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OUTOKUMPU

Why Clad when there is Duplex?

Dear Reader

You are probably aware of that stainless steel prices are rather high for the moment, mainly due to all time high prices for the very important alloying elements nickel and molybdenum, i.e. factors outside the control of the stainless steel industry. One alternative to solid austenitic stainless steel could consequently be taking a step backwards in technology and looking for clad steel. I strongly advice against such a concept when you have another more cost effective alternative, i.e. using an austenitic-ferritic or duplex grade. There are quite a few advantages in using solid duplex steel, far easier fabrication, welding included, normally no need for a post fabrication stress relieving, no need for an external coating and consequently no need for maintenance.

And on top of that, twice the strength of the austenitic 300-series, implying possibilities to reduce the gauge and costs. Furthermore, lower contents of nickel and molybdenum resulting in a lower alloy surcharge, i.e. more stable and predictable costs.

This issue of Acom contains an updated version of an article published in Stainless Steel World a year ago where these issues were addressed.

One obvious drawback of clad steel is the compromise in rolling and annealing temperatures for the stainless steel cladding and the mild steel substrate, which can result in surface defects of the stainless steel cladding. There is one such case briefly described in the article where the fabricator tried to remove surface defects by grinding, but accidentally the grinding became too deep, exposing the mild steel to the corrosive environment with a disastrous result. I cannot give any more details then mentioned in the article since I got this case in confidence, trying to explain what had happened. I could be mentioned, however, that Outokumpu Stainless does not produce clad plate, we are more solid.

Apart from being twice as strong, the duplex grades have a corrosion resistance well matching that of austenitic 1.4404 (316L) and upwards. Besides, the new Outokumpu LDX 2101 has developed a tremendous interest by industries traditionally using mild steel and it has been used for bridges, flood gates, garbage trucks and of course large storage tanks to mention a few applications.

Enjoy the reading and have a serious look upon duplex before thinking clad.

Yours sincerely
Jan Olsson
Technical editor of Acom

Why Clad when there is Duplex?

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Introduction

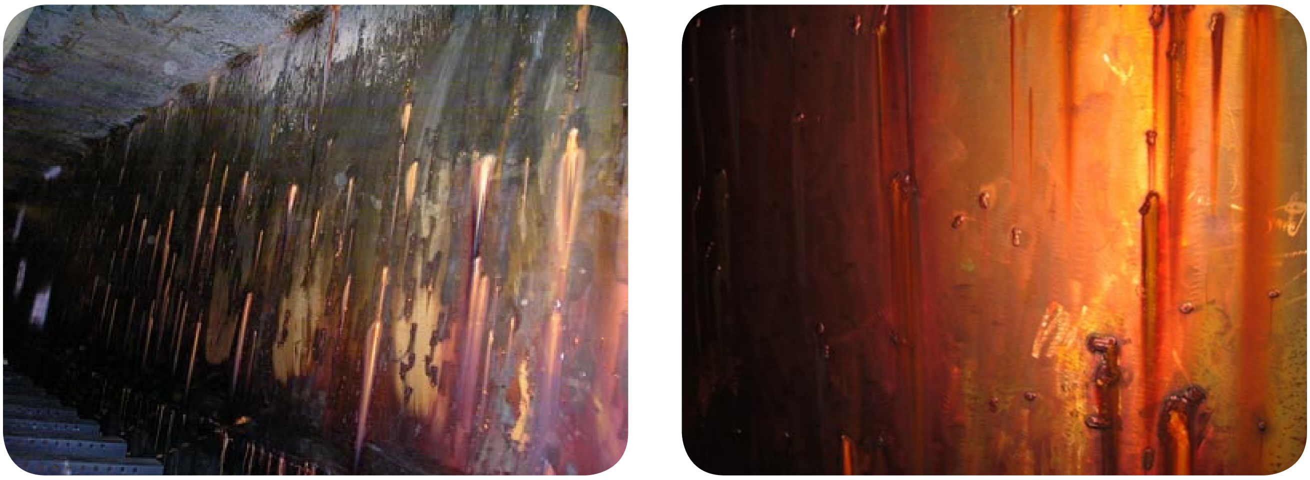
Once upon a time stainless steel was considered as a very costly material and the use of it was restricted to areas where there was a demand for its corrosion resistance.

