Duplex stainless steels for chemical tankers

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Abstract

Material selection for chemical tanks is of prime concern when considering building costs, and maintenance costs. This paper outlines why duplex stainless steels have been more and more selected instead of 316 LN or 317 LN grades for the erection of new chemical tankers. The main advantages of duplex stainless steels, including their resistance to different corrosion mechanisms, their high mechanical properties which allows the designer to reduce weight when properly used, and their good weldability are emphasized.
The paper gives also some practical advices when selecting duplex stainless steels, i.e. how to specify and how to weld them. Finally, some practical experience gained from the use of the material in marine chemical tankers is summarised.

1 Introduction

The number of products carried by chemical tankers increases continuously with time. The cargoes range from very aggressive solution like phosphoric acid, sulphuric acid to more complex compounds like molasses, fish oil, chemical products, lubricants, methanol or even wine. Some of the products are heated and may contain several quantities of highly corrosive elements like chloride, fluorides, combined with acids.
The steel used for the tanks must then be resistant to several mechanisms of corrosion in order to avoid contaminations effects of the cargoes as well as damages on the tanks. Furthermore, the steel must also be resistant to sea-water. To-day, material selection must also take into account the future needs which will include the transportation of again more sophisticated and possible corrosive products as well as more tight regulations concerning the protection of the nature.
In the past, for most of cargo tanks, austenitic stainless steels were selected. This included the 304 LN grade, but more often the 316 L or 316 LN with 2.5 or 2.75 Mo minimum.
Creusot-Loire was the first steel company to introduce duplex stainless steels for the erection of chemical tankers. This was the case in 1970, when Dunkerque Shipyard built the 3 chemical tankers (Zambeze, Zeebrugge and Zeeland), with UR 50 grade. Those ships have successfully been used in service. In that time, the production of duplex stainless steels was almost marginal and CLI was already the world leader in the manufacture of duplex stainless steels.
Since that time, steel industries have made continuous developments of their process, up to the present time. This had led to a significant improvement in the control of the residual elements such as oxygen, sulphur... while at the same time guaranteeing narrow composition range including that for nitrogen.
As will be seen below, the accuracy and reproducibility of the chemical composition enable the amounts of the two phases α and γ to be closely adjusted. Furthermore, increased control of nitrogen levels made it possible to improve the corrosion resistance and the high temperature stability of the duplex structure, particularly in the heat affected zones of welds. Finally, the reduction in the levels of residuals has resulted in a marked beneficial effect on the hot workability, making possible the production of wide plates.
All those improvements have also led to a significant reduction in production costs, making them more and more cost saving materials. This explains why they have increased in popularity.

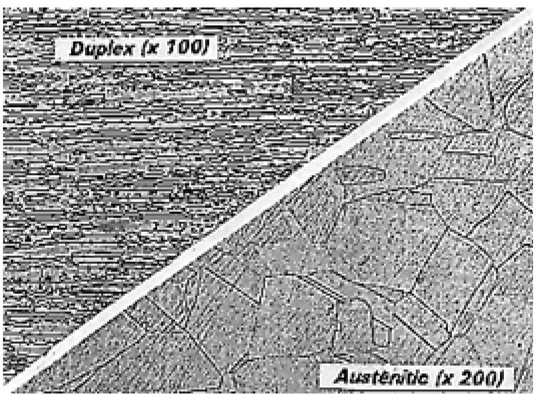

Figure 1.

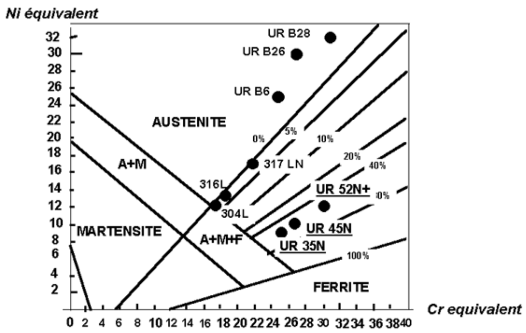

Figure 2. Ni – Cr equivalent.

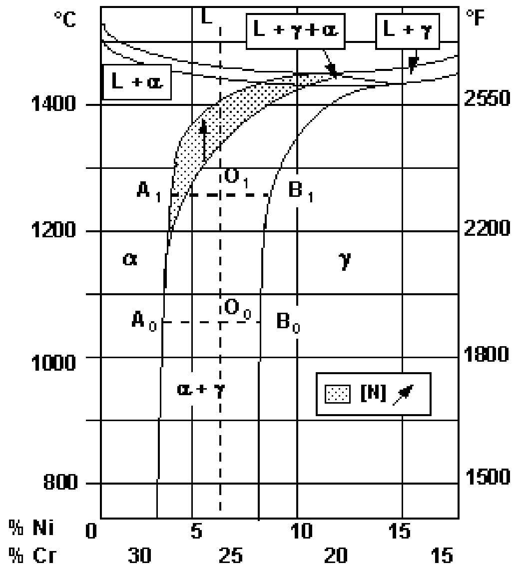

Figure 3. Schematic effect of nitrogen additions on the pseudo binary Cr-Ni 68Fe phase diagram.

