

**SPECIALITY STAINLESS FOR SOLVING CORROSION PROBLEMS
IN THE OIL & GAS INDUSTRY**

***AÇOS INOXIDÁVEIS ESPECIAIS PARA A SOLUÇÃO DE PROBLEMAS NA
INDÚSTRIA DO PETRÓLEO E DO GÁS NATURAL***

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Abstract

Stainless steels cover a wide range of alloys, each with a particular combination of corrosion resistance and mechanical properties. Lean duplex stainless steel LDX 2101[®] combines high mechanical strength, with pitting corrosion resistance on par with standard austenitic grades and high resistance to stress corrosion cracking. At the other end of the spectrum, the high alloy content of the super austenitic grades 254 SMO[®] and 654 SMO[®] makes them the materials of choice for many very demanding applications.

Resumo

Os aços inoxidáveis cobrem uma vasta gama de ligas, cada qual com uma determinada combinação de resistência à corrosão e propriedades mecânicas. O aço inoxidável LDX 2101[®] (conhecido como Lean duplex) combina alta resistência mecânica, com resistência à corrosão por pite comparável ao dos tipos austeníticos padrão e alta resistência à corrosão sob tensão. No outro extremo do espectro, o alto teor de ligas dos tipos superausteníticos 254 SMO[®] e 654 SMO[®] os torna materiais de escolha para muitas aplicações muito exigentes.

Introduction

Stainless steels cover a wide range of alloys, each with a particular combination of corrosion resistance and mechanical properties. In oil and gas applications many of these stainless steel grades are used, depending on the demands of the particular service environment. To achieve good corrosion resistance several damage mechanisms have to be considered, such as uniform corrosion, pitting corrosion and environmentally-induced cracking. Different strategies are used for developing specialty stainless steels which have properties far superior to those of the basic 304L and 316L grades. This paper will focus the attention on some duplex and superaustenitic grades and their corrosion properties and applicability to the oil and gas industry.

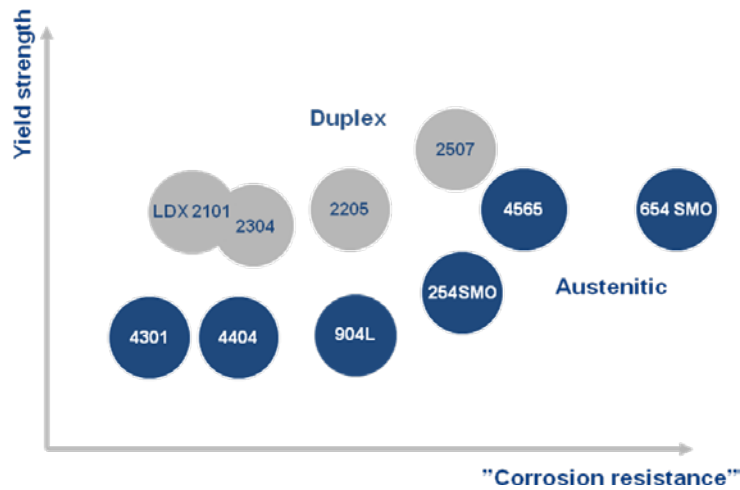


Figure 1. Austenitic and duplex stainless steel grades and their yield strength (R_{m2}) and corrosion resistance.

Stainless steel grades

The resistance to localized corrosion of stainless steels can be estimated from the steel composition using the pitting resistance equivalent ($PRE = \%Cr + 3.3x\%Mo + 16x\%N$). In Table 1 PRE values for some stainless steels grades are listed. The standard austenitic grades 304L and 316L contain 17-18% chromium, 8-10% nickel, and in the case of 316L also some molybdenum, and have relatively low strength and corrosion resistance, as illustrated in Figure 1. From this starting point two development directions have been pursued. In order to increase the corrosion resistance of austenitic grades higher contents of chromium, molybdenum and nitrogen are added. Two examples of such superaustenitic stainless steels are 254 SMO[®] (20Cr 18Ni 6Mo 0.2N) and 654 SMO[®] (24Cr 22Ni 7.5Mo 3Mn 0.5N), which have typical PRE-values of 43 and 56 respectively (see Table 1). The mechanical properties such as the yield strength also increase with increasing alloying content, this is especially noticeable in the case of 654 SMO[®] that has around twice the yield strength compared to standard austenitic grades (Table 2). Another way to increase the yield strength is to decrease the nickel content so that the microstructure becomes duplex (ferritic-austenitic). LDX 2101[®] (21.5Cr 1.5Ni 5Mn 0.3Mo 0.22N) is a lean duplex grade with comparable corrosion properties of standard austenitic grades ($PRE = 26$), but with twice the yield strength as shown in Table 2.

Table 1. Austenitic and duplex stainless steel grades

Grade	Typical chemical composition [wt%]						PRE ¹⁾	Micro-structure
	Cr	Ni	Mo	C	N	Others		
304L	18.1	8.1	—	0.02	—	—	18	Austenitic
316L	17.2	10.1	2.1	0.02	—	—	24	Austenitic
LDX 2101 [®]	21.5	1.5	0.3	0.03	0.22	5Mn	26	Duplex
2205	22	5.7	3.1	0.02	0.17	—	35	Duplex
254 SMO [®]	20	18	6.1	0.01	0.20	Cu	43	Austenitic
654 SMO [®]	24	22	7.3	0.01	0.50	Mn, Cu	56	Austenitic

¹⁾ $PRE = \%Cr + 3.3x\%Mo + 16x\%Mo$

Table 2. Mechanical properties (min values at 20°C according to EN 10088)

Grade	R _{p0.2} [MPa]	R _m [MPa]	A ₅ [%]
304L	200	500	45
316L	220	260	45
LDX 2101 [®]	450	650	30
2205	460	640	25
254 SMO [®]	300	650	40
654 SMO [®]	430	750	40

Corrosion properties of LDX 2101[®]

One way to evaluate the resistance to pitting corrosion in chloride environments such as seawater is by determining the critical pitting temperature (CPT) using the ASTM G 150 method. In Table 3 typical CPT values for some stainless steels are listed and according to these values LDX 2101[®] has a resistance to pitting intermediate between 304L and 316L. This is also confirmed using ASTM G48 Method E to determine the CPT in ferric chloride solution as shown in Table 3.

A particular characteristic for duplex stainless steels is their high resistance to chloride-induced stress corrosion cracking (SCC) compared to standard austenitic grades. There are a large number of test methods and environments used to assess SCC in stainless steels. Table 4 shows results from evaporative conditions in the Wick test (ASTM C692), and the Drop Evaporation test (DET, based on test method MTI-5), also from immersion testing of U-bends in concentrated calcium and sodium chloride solutions. The results demonstrate the superior resistance of LDX 2101[®] to SCC compared to standard austenitic grades in all these types of tests.

Materials intended for service in sour environments in the oil and gas industry also need sufficient resistance to sulphide stress cracking (SSC). SSC can be influenced by many factors such as the partial pressure of H₂S, the pH, chloride concentration and temperature, making it complex to define limits for when SSC occurs. In table 5 the resistance to SSC of LDX 2101[®] is compared to that of a 13Cr supermartensitic stainless steel. The tested material was girth welded using TIG with 2209 filler without any post weld heat treatment. 4-point bend samples were tested at 100% of the actual proof strength at room temperature under conditions shown in Table 5. The total pressure in this test was 100 kPa and the pH at the start of the test was 4.7. The results showed that all the 13Cr specimens cracked while none of the LDX 2101[®] specimens exhibited any cracking, even though tested at ten times higher H₂S partial pressure. Figure 2 shows a simple schematic illustration of limits of SSC resistance for LDX 2101[®] compared to some other stainless steels which is based on the results of this type of comparative investigations.

Lean duplex stainless steels are suitable for subsea oil and gas applications, such as flowlines and umbilicals in milder well conditions, as well as for topside applications where their combination of corrosion resistance and high mechanical strength can be utilized. They can be an alternative to standard austenitic grades such as 304L, supermartensitic stainless steels, 2205 duplex stainless steel and coated carbon steels.

Table 3. Typical