If heavy walls were required and if the corrosion resistance of mild steel was inadequate it could be lined or "wallpapered" with thin sheets of stainless steel. The mild steel carried the entire load and the stainless steel, normally an austenitic grade, was there to protect against corrosion, it was used as an "umbrella" only. The drawback was obvious; the attaching of this "wallpaper" by welding was not always that easy and differences in thermal expansion caused often stresses and occasionally thermal fatigue.

As times passed by it was realised that the lining could be bound atomically to the substrate; clad steel was born. The cladding was initially achieved by hot rolling of a sandwich where two heavy mild steel plates were the bread and the thinner stainless steel plates the butter, which was partly smeared into the bread by hot rolling. The buttered sides were turned against each other and to avoid them to weld together, a partition agent, like a greaseproof paper, was used. Later on also explosive bonding was developed. The stainless steel was now an integrated part of the material although it was still not included in the dimensioning; its strength was just too low in comparison to the substrate.

However, clad steel has obvious drawbacks. There is often a compromise in hot rolling temperature, too low for stainless and too high for the mild steel. One possible consequence is illustrated in Figure 1 showing a 1.4438 (317L) clad steel item. Surface defects from the hot rolling were removed by grinding, but the grinding became too deep, exposing the mild steel substrate to the corrosive environment with disastrous result.

Fig. 1 Corrosion of the mild steel substrate in a 1.4438 (317L) clad steel component (left) and failed repair welding (right).



The subsequent repair welding did not solve the problem.

There is occasionally also poor adhesion between the cladding and the substrate and above all, complex welding procedures with three or maybe four different types of welding consumables. The welding has to start with 2–3 beads for the mild steel backing to assemble the vessel or plates for further fabrication, then removal of the welded surface layer from the stainless steel side by grinding. This is followed by welding from the stainless steel side with an over alloyed filler to get a ductile transition zone between the mild steel and the stainless steel and also to avoid dilution of the stainless steel surface by mild steel. Then follows one or two beads of stainless steel with a composition matching that of the stainless steel cladding. Then it is necessary to turn around the plates or get to the outside of the vessel to fill up the mild steel weld by submerged arc or some other high productivity welding process.

On top of that there are often requirements for post weld heat treatment implying a compromise in annealing temperature for the substrate and the stainless cladding. And then comes the need for an external coating, paint or epoxy, which often has to be maintained.

Today there is another concept available, austenitic-ferritic or, more commonly, duplex stainless steel. Duplex stainless steel was developed around 75 years ago, but the austenite-ferrite balance was far from perfect in those days and fabrication was more an art than science. However, the introduction of modern metallurgical processes in the late 1960s, such as AOD (argon-oxygen-decarburising), enabled large-scale production of an excellent engineering material with high strength and an adopted corrosion resistance, i.e. there are several grades with different levels of corrosion resistance, suitable for a variety of environments.

Duplex stainless steels can be fabricated more easily than clad steel and they can be welded in heavy gauges without any pre-heating or post weld annealing. And there is no need for an external coating, i.e. no future costly maintenance. Duplex stainless steels are today standardised in most countries and design and pressure vessel codes are available.

This article will give case stories from four different industry sectors showing that duplex stainless steel can be a cost effective alternative to clad steel because of its corrosion resistance and likewise to solid austenitic steel due to the higher strength and even to mild steel because it eliminates the demand for future maintenance.

One of the industries, the pulp and paper industry, has more or less converted all manufacturing of pressure vessels and large tanks into the use of solid duplex steel, another has partly turned away from clad steel, chemical tankers, and the third, the desalination industry, has just started to use duplex. Clad steel has rarely been an option for the fourth sector, civil engineering, but the use of duplex as a replacement for mild steel is increasing rapidly.