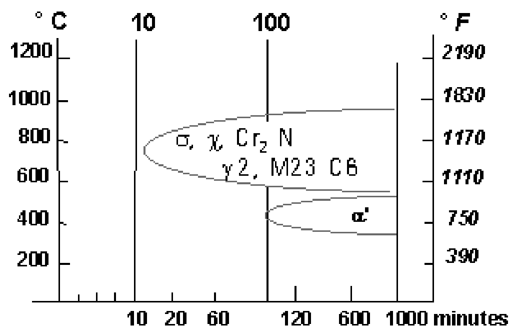

Figure 4. Typical time temperature precipitation diagrams for duplex stainless steels.

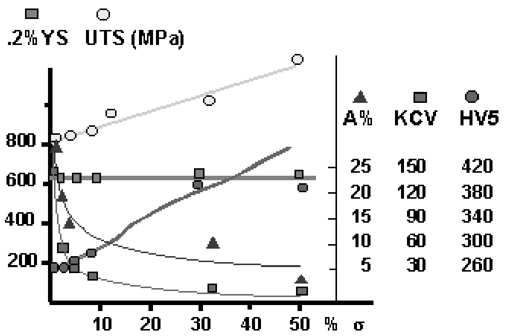

Figure 5. Mechanical properties of UR52N+ duplex alloy, as function of sigma phase precipitation by thermal ageing.

2 Duplex stainless steels compared to austenitic stainless steels

Figure 1 shows micrographs of both duplex and austenitic alloys. The duplex stainless steel has a balanced 50 α/ 50 γ microstructure obtained by controlled chemical analysis and heat treatment.

Figures 2 and 3 present phase diagrams of duplex alloys. It is observed that the duplex alloys have a lower nickel content while the chromium, molybdenum and nitrogen additions which contribute to the corrosion resistance properties, are high. Furthermore nitrogen additions, increase the structure stability of the duplex grades at high temperature.

Table 1 presents typical analysis of stainless steel grades. The PREN value = [%Cr]+3.3[% Mo]+16[%N] is also given. This index (PREN value) is the most commonly used in order to compare the corrosion resistance behaviour between the stainless steels.

Table 2 presents the mechanical properties of duplex stainless steels compared to them of the austenitic stainless steels. The yield strength of the duplex stainless steels is almost twice that of the austenitic grades.

Table 3 gives some allowable design stresses values, following several codes, for the erection of pressure vessels. Those results show clearly that thickness reductions may be considered with duplex grades when vessels are properly designed.

3 Duplex stainless steels and structure stability

Figure 4 presents typical time temperature precipitations diagrams for duplex stainless steels. An increase of molybdenum and chromium contents makes the alloy more prone to intermetallic phase precipitations. This is particularly the case for the 650–900°C temperature range where intermetallic phases like σ or χ are formed in the ferritic grains. This result, as observed in figure 5, in a sharp decrease of the mechanical properties.

This concerns particularly the toughness properties. With a σ content of 5%, the alloy may suffer from big losses in toughness as well as in corrosion resistance properties. When forming those plates containing 5% sigma phase, we can be faced to cracks formations particularly in the segregated areas. Fatigue life properties may also be affected.

CREUSOT-LOIRE INDUSTRIE aim is the production of hot rolled plates totally free of intermetallic phases. This is obtained by a close control of the chemistry, solidification process and solution annealing treatment performed on the most efficient equipments in the world. The plates are fully water quenched by immersion few seconds after a plate by plate heat treatment where the temperature and holding time are optimised for each treatment i.e. plate sizes and chemistry. Since more than 30 years, CREUSOT-LOIRE INDUSTRIE has developed the duplex grades because they are cost effectiveness, but always provided a high quality product. Duplex grades are less forgiven than austenitic stainless steels.

4 Duplex stainless steels and physical properties

Table 4 presents typical physical properties of stainless and structural steels. The most interesting characteristics of the alloys include:

- A low thermal expansion coefficient for duplex stainless steels when compared to that of the austenitic stainless steels. The thermal expansion coefficient is similar to that of C.Mn steels. This makes it possible to reduce thermal stresses when the cargoes carried are heated. As a result the number of expansion joints are limited.
- A thermal conductivity similar to that of austenitic stainless steels (slightly higher) but much lower than that of the structural steel (C.Mn steel).
- A strongly magnetic behaviour when compared to austenitic stainless steels, enabling the use of magnetic clamps during machining.

