Introduction

Duplex stainless steels are alloys of the Fe-Cr-Ni(-Mo) system having a microstructure comprising typically 40 to 50% ferrite and the rest austenite.

Alloying steel with chromium, being a ferrite stabilizer, to improve corrosion resistance, will result in a material with a bcc crystal structure. Solubility of elements like carbon and nitrogen in such a crystal structure is very low. Rather low heat input causes precipitations (like chromium carbides) having a negative influence on the corrosion resistance. In case of presence of about 18% Cr some 10% of Ni as an alloying element will result in a fully austenitic structure with fcc crystal lattice. Austenitic materials are much more stable with respect to chromium carbide and chromium nitride precipitation and have as a consequence a very good resistance to intergranular corrosion but having disadvantages regarding strength and chloride SCC resistance.

It will be clear that there was a strong desire to combine the good properties of the austenitic materials with the good properties of the ferritic materials.

Just after world war II one succeeded to manufacture a material with a duplex (ferrite-austenite) structure by alloying steel with a certain amount of ferrite and austenite transformers. From the schematic pseudo-binary phase diagram for Cr and Ni (with 70% Fe) as shown in figure 1 ferrite as well as austenite are stable in the area of 20 to 25% Cr and 5 to 10% Ni.

At high temperatures duplex stainless steel alloys are more or less ferritic. The partial re-transformation to austenite is controlled by the diffusion of the ferrite respectively the austenite stabilizing elements and thus favoured by a low cooling down rate in the range between 1200 and 800 °C. The obtained microstructure consists of a ferritic matrix, enclosing uniformly distributed austenite islands.

The typical microstructures of duplex stainless steel are shown in Photo’s 1 and 2. The microstructure as shown in Photo 1 is obtained after electrolytic etching by means of KOH; the microstructure as shown in photo 2 is obtained after etching by means of the colour etching technique according to Lichtenegger and Bloech.
### Types of duplex stainless steels

The first generation of duplexes, such as type 329, Uranus 50 and 3RE60, as listed in Table 1, offer good localized corrosion resistance, due to their high Cr and Mo contents. However, when welded, these materials lose some of this corrosion resistance and ductility, both of which can be restored by a post-weld heat treatment. Due to the decrease in corrosion resistance after welding these duplexes found only limited application. A break-through in the development of duplex stainless steels took place in the nineteen seventies with addition of nitrogen as alloying element.

In the second generation of duplex stainless steels, the addition of 0.15% to 0.25% nitrogen reduces chromium partitioning between the two phases, and enhances the pitting and crevice corrosion resistance of the austenite. When properly welded, the second generation of duplex stainless steel grades have the same level of corrosion resistance and ductility as does mill annealed material. Each reputable stainless steel producer developed its own type or types. Thus, duplexes became more readily obtainable and more cost competitive. They combine the advantages of the austenitics (good processability, including weldability, and overall corrosion resistance) with those of the ferritics (good mechanical properties and chloride SCC resistance).

During the development of the second generation of duplexes two different types were fabricated: 22% Cr-type and the 25% Cr-type. In Table 2 some second generation 22% Cr duplexes are listed. In Table 3 some second generation 25% Cr duplexes are listed.

For improved corrosion resistance several manufacturers developed super duplex stainless steel types. The PREN (Pitting Resistance Equivalent Number) of these steels is above 40. PREN = Cr + 3.3Mo + 16N >40 or Cr + 3.3(Mo + 0.5W) + 16N >40. These duplexes are also called the third generation duplexes. Some well known super duplexes are listed in table 4.