Metallurgy

There are a variety of duplex grades available and their corrosion resistance range from close to that of conventional 1.4404 (316L) up to that of the 6Mo austenitic grades, which to some extent also is illustrated by the PRE-numbers (Pitting Resistance Equivalent) given in Table 1.

Chemical compositions of some duplex grades, typical values, with some austenitic grades included as reference.

Table 1

Outokumpu	EN	ASTM	Cr	Ni	Mo	N	PRE[1)]
4307	1.4307	304L	18	8	–	0.06	19
LDX 2101 ®2)	1.4162	S32101	21.5	1.5	0.3	0.22	26
4404	1.4404	316L	17	11	2.1	0.04	25
SAF 2304 ®3)	1.4362	S32304	23	4.8	0.3	0.10	26
904L	1.4539	N08904	20	25	4.5	0.06	36
2205	1.4462	S32205	22	5.7	3.1	0.17[3)]	35
254 SMO ®2)	1.4547	S31254	20	18	6.1	0.20	43
SAF 2507 ®3)	1.4410	S32750	25	7.0	4.0	0.27	43

1. PRE = % Cr + 3.3 x % Mo + 16 x % N.
2. Registered trade name by Outokumpu Stainless.
3. Should preferably be min 0.14% as in ASTM S32205!
4. Registered trade name by Sandvik AB.

The mechanical properties are given in Table 2 and the max allowable stresses for designing a pressure vessel with a design temperature of 200°C in Table 3.

Mechanical properties of some duplex grades including the austenitic 1.4307 as reference.
Min values at room temperature for plate material according to EN 10088. Table 2

EN	ASTM [1)]	Rp0.2 (N/mm²)	Rm (N/mm²)	A_5 (%)
1.4307	304L	200	500	45
1.4162[2)]	S32101	450	665	30
1.4362	S32304	400	630	25
1.4462	S32205	460	640	25
1.4410	S32750	530	730	20

1. ASTM is included to give the corresponding grades only; the mechanical properties deviate from those given for EN.
2. Not yet included in EN 10088.

Max allowable design stresses at 200°C for duplex stainless steels including
1.0481 and 1.4307 for reference. Table 3

Grade	EN (N/mm²)	ASME (N/mm²)
1.0481[1)]/ A 516 grade 70[1)]	150	122
1.4307/ 304L	120	109
1.4162/ S32101	210[2)]	165[3)]
1.4362/ S32304	187	150
1.4462/ S32205	210	165
1.4410/ S32570	267	208

1. Mild steel used as substrate for clad steel.
2. Not yet included in EN 10028-7.
3. Code Case 2418.

Cellulose Pulp Industry

One industry that has passed through all the development stages illustrated above is the kraft or sulphate pulp industry. Initially the digesters, the heart of such plants, were made of plain carbon steel since the process environments were not that hostile and the mass lost due to corrosion could easily be compensated for by a corrosion allowance. Large scale kraft pulp processing started during the 1870s, i.e. more than 130 years ago. Those were the days when the vessels were riveted, not welded.

However, the processes were modernised and the demand for better materials of construction resulted in the use of stainless steel wallpapering or lining around 80 years later, i.e. in the late 1950s. The conditions were still suitable for an ordinary stainless steel and the grade commonly used was 1.4301. In those days the cooking was done in batch digesters resulting in thermal cycling from ambient temperature to 150 or 160°C, occasionally even higher, several times a day. To avoid fatigue problems the pieces of stainless steel used were rather small, less than 1x2 m, and the internal side of the digester looked like a king size patchwork quilt.

Thermal fatigue problems could still not be avoided, Figure 2, and the introduction of clad steel around 10 years later, i.e. in the late 1960s, came as a gift from heaven. However, fabrication was still complicated and especially the welding procedures, as described above, caused a certain concern. On top of that were occasional problems with poor adhesion and also carbon pick-up in the stainless steel surface resulting in superficial intergranular corrosion during service.