5 Duplex stainless steels and corrosion resistance properties

When considering the different corrosion mechanisms, i.e. general corrosion, pitting, crevice, stress corrosion cracking or corrosion fatigue resistance duplex stainless steel UR 45N performs better than austenitic 304L, 316LN or 317 LNM grades.

5.1 General corrosion resistance

5.1.1 Phosphoric acid

General corrosion resistance properties of duplex stainless steel 31803 (UR 45N, 2205) are generally much better than austenitic 316 and 317LN grade. Figure 6 presents the corrosion resistance properties of the duplex grade UR 45N of CLI when compared to 316L and 317LN grades in 54% P_2O_5 industrial solution. Temperature and chloride contents may be increased when considering duplex grades compared to austenitic stainless steels.

This is explained by the high chromium and molybdenum contents of the duplex grades. Duplex alloy UR45 is thus particularly well designed for phosphoric acid transportation even if chloride species are encountered.

5.1.2 Sulphuric acid

The behaviour of duplex UR 45N – 2205 is also particularly good when comparing the alloys for sulphuric acid transportation. In the case of diluted sulphuric acid solutions (when the cleaning operations occur) together with an increase of temperature – which always occur when the remaining acid is diluted with water – the duplex grade UR 45N performs very well when compared to the more classical austenitic grades. For the most concentrated solutions > 95% H_2SO_4 duplex alloy UR45N behaves as well as 316LN or 317LN grades (figure 7)

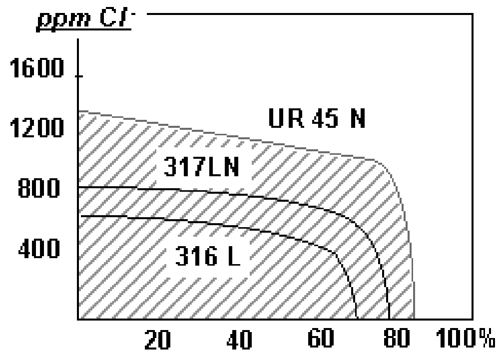

Figure 6. 54% P205 – H_2SO_4 < 4% Industrial solution.

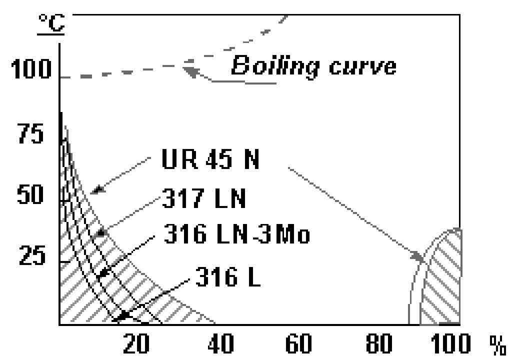

Figure 7. % H_2SO_4 = 2.000 ppm Cl^-.

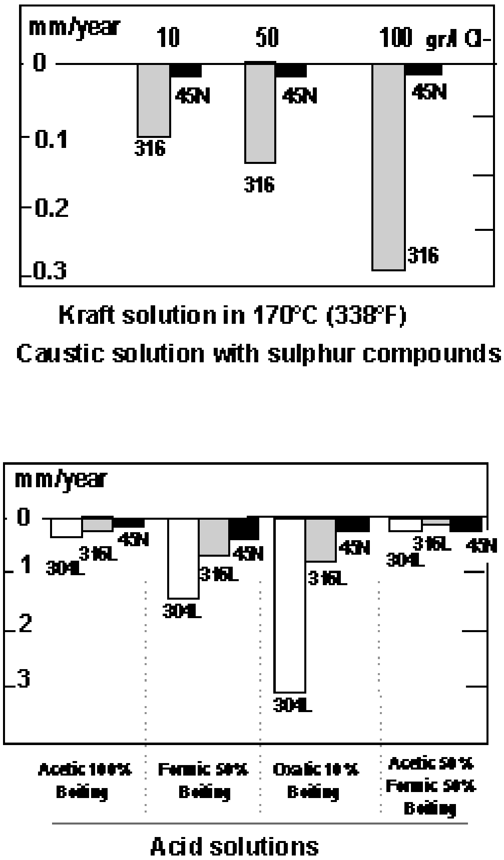

Figure 8. General corrosion resistance in organic and caustic solutions.

5.1.3 Organic acids and caustic media

General corrosion resistance in organic solutions as well as in caustic solutions are also increased when using UR45N grade instead of austenitic 316L grade as presented figure 8.

5.2 Localised corrosion resistance

Figures 9 and 10 present compared pitting and crevice corrosion resistance of austenitic 304L, 316L, 317LN grades and duplex grades. Without any doubt, the high chromium, molybdenum and nitrogen contents of the duplex grade UR 45N, or better UR 45N+, make those alloys very resistant to pitting or crevice corrosion. This makes them much more resistant in solutions containing chlorides, fluorides, as well as corrosion under deposits or in crevice like configurations. Such a resistance increases a lot the safety of the tanks under nominal in-service conditions. Extra-pollution of the cargoes, including seawater, are accepted (without any heating).
The use of 316 LN complementary product (bolts, nuts, clamps, pipes), combined with duplex grades is acceptable, but the 316 LN grade will be more prone to localised corrosion when considering heated chloride containing solutions.