### Table 1. First generation of duplex stainless steels.

<table>
<thead>
<tr>
<th>Type</th>
<th>Manufacturer</th>
<th>Chemical analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>329</td>
<td>Carpenter</td>
<td>0.10 26 4 2</td>
</tr>
<tr>
<td>HVD 1</td>
<td>Henricot</td>
<td>0.08 26 8 3 2</td>
</tr>
<tr>
<td>3RE60</td>
<td>Sandvik</td>
<td>0.03 18.5 4.7 2.7</td>
</tr>
<tr>
<td>DP1</td>
<td>Sumitomo</td>
<td>0.03 18.5 5.5</td>
</tr>
<tr>
<td>Uranus 50</td>
<td>Creusot-Loire</td>
<td>0.03 21 7.5 7.5</td>
</tr>
</tbody>
</table>

### Table 2. Second generation 22% Cr duplex stainless steels.

<table>
<thead>
<tr>
<th>Type</th>
<th>Manufacturer</th>
<th>Chemical analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF 2205</td>
<td>Sandvik</td>
<td>0.03 22 5.5 3</td>
</tr>
<tr>
<td>223 FAL</td>
<td>Avesta</td>
<td>0.03 25 6.5 3.0 0.5</td>
</tr>
<tr>
<td>Uranus 45 N</td>
<td>Creusot-Loire</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>DMV 225</td>
<td>DMV</td>
<td>0.03 25 6.5 3.0 0.5</td>
</tr>
<tr>
<td>A903</td>
<td>Böhler</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>AF21NMMN</td>
<td>Junker</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Cronifer 2205 LC</td>
<td>Krupp-VDM</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>DP8</td>
<td>Sumitomo</td>
<td>0.03 25 6.5 3.0 0.5</td>
</tr>
</tbody>
</table>

### Table 3. Second generation 25% Cr duplex stainless steels.

<table>
<thead>
<tr>
<th>Type</th>
<th>Manufacturer</th>
<th>Chemical analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF 2507</td>
<td>Sandvik/Avesta</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Falc 100</td>
<td>Krupp-VDM</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Zeron 100</td>
<td>Mather &amp; Platt</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>DMV 25.7 N</td>
<td>DMV</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Uranus 52 N+</td>
<td>Creusot-Loire</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
</tbody>
</table>

### Table 4. Third-generation (Super-) Duplex Stainless Steels PREN = Cr + 3.3Mo + 16N >40.

<table>
<thead>
<tr>
<th>Type</th>
<th>Manufacturer</th>
<th>Chemical analysis %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAF 2205</td>
<td>Sandvik/Avesta</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Falc 100</td>
<td>Krupp-VDM</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Zeron 100</td>
<td>Mather &amp; Platt</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>DMV 25.7 N</td>
<td>DMV</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
<tr>
<td>Uranus 52 N+</td>
<td>Creusot-Loire</td>
<td>0.03 25 7.5 3.0 0.5</td>
</tr>
</tbody>
</table>
For specific applications some special types of duplex stainless steels were developed. Some well known types of special duplex stainless steel types are listed in Table 5.

**Field of application of duplex stainless steels**

Ferrite-austenitic stainless steels have gained wide acceptance in the chemical and petrochemical process industries for numerous services. They are often used where typical austenitic stainless steels, such as type AISI 304L and AISI 316L, failed because of stress corrosion cracking. Also they have proved a good substitute for more or less exotic materials, such as titanium and high-nickel alloys which until recently were the sole option for a number of media.

At DSM, duplex stainless steels were first applied in the mid-sixties, mainly for non-welded parts of carbamate pumps and valves in urea plants.

In the late nineteen sixties, the drum of a centrifuge in a polyethylene plant was fabricated from X2CrNiMoCu21-8-3 to replace a type AISI 316 drum exhibiting serious chloride stress corrosion cracking.