Fig. 2 Thermal fatigue in stainless steel lining.

Fig. 3 A kraft batch digester made of 2205.

Fig. 4 A continuous kraft digester made of 2205 during erection in China (Courtesy Kvaerner Pulping).

The first kraft pulp digesters made of duplex stainless steel were erected in New Zealand in 1988, two batch digesters of 125 m³ each, manufactured as knocked down vessels in Avesta and assembled at the site, Figure 3.

Then there was a period with no duplex digester installations while experience was collected from this first installation. The next three were installed in 1990 and then it all accelerated with three sulphite digesters in 1992, four more kraft digesters in 1993, another 19 in 1994 and the ball was rolling [1]. Today more or less all pulp digesters are made of solid duplex stainless steel, including the huge continuous kraft digesters having a diameter at the lower part of around 10 – 12 m and a height of around 60 m.

The biggest of them all and probably also the biggest pressure vessel in the world, a continuous kraft digester with a diameter of 12 m, a height of 60 m and a shell weight of 550 tons is right now being erected in China, Figure 4. The design is according to the new European pressure vessel code, EN 13445, and the max gauge in the lower part is 52 mm, all in grade Outokumpu 2205.

The allowable stress at the design temperature, 200°C, is 210 N/mm^2 for 2205 while the corresponding value for a clad plate with the grade 1.0481 (EN 10028-2) as substrate is 150 N/mm^2. If built in clad steel the shell weight should have been close to 800 tons and the welding should have been far more costly. And post fabrication heat treatment would just be impossible.

By using the more conservative ASME code solid duplex stainless steel will be less cost effective than with the European code, but since this goes also for the mild steel substrate for clad steel, e.g. ASTM 516 Grade 70, the advantage of using duplex is still considerable.

It is difficult to get exact numbers in cost savings by the use of solid duplex stainless steel for these digesters, but a statement by one leading engineering company, "We don't pay more for having them made in duplex", speaks for itself.

Also other pressure vessels within the pulp industry are commonly made of duplex stainless steel today. Not because it is required by its superior corrosion resistance but because of the possibility to save costs due to the high strength. Typical examples are oxygen delignification reactors, pressurised peroxide reactors and black liquor evaporators. The first two items are used in modern bleach processes to reduce the demand for chlorine containing bleach stages and the third for recovery of chemicals used at cooking.

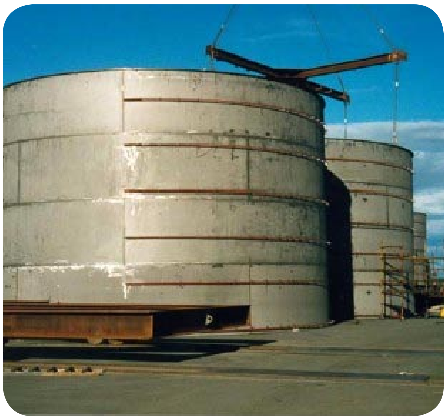
Most of the equipment described is made of 2205 (1.4462). The lower alloyed grade SAF 2304 (1.4362), which actually has better corrosion resistance in the strongly alkaline solutions handled, has so far mainly been installed in critical stages of the evaporation plant, where the strive for higher temperatures and more efficient recovery has increased the corrosiveness of the black liquor. The use of the slightly more costly 2205 has been justified by the extremely positive experience achieved and the higher strength, which has counterbalanced the higher price per kilo.

The high strength can also be used for atmospheric tanks, which are so high that the proof stress is used for the design of the lower parts of the tanks due to the internal pressure from the product stored. Examples are pulp towers, i.e. for intermediate storage of pulp during the processing, Figure 5a, black, green and white liquor tanks, i.e. for chemicals used for the recovery and preparation of the cooking liquors, Figure 5b, and as shown in Figure 5c, marble slurry tanks.