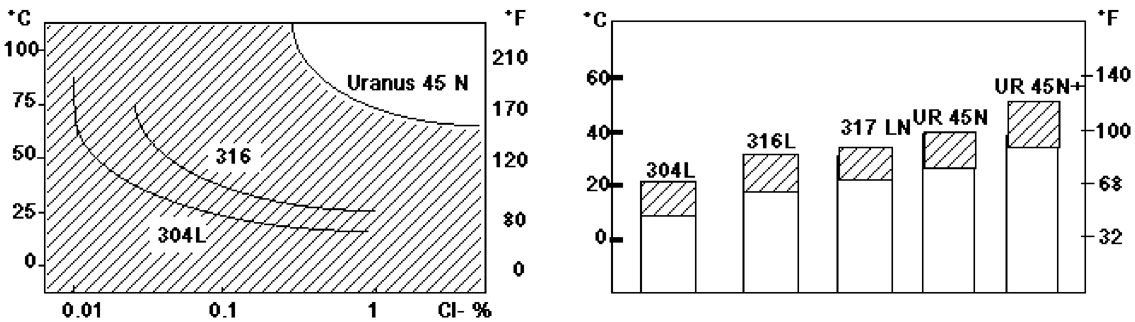

Figure 9. Pitting corrosion resistance.
(1) Sensitivity to pitting corrosion – Effects of temperature and chloride content.
(2) ASTM G48A test results – 10% Fe Cl_3 $6H_20$.

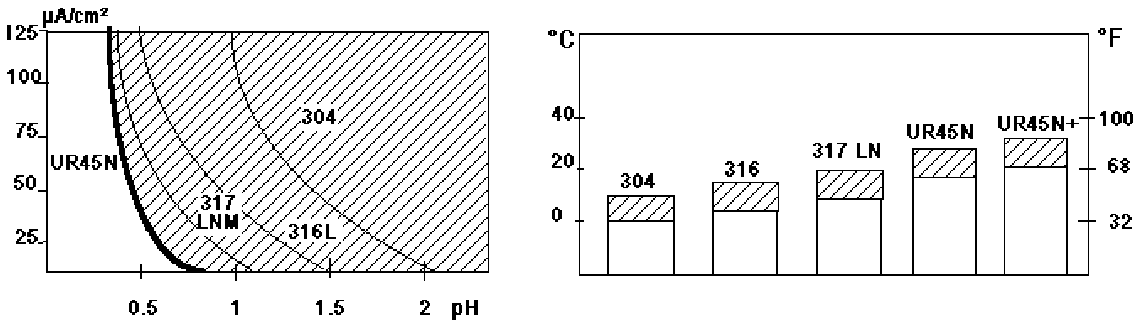

Figure 10. Crevice corrosion resistance.
(1) Depassivation conditions of several stainless steels – Solution : 30 g/l Na Cl 20°C.
(2) ASTM G78 – Crevice – 10% Fe Cl_3 6 H_20 solution.

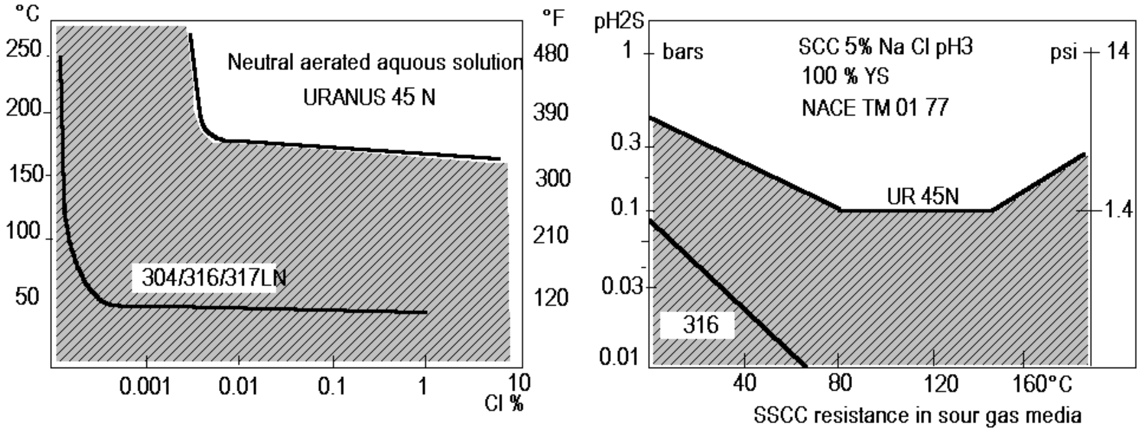

Figure 11. Stress corrosion cracking resistance.