Large-scale introduction of duplexes began in the early eighties, initially for pipework and equipment components and later for large-size equipment. At present time in a lot of different DSM plants many items of equipment and piping is manufactured out all kinds of duplex stainless steels. Applications include the following:

- Pumps, pipework, heat exchangers, scrubbers, vessels, cyclones of X2CrNiMoCu22-5-3 in carbamate solutions at temperatures up to about 150°C where titanium and high-nickel alloys were used hitherto.
- Pipework in X2CrNiMoN22-5-3 carrying benzoic acid medium at temperatures of 240 to 260 ºC, where previously high-nickel alloys were used.
- Pumps in GX6CrNiMoCuN25-6-3 for phosphoric acid solutions.
- Heat exchangers, vessels, distillation columns, pipework and centrifuges handling chloride-containing media, which, if fabricated from a typical austenitic stainless steel, would be susceptible to stress corrosion cracking and/or corrosion fatigue. Various types of duplex have been used here, including 22 and 25% Cr grades.
- MVC strippers handling vinyl chloride slurries (X2CrNiMoN22-5-3 and X2CrNiMoCuN25-7-3).
- Heat exchangers for caustic fluids at temperatures up to 180 ºC (X2CrNiMoN22-5-3).
- Granulator drum (X2CrNiMoN22-5-3) for calcium ammonium nitrate and NPK fertilizer.
- In Stamicarbon urea plants several HP carbamate condensers and a HP scrubbers have been manufactured out of X2CrNiMoN22-5-3.
- Recently several HP carbamate condensers and HP strippers for urea service have been manufactured out of Safurex.

Safurex has been developed in cooperation between Sandvik and Stamicarbon specifically for application in Stamicarbon Urea plants to withstand extremely corrosive (nearly oxygen free) ammonium carbamate solutions.

The list of applications might suggest that duplexes are a cure for all corrosion problems. This is not the case. In general, experience has been much favourable but we have also experienced that duplexes have their limitations.

Limitations of duplex are related to several aggressive components as well as service temperature. At temperatures above about 250°C, long term exposure will result in 475°C embrittlement.

At temperatures in between 600 and 900°C other phases or precipitations may develop such as: CrN-nitrides, M23C6-carbides, /H9273-phase, /H9268-phase, /H9261-phase, etc.

Figure 2 shows the temperature versus time diagram for harmful precipitations in duplex stainless steel.

At low temperatures duplex stainless steels show a brittle character due to the ferrite matrix of the material. The applied duplex stainless steels have to fulfill the requirements as described in paper M 0110 “Notch ductility testing” in the Rules for Pressure Vessels (Published for Dienst voor het Stoomwezen, The Netherlands).
Hague). For application of duplex stainless steel down to -20 ºC a Charpy-V notch testing has to be performed at -20 ºC; the minimum required Charpy-V notch value for as delivered (wrought and forged) material is 60 Joule and for weld deposit material 40 Joule.

At temperatures below -20 ºC the Charpy-V notch ductility value is decreasing. Actually, the application of duplex stainless steel is restricted to the temperature area of -20 ºC to +250 ºC. For each specific case outside this temperature range it has to be checked whether application is acceptable.

Some applications, indicating limitations of duplexes are discussed in several cases.

**Case 1: Application of duplex stainless steel in a condenser.**

*Selective attack of austenite phase*

Titanium and high-nickel alloys have often been used for oxygen-free acidic solutions. Exposure tests of welded and unwelded test plates and equipment internals indicated that good corrosion resistance may be expected of duplex stainless under the prevailing service conditions.

In late 1983, a titanium condenser with tubes 3 mm thick had to be replaced after six years on stream. The tubes had developed overall corrosion as well as embrittlement due to titanium hydride formation. In selecting the material of construction of the replacement unit high-nickel alloys and duplex were considered. Field exposure tests of duplex materials, lasting about one year, revealed selective attack of the austenite phase to a depth of about 0.1 mm (Photo 3). On this photo, the austenite phase is light-coloured due to etching with NaOH.

High-nickel alloys, too, are susceptible to corrosion in this service, especially the heat-affected zones of welds.

Equipment vendors quoted 1,000,000 Euro for a unit fabricated from high-nickel alloy and 220,000 Euro for a unit in duplex stainless steel. It was decided to opt for the duplex material due in part to its ready availability. No sooner had the replacement unit been started up than we observed serious contamination of the process stream exiting from this heat exchanger.