Fig. 5 a) Pulp towers made of 2205

b) white liquor tank made of SAF 2304

c) marble slurry tanks made of LDX2101.



The latter case is interesting since it required only a stainless steel to avoid contamination of the marble slurry, which is used for whitening of the paper. However, by utilising the high strength duplex grade LDX 2101 instead of 1.4301 (ASTM 304) it was possible to reduce the gauge and weight by around 40% and the cost by 30%. Another design concept had been used for other similar tanks built some years earlier, a case that was described in a previous issue of Acom [2].

Chemical tankers

The shipping sector using tankers for the transportation of chemical compounds has not gone through all the material selection concepts as the pulp industry. Naked mild steel has never been an issue for the transportation of aggressive chemicals also if concentrated sulphuric acid can, according to the textbook, be handled in mild steel tanks, nor has lining with stainless steel patches. The tanks are consequently made of either epoxy coated mild steel or stainless steel, either as cladding or solid.

The stainless steel grades have mainly been selected in accordance with chemicals transported, but also to resist seawater cleaning. With the exception of tankers for dedicated trades, such as orange juice transportation where seawater cleaning is not applied, it has been found necessary to use grades with rather high content of alloying elements. EN 1.4429 (316LN) modified with minimum 2.75% Mo is today used in about 50% of the total world fleet of chemical tankers.

Initially, i.e. in the beginning of the 1960s, clad plate was used for all external parts of the cargo tanks whereas solid stainless plate was used for internal bulkheads exposed to the cargo on both sides. One reason for clad steel was to reduce the risk of galvanic corrosion between the hull and a stainless steel surface, since the space between the two often was used for ballast water, another the cost of solid stainless steel.

The cargo tanks are integral parts of the ship and therefore contributing to the total strength of it, Figure 6. Due to the high strength of the duplex stainless steel 2205 it is possible to save weight and costs in comparison with other materials when building a chemical tanker. The corrosion resistance of 2205 to cargoes and seawater is equal to or better than that of any other stainless steel grades used for this application, implying less risk of corrosion and consequently higher degree of flexibility in cargoes [3].

Fig. 6 Chemical tanker with 2205 tanks under construction.

There are today around 200 chemical tankers with solid 2205 used for the cargo tanks in service worldwide, sizes range from small barges and coast vessels to big tankers of 40,000 dwt.

Clad steel is still, however, the most common concept in certain countries, which seems slightly old-fashioned considering the complicated welding processes and other drawbacks described in the introduction. The reluctance to use solid duplex might originate from the days when it was introduced for chemical tankers, i.e. during the late 1970s. The importance of nitrogen was not fully understood in those days and pre-heating was occasionally recommended to achieve a cooling rate slow enough to get the correct austenite-ferrite balance in the heat-affected zone, thereby avoiding precipitates of carbides and nitrides.

Desalination

The desalination industry, where distillation is applied, has passed through all the development stages in materials selection, just as the pulp industry, but in shorter time.

Large-scale desalination of seawater was introduced during the 1950s by professor Silver's multi stage flash (MSF) concept. Boiling seawater was led into a first evaporation vessel, a flash chamber, where the vapour was condensed and collected as fresh water. During this evaporation the temperature of the seawater dropped below the boiling point at atmospheric pressure, which was compensated for by applying a vacuum, allowing the remaining seawater to boil in the next stage, despite the reduced temperature. This procedure was then repeated in a series of steps, more than twenty stages in modern plants, resulting in a brine of around 35°C in the last stage.

Another consequence of the applied vacuum was a more or less oxygen free environment inside the evaporators, i.e. not more than some decades of ppb of oxygen. According to the textbook this oxygen free environment should be harmless from corrosion point of view and mild steel was a natural selection for the flash chambers, internals included. However, there were leaks, allowing oxygen to enter the evaporation vessels, especially during shutdowns, and corrosion was experienced, occasionally with a rate of several mm per year.

The remedies were to use a corrosion allowance of maybe 10 or even up to 20 mm, or to coat the internal surfaces with epoxy. In the early 1970s, i.e. 20 years later than in the pulp industry, stainless steel lining or wallpapering was introduced and for a period of close to 10 years the inner surfaces of flash chambers had the same appearance as the old kraft digesters, they looked like a patchwork quilt. The most common steel grade used for the lining was 1.4404 (316L), but also higher alloyed grades were used, e.g. for some of the later phases of the Jeddah plants the very highly alloyed grade 1.4439 (317LMN) was utilised.

Clad steel was introduced in the late 1970s and is still the most common concept used, mostly with 1.4404 cladding.

Solid austenitic stainless steel of type 1.4404 has also been used for some plants out of which Hidd in Bahrain is the largest, but there are other plants with a slightly modified process called "MSF once-through" where the feed to the first flash chambers is air saturated, implying far more aggressive conditions than in the conventional "MSF recycling" plants. A highly alloyed austenitic grade of type 6Mo, i.e. 254 SMO (1.4547, ASTM S31254), has successfully been installed in such plants in Chile.

However, solid duplex stainless steel has also entered this industry and the first MSF plant with 100% solid 2205 plate in the evaporators, i.e. the roofs, floors and lateral walls was erected in Libya in 2003, Figure 7. By using the high strength duplex grade instead of 1.4404 it was possible to reduce the gauge from 12 to 8 mm and instead of using 400 tons of stainless steel they required 280 tons only [4].

Fig. 7 The first MSF recycling plant with 100% solid 2205 evaporator vessels.

A second MSF plant with solid 2205 evaporator shells, the 500 m³/day Skikda plant, is being built in Algeria and water production is expected to start during 2005.

The Libya plant was described at the IDA (International Desalination Association) conference in Bahamas in October 2003 and at the same conference there was a paper by the Italian engineering company FISIA Italimpianti where they had looked upon the possibility to use solid 2205 instead of the more common concept with clad steel. Their comparison covered clad steel, not solid as for the Libyan plant, the size was three times larger than the Libyan plant, and their calculations ended in a cost saving of 1.2 million US-dollars if solid 2205 should be used instead of clad steel with 1.4404 cladding [5]. A remarkable number!

Civil engineering

Civil engineering is a fourth industrial sector where the interest for duplex stainless steel has grown tremendously during the last years. One driving factor is the high strength enabling lightweight constructions, but even more in combination with the stainless feature.

Maintenance of coated mild steel imply often a combination of shot peening and re-coating, processes that can be very complicated and costly for certain almost inaccessible components, e.g. bridges and flood gates. The use of duplex stainless steel for such applications is illustrated in Figures 8 – 10.

Fig. 8 Bridges for pedestrians and cyclists in Bilbao (left) and Stockholm (right) made of SAF 2304 and 2205 respectively.

Fig. 9 An old concrete bridge (left), which will be replaced by a new 2205 bridge (below) in Menorca.

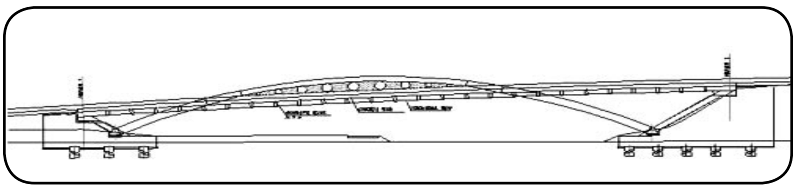


Fig. 10 Footbridge along a Norwegian mountain track (left) and a floodgate in Sweden (right), both made of LDX 2101.

Conclusions

1. The use of duplex stainless steel implies easier fabrication than for clad steel.
2. The use of duplex stainless steel implies lighter constructions than for clad steel.
3. The use of duplex stainless steel implies reduced investment costs compared with clad steel or solid austenitic stainless steel.
4. The use of duplex stainless steel implies reduced life cycle costs when compared with mild steel components where maintenance can be difficult to perform.

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