The duplex stainless steels will also resist better when considering cleaning heated seawater operations between two cargoes. We thus recommend the use of duplex stainless steels for all complementary products.

5.3 Stress corrosion cracking resistance

Stress corrosion cracking may occur generally in heated solutions containing chlorides or other species like H_2S and when the plates are stressed. Residual stresses or thermal stresses may in those conditions, particularly on pitting initiation areas, assist the crack propagation.
When they occur, those damages are particularly dangerous and difficult to repair. In such conditions, here also duplex stainless steels present a very good behaviour (figure 11). They perform much better than the austenitic grades 304L or 316L. This is particularly due to their microstructure and low nickel content.

5.4 Corrosion fatigue resistance

Due to their high mechanical properties and two phases microstructure, fatigue properties of duplex UR45N grade are twice that of the 316 2.5Mo grade. That result has been obtained on sea-water rotating beam bending tests on smooth samples. Such a result is particularly interesting when considering the cyclic stresses induced on the tanks by the ocean (waves) – figure 12

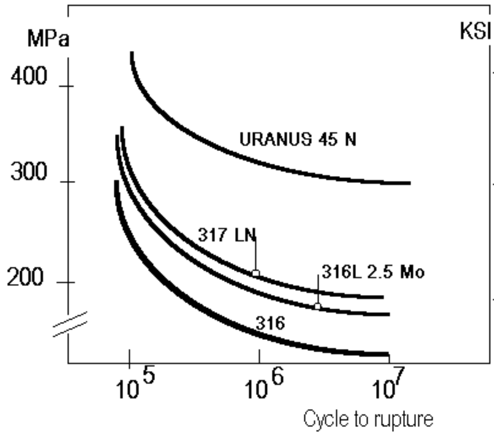

Figure 12. Synthetics sea-water rotating beam bending of smooth samples.

6 Duplex stainless steels and processing

6.1 Forming

UR 45N can be cold formed without any problem on all equipments suited to work stainless steels. Duplex stainless steels, due to their high mechanical properties, require more strength than austenitic stainless steels. Intermediate full annealing heat treatment at 1040/1080°C followed by water quenching is required for cold working deformations higher than 20%. The ductility of duplex grades are lower than that of austenitic stainless steels, but equivalent to that of normalised C.Mn steel which are often used on the yards. Hot forming should be carried out in a temperature range of 1150-950°C. A final full annealing heat treatment followed by rapid quench to restore the phase balance and corrosion resistance properties is requested (1040/1080°C – 1900/1980°F interval).

6.2 Pickling

Duplex UR45N grade can be pickled with the same solutions than that of alloy 316LN grade. Due to the higher corrosion resistance properties, the pickling time will be about twice that used for the 316LN grade. Typical pickling baths are 10% HNO_3-2% HF with a temperature which may be in-

creased up to 60°C. Final pickling operations on the yard are very important to restore to the grade, after weldings, all the properties, including the corrosion resistance properties of the alloy.

7 Welding

Duplex grades, like UR45N are now standard grades for most of the manufacturers. They can be welded following all of the processes, i.e. TIG-Manual or automatic, Plasma, MIG or manual arc welding with covered electrodes or submerged arc welding. CLI is ready to provide technical assistance staff for specific projects. The general guide lines are now well known. They include a control of the heat input which is almost close to 10 KJ/cm and must be optimised following the plate thicknesses in order to obtain a correct microstructure in both HAZ and weld metal. Welding energy should always be lower than 15 KJ/cm, interpass temperature lower than 150°C and better 120°C. Heat input will be particularly controlled for cross multipass weldings when multi HAZ may affect the microstructure, and thus the corrosion resistance behaviour, if not properly done.
Pre or post weld heat treatments are not recommended. Usual precautions including cleaning and degreasing of weld areas, protection against weld sputters must be taken to ensure corrosion resistance of finished products. Careful final descaling and/or cleaning of the welds is highly recommended. In order to optimise the properties, the weld consumables will be slightly over-alloyed in nickel and chromium + molybdenum.
Nitrogen contents of the base metal should be better controlled on the level of 0.16N in order to obtain a better stability in the HAZ. The nitrogen content of the weld should be controlled and limited to 0.22 maxi. Some additions of nitrogen (2%) in the shielding gas are recommended while hydrogen contaminations will be strictly avoided in order to obtain enough ductility of the welds and no cold crackings. Lower oxygen contents are also recommended in order to have the best properties including the corrosion resistance and ductility.
One more important advantage of duplex stainless steels, when compared to other 316LN grades: the yard may use only one filler material i.e. the same welding consumables may be used for welding duplex grade with duplex grade or duplex grade with structural steel! This makes the erection conditions much more easier and safer. The use of wrong welding consumable is no more possible (two products are used to weld 316 LN grade or 317 LN grade with structural steel in order to avoid martensitic structures).

8 Summary: why duplex grades instead of austenitic grades for chemical tankers

Table 5 gives a summary of the advantages of duplex UR45N grade when compared to 316LN 2.5 Mo mini.
Without any doubt, duplex stainless steels are the right choice for multipurposes applications for the new generation of chemical tankers. They offer more safety at a lower cost when tanks are properly designed.

9 How to specify duplex stainless steels for chemical tankers

Generally, when specifying stainless steels following general specifications (European or American standards) the steel industry provides heats with the minimum allowable level of alloying elements. i.e. for a 316L grade, the molybdenum content will be ≈ 2.00%. For austenitic stainless steels, this doesn’t affect the microstructure, but only the corrosion resistance properties. In order to obtain the required properties, heats for chemical tankers are then specified with a minimum level or molybdenum (2.5% or 2.75 or even higher).
When specifying duplex stainless steels following international standards, some more requirements are needed in order to obtain the right properties including an almost 50 α /50 γ microstructure, and enough corrosion resistance properties.
Table 6 gives the chemical analysis ranges for Euronorm and American standards for two duplex grades as well as typical CLI chemical analysis.
The most important point is the fact that when considering the lowest level of alloying elements for international codes both structure balance and corrosion resistance properties will be poor.
Nitrogen additions in the base metal furthermore increase the structure stability of the HAZ. For this reason, nitrogen additions will be at least 0.15% and 0.16% will be an aim. In order to obtain the best product, the following guidelines may be proposed when specifying duplex stainless steels.

9.1 Chemical analysis duplex 31803 / 1.4462

C ≤ 0.030 Ni 5/6.5
Si ≤ 0.75 Cr 21.5/23
P ≤ 0.030 Mo 2.7/3.5
S ≤ 0.005 N 0.15/0.20
Mn ≤ 2 PREN value = [%Cr] + 3.3[% Mo] + 16[%N] ≥ 34

9.2 Structure

The plates will be delivered in the solution annealed condition followed by water quenching. They will be free of intermetallic phase precipitation. The microstructure will be balanced in order to obtain an austenitic ratio included in the 47–57% range. The remaining being ferrite.

9.3 Mechanical properties

Mechanical properties will be specified following the tables 7 and 8.

9.4 Corrosion tests

The CPT temperature following ASTM G48A test will be at least 25°C.
At 25°C, no pits will be recorded after 24h. Immersion test and the weight loss will never exceed 1 $g/m^2/24$ h.

10 Some specific CLI assistance for chemical tankers orders

Technical assistance has always been a must when considering chemical tanker business. In CLI, a team of about 100 peoples is prepared to provide all technical advices needed. This includes a technical assistance for the forming and welding operations as well as a strong team involved in the evaluation of the corrosion resistance properties of stainless steels in several media. This experience has been centralised and a service known as 'SVP Corrosion' has been built up. An extensive 'cargo list' has been made available to help the owners in the selection of products to be carried with their chemical tankers. Special services and particular requests, including corrosion tests results for specific cargeos, are available.

11 Experiences

CLI duplex plates have been ordered for the three first chemical tankers projects and built in 1970 at the Dunkerque Yard. Since that time, more than 30 000 Tons of duplex stainless steels have been ordered to CLI for chemical tankers. This includes 7 deck

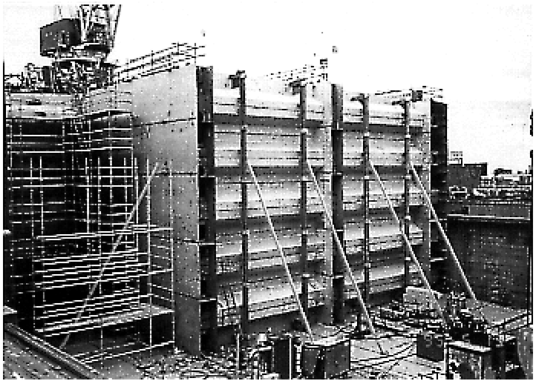

Figure 13. Erection stage at Danyard field. (Photo Danyard)

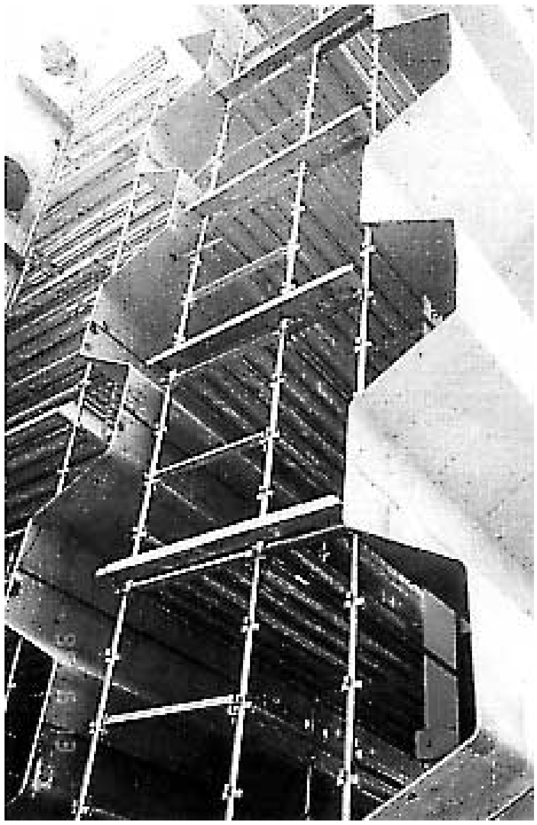

Figure 14. Erection stage at Danyard field. (Photo Danyard)

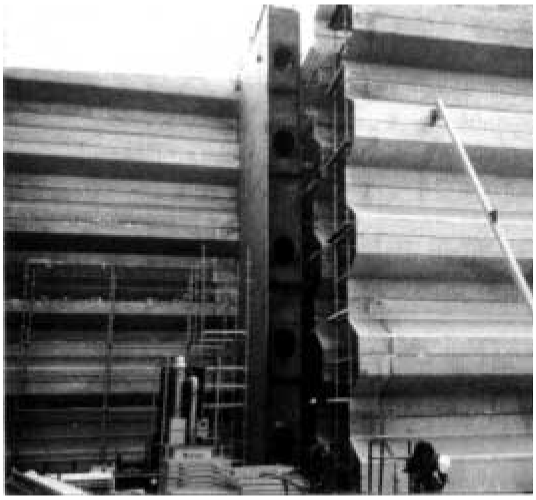

Figure 15. Erection stage at Danyard field. (Photo Danyard)

cargeos tanks for Korean ship yards, 7 ships for Stolt Nielsen order now in progress at Danyard, as well as part or the latest order placed again by Stolt Nielsen at the Ateliers et Chantiers du Havre (ACH – FRANCE). Figures 13, 14 and 15 present some of the erection stages of the Danyard field.

12 Conclusion

Duplex stainless steels are used since 1970 as cargo tank material. The first use was the building of three chemical tankers at Dunkerque shipyard with CLI grade UR50. Since that time, duplex stainless steel chemistry has been modified by increasing the molybdenum and nitrogen contents. This has made the duplex grades even more attractive and much more stable in microstructure. As a result, the nowaday main advantages of duplex stainless steel of the 2205 type – UR 45N – compared to austenitic 316LN 2.5Mo grade or 317 LN grade are

- Much better corrosion resistance, particularly when considering localised corrosion (pitting, crevice...).
- Much higher mechanical properties – almost twice of the austenitic grade which makes it possible to reduce weight when the vessels are properly designed.
- Much more compatible with C.Mn structural steel i.e. the thermal expansion coefficients are closed which result in lower thermal stresses.
- Only one weld product for duplex-duplex or duplex-CMn steel welds which makes the erection more efficient and safe.
- Chemical analysis less affected by nickel price escalation.

All those advantages make the duplex stainless steels cost effective and explain why they are now extensively used as cargo tank material. The only weak point is the need of high quality products i.e. free of intermetallic phases. This is the only way to obtain the optimum properties including corrosion resistance, formability as well as fatigue properties.
Such a quality of steel is a CLI standard and achieved tanks optimum equipments when considering melting facilities as well as heat treatment facilities. This is probably one of the main reasons why CLI is the world leader in the manufacture of duplex plates, and that more than 30 000 Tons of duplex grades have been placed with CLI in the chemical tank business.

References

1 J. Charles, 'Duplex Stainless Steels for Chemical Tankers' – Marichem – Cologne – November 1995.

		Ni	Cr	Mo	N	PREN
AISI 304 LN		10	18	-	0.15	> 19
AISI 316L		11.5	17	2	-	> 23
AISI 316 LN mod		11.5	17	2.5	0.15	> 27
AISI 317 L		13	18.5	3.2	0.08	> 30
AISI 317 LN		13	18.5	3.3	0.15	> 30
Duplex 32304	UR35N	4.2	23	0.2	0.10	> 24
Duplex 31803 (*)	UR45N	5.5	22	3	0.16	> 34
Duplex 31803(**)	UR45N$^+$	6	22.8	3.4	0.18	> 36

Table 1. Chemical analysis of duplex and austenitic stainless steels.

	Tensile test results				
	YS 0.2 %		UTS		El %
	MPa	KSI	MPa	KSI	
AISI 304 LN	290	42	590	86	40
Duplex 32304	400	58	600	87	25
AISI 316 LN 2.5 Mo	300	43	600	87	40
Duplex 31803	480	69	680	98	25
AISI 317 LN	310	44	600	87	40

Table 2. Mechanical properties of duplex and austenitic stainless steels.

Country	Code	Allowable stresses e > 5 mm - 20°C / MPa		Weight Savings
		316L	UR 45N	UR 45N /316L
USA	ASME VIII	115	155	26 %
F	CODAP 90, f.1	170	275	38 %
UK	BS 5.500	150	289	48 %
D	ADW 2	150	300	50 %

Table 3. Allowable design stress values for several pressure vessel codes.

Grade			Temperature		Young modus	Thermal expansion	Specific heat	Thermal conduction
Structure	CLI	AISI/UNS	°C	°F	GPa	10-6 K^{-1}	J kg^{-1} K^{-1}	Wm-1K^{-1}
		A 516	20	*70*	205	12.5	450	60
α	Soleil B2	410	20	*70*	205	10	480	22
γ	CLI 18.10	S 30400	20	*70*	205	16	520	16
	UR B6	S 08904	20	*70*	205	16	544	15
			20	*70*	205	13.5		17
$\alpha + \gamma$	UR 45N	S31803	100	*200*	195	14	500	18
			200	*400*	185	14.5	530	19

Table 4. Typical physical properties of stainless steel alloys.

	316 - 2.5 Mo mini Austenitics	317 LN Austenitic	UR 45 N Duplex	Advantages with Duplex UR 45 N
CHROMIUM MOLYBDENUM NITROGEN NICKEL PREN	17 % 2.5 % - 11.5 ≥ 27	18.5 % 3 % 0.12 % 13 ≥ 30	22 % 2.8 % mini 0.15 % mini 5.5 ≥ 34	More corrosion resistance - general corrosion - pitting - crevice - stress corrosion - fatigue corrosion less affected by nickel price evolutions
Y.S. 0.2 % YS. 1% Rm KV (+20°C)	> 300 MPa > 330 MPa > 600 MPa > 150	> 310 MPa > 340 MPa > 610 MPa > 150 MPa	> 470 MPa > 500 MPa 660-800 MPa > 100	More strength → less stiffeners → weight saving
THERMAL EXPANSION	16 10-6 / °K	16 10-6 / °K	13.5 10-6 / °K	Less thermal stresses More compatible with C.Mn steels
WELDABILITY	2 types of weld consumables	2 types of weld consumables	Only 1 type of weld consumable	No risks of mistakes with weld consumables when welding duplex

Table 5.

	Ni	Cr	Mo	N	PREN
UNS 32304	3/5.5	21/24.5	0.05/0.60	0.05/0.020	≥ 22
EURONORM 1.4862 X2CrNi23-4	3.5/5.5	22/24	0.10/0.60	0.05/0.20	> 23
UR 35N	4.2	23	0.2	0.10	> 24
UNS 31803	4.5/6.5	21/23	2.5/3.5	0.08/0.20	> 29
EURONORM 1.4462 X2CrNiMo22-5-3	4.5/6.5	21/23	2.5/3.5	0.10/0.22	> 29
UR 45N	5.5	22	2.8	0.16	≥ 34
UR 45N+	6	22.8	3.4	0.18	≥ 36

PREN value = [%Cr] + 3.3[% Mo] + 16[%N]

Table 6.

Steel quality	Thermic treatment	Tensile test							Other characteristics
		Rp 0.2 min (MPa) YS 0.2 (*KSI*)		Rp 1 min (MPa) YS 1 (*KSI*)		Rm N/mm²	El % min		
	Austenitizing	e≤5	5<e≤75	e≤5	5<e≤75		e≤5	5<e≤75	
Austeno-ferritic steel									
Z2CND22-05 AZ UNS 31803 1.4462 - UR45N	1040-1080°C	480 (*69*)	470 (*68*)	510 (*74*)	500 (*72*)	660-800 (*96-116*)	20	25	KV (+20°C) ≥ 100 J KV (-20°C) Transv. ≥ 60 J Long ≥ 80 J

(1) 1N/mm² = 1 MPa

Table 7.

Austéno-ferritic steel
Z3 CND 22-05 AZ - UNS 31803 - 1.4462

	Rp 0.2 - YS 0.2% (1)							Rp1 - YS 1% (1)						
°C→	50°	100°	150°	200°	250°	300°	350°	50°	100°	150°	200°	250°	300°	350°
°F→	*122°*	*212°*	*302°*	*392°*	*482°*	*572°*	*660°*	*122°*	*212°*	*302°*	*392°*	*482°*	*572°*	*660°*
MPa	420	360	340	320	310	290		455	395	370	350	340	330	
KSI	61	52	49	46	45	42		66	57	53	51	49	48	

(1) 1N/mm² = 1 MPa

Table 8. Mechanical characteristics according to the temperature.