Analysis revealed high Fe concentrations. The corrosion rate at this iron level was calculated to be some millimetres per year. The iron could not but originate from the newly installed duplex heat exchanger.

After three days, the Fe concentration suddenly changed to normal, suggesting that corrosion had stopped. Examination of a heat exchanger tube after one year on stream revealed selective attack of the austenite phase to a depth of 0.2 to 0.3 mm, quite similar to the exposure test. Apparently, the austenite phase becomes passivated after a few days. The mechanism involved is believed to be anodic protection of the austenite phase developing when the ferrite/austenite area has become large enough as a result of corrosion of the austenite.

Inspections have confirmed that corrosion hardly progresses as service is continued. This heat exchanger was in service for about 14 years. Replacement was necessary due to severe corrosion of nickel based weld deposit material.

Some time before the titanium heat exchanger was replaced, a perforated duplex stainless steel support plate and a hold-down plate were installed in the intermediate chamber above the top tube sheet of the heat exchanger to serve as impingement plates. After three years, the plates proved embrittled throughout. (Photo 4).
Again, microscopic examination revealed selective attack of the austenite phase (Photo 5) as well as intergranular corrosion progressing along the ferrite/austenite grain boundaries (Photo 6), mainly originating from the stirr face in the drilled holes of the plates.

Apparently, in this case, the selective attack (and intergranular attack) did not stop after a few days. Microscopic examination indicated also that the structure could hardly be classified as one with a ferrite matrix surrounding uniformly distributed austenite islands. In effect, it was more akin to an austenite matrix containing ferrite (Photo 7).

Also, the austenite content was quite high, i.e. 60 to 70%. Apparently, the austenite is more difficult to repassivate if intercrystalline corrosion is leading selective attack and if the microstructure is more like an austenite matrix containing ferrite than a ferrite matrix containing austenite.

**Laboratory experiments concerning anodic protection of active austenitic materials by means of passive ferritic material.**

Laboratory experiments have been conducted in an attempt to establish whether an active austenitic stainless steel is amenable to passivation through galvanic coupling with a passive ferritic stainless steel. This has proved possible for X1CrNiMoNb28-4-2 and X2CrNiMo17-13-2 in a mixture of sulphuric acid and oxalic acid at a temperature of 50 ºC. In this medium, on activation, X2CrNiMo17-13-2 remains active while X1CrNiMoNb28-4-2 repassivates spontaneously. A potential of -300 mV versus an Ag/AgCl reference electrode is applied to the austenite for five minutes from t2 until t3 (Figure 3), the free corrosion potential being measured from t3 until t4.

At t4, when the material has stabilized, the austenitic material is coupled with the ferritic material, whereupon the mixed potential assumes a different value depending on the surface ratio of ferrite/austenite. At a surface ratio of 200/1, the austenite appears to passivate on coupling. On the other hand, at a surface ratio of 1/1, if there is galvanic coupling of the passive ferrite with the active austenite, the ferrite becomes active also.

**Acceptance testing**

Experience shows that duplex stainless steels, especially if used in media likely to initiate selective attack
of the austenite phase, must meet specific requirements that should be incorporated in a material specification.

The following preliminary requirements have been drawn up on the basis of experience and laboratory tests:

- Duplex material shall after final heat treatment have a homogeneous ferritic-austenitic structure with a ferrite content of 40 to 60 vol. % but preferable 50 to 60 vol. %.
- The material shall have a uniform, ferritic structure with austenite islands fully enclosed by ferrite.
- The weld filler metal shall be compatible with the selected material. To ensure a proper ferrite-austenite balance in the deposit weld metal, the nickel content of the weld filler metal shall be higher than that of the base metal.
- The ferrite content of the deposit weld metal as well as the heat-affected zone shall be between 30 and 70 vol. %.
- The material shall be Streicher-tested (solution of ferric sulphate in sulphuric acid) in accordance with ASTM A 262, Practice B and shall meet the following requirements:
  - The rate of the overall attack in as-delivered condition and in welded condition, as measured by the gravimetric method, shall not exceed 0.1 mm/year for 25% Cr duplex stainless steels or 2 mm/year for 22% Cr duplex stainless steels.
  - Seamless heat exchanger tubes shall be tested for homogeneity (ferrite/austenite ratio) by eddy current testing.
  - In our experience, the Streicher test is well capable of identifying those material properties which are influenced by precipitations on the grain boundaries. We have found that it can reveal intergranular corrosion along both the ferrite-ferrite crystal boundaries and the ferrite-austenite crystal boundaries. On the other hand, we do wonder if this test is really suitable to detect duplex materials with an unacceptable ferrite-austenite ratio or distribution.
  - Additional to the Streicher test a microscopic examination is mandatory to establish the depth of selective or intergranular attack. This microscopic examination can also reveal the more or less subjective assessment criteria such as the ferrite-austenite ratio and distribution.

Conclusions

- Where a duplex is used in a medium likely to cause selective corrosion of the austenite phase, it is essential that the structure consist of a ferrite matrix, enclosing uniformly distributed austenite islands. In that case, selective attack of the austenite phase will develop but cease soon after probably because of anodic protection.
- The quality requirements should be laid down in a material specification. To that end, a quality test needs to be performed to distinguish between good and bad grades of duplex.

Literature


Case 2: Application of duplex stainless steel in MVC strippers PVC plant.

Stress corrosion cracking

Stripper columns in type AISI 316L handling a vinyl chloride slurry with a pH of 2.8 to 3.5 and 20 to 50 ppm chlorides developed stress corrosion cracking after only a half year on stream. A process flow diagram of MVC stripping in a PVC plant is shown in Figure 4. The service temperature is about 105 deg. °C and the pressure 1.05 bar. In late 1986, after eight years in service, the four strippers were...
replaced by similar units in type X2CrNiMoN22-5-3 duplex. A year later, in a similar plant, four strippers in X2CrNiMoCuN25-7-3 were installed. Inspections after eight to twelve months revealed stress corrosion cracking in all strippers.

The incidence of cracks in the 22% Cr grade is greater than in the 25% Cr grade.

Inspections after another year showed that crack formation had practically come to a halt and that there had been only little propagation of existing cracks. The cracks originate from the welds and propagate into the plate material, perpendicularly to the weld, over a length of maximum 20 mm (Photo 8). Occasionally, crack indications were also found in the sieve trays adjacent to the punched holes. Microscopic examination revealed that the branched cracks progress mainly through the austenite phase of the plate material (Photo 9). On the photos, the austenite phase is darkish as a result of etching in accordance with LB1 (Lichtenegger and Bloech). In weld deposit material, too, cracking propagates preferably through the austenite phase albeit less markedly than in plate material (Photo 10). As a secondary observation we have noted localized selective subsurface attack that progresses through the austenite phase (Photo 11) although we have also identified localized selective ferrite attack.

It is remarkable that cracks are located at the inside surface in and adjacent to the double-sized SAW welds. The closing seam of the stripper was welded from the outside with a GTAW root and SAW filler layers (Figure 5). After two years on stream, this weld did not exhibit any cracks.

The double-sized GTAW welds of the nozzles, too, show cracks emanating from the inside surface. We should add that the seam welds had not been pickled. We believe this omission promotes selective adsorption of chlorides in the porous oxide skin resulting from welding operations. The chlorides so adsorbed increase the risk of stress corrosion cracking. After some 4 years on-stream in the weld indicated B also cracking was observed.
Constant Extension Rate Testing (CERT)

A comparative evaluation was made of the susceptibility to SCC of duplex steels and Type AISI 316 steel in a calcium chloride environment as a function of pH. These tests were carried out by means of computer-controlled tensile testing machines.

It is remarkable that in calcium chloride solutions lower than 25% the relative elongation fails to give any clear indication of SCC. Tests in vinyl chloride slurry with 50 ppm chlorides and a pH of 2.8 yielded no indications of SCC in duplex either. At 40% calcium chloride, a higher susceptibility to SCC can be observed at lower pH values.

Figure 6 shows the relative elongations at fracture of duplexes and Type AISI 316L in a 40% calcium chloride solution in relation to the elongation in glycerine, as a function of the pH value.

Figure 7 shows a stress strain curves determined by constant extension rate test (CERT); temperature: 123°C; \( \epsilon = 10^{-6} \) sec\(^{-1}\).

Conclusions

- Duplexes may be used in numerous applications to replace common austenitic stainless steels because of their superior resistance to SCC or to replace high-nickel alloys and titanium, in which case they offer comparable or even better corrosion resistance.
- Resistance to chloride SCC at low pH values (about 3) is hardly any better than that of, say, X2CrNiMo17-13-2.

Literature


Case 3
Catastrophic failure of a duplex stainless steel X2CrNiMoN22-5-3 (1.4462) pipeline in a chemical plant

The situation
- A polypropylene pipeline in a chemical plant was suffering from embrittlement by:
  - chemical oxidation from inside.
  - photochemical degradation (UV radiation) from outside.
- About every four years replacement was necessary.
- To find a better construction material, different samples have been exposed for about 4 years at different locations in the polypropylene pipeline.
- Conclusion: duplex stainless steel X2CrNiMoN22-5-3 (1.4462) should be an excellent option.
- Action: during a turnaround about 50 meters polypropylene pipeline have been replaced in 1.4462.

Initially, in the early fifties, the pipeline in between graphite heat exchangers and hydrolysis vessels was constructed out of glass. After a couple of years the glass line was replaced in polypropylene. The hydrolysis vessels were initially constructed out of Kera S (furane resin). The furane resin was subject to chemical oxidation; occasionally oxidizing components are present in the environment. In the early seventies new hydrolysis vessels were installed, the first vessel (of 3 in series) constructed out of austenitic stainless steel X5NiCrMoCuNb20-18-2-2 and the other 2 vessels out of X2CrNiMo17-13-2.

Description of corrosion failure of X2CrNiMoN22-5-3 pipeline
- Only three days after start-up the DN100 duplex stainless steel (X2CrNiMoN22-5-3) pipeline ((114.3 x 6.02 mm) started leaking due to very severe uniform attack (see photo 12).
- Uniform corrosion rate: up to 2 mm/day (700 mm / year).
- Actions:
  - immediate replacement of the duplex stainless pipeline in again polypropylene; (recently the pipeline was replaced in FRP PVDF lined).
- Root cause analysis.
  - Visual examination and NDT of the replaced pipeline
  - there were locations with serious (2 mm/day) corrosion and locations with hardly any attack.
  - Examination of the microstructure of the material
    - no irregularities in composition and microstructure were found
  - Investigation of start-up conditions
    - start-up conditions were the same as normal process conditions
  - Investigation of the reaction mechanisms

The failure mechanism of the duplex stainless steel pipeline
- The pipeline is in fact a “reactor” composition in is not equal to composition out.
- In some parts of the “tube reactor” there is a side-reaction in which sulphuric acid (locally up to 40%) is being formed.
- In the polypropylene pipeline this sulphuric acid reacts quickly to ammoniumbisulphate.
- In (duplex-) SS the sulphuric acid (80 / 100°C) also attacks the metal in which metal-ions are being formed.
- Fe and Mo catalyze the side-reaction to sulphuric acid so even more sulphuric acid is being formed.

What can we learn from this incident?
- Always pay attention to the understanding of the reaction mechanisms (all steps) and all possible side-reactions.
- Always ask yourself if the metal (or ions from the metal) in the process environment may influence reactions.
- Exposure tests can be misleading:
  - exposure locations are not always representative.
  - influence on the reaction mixture is not taken into account.
- Support exposure tests with (electro)chemical research to get a better understanding of the corrosion mechanism.

Photo 12. Catastrophic corrosion in X2CrNiMoN22-5-3 (ø114.3 x 6.02 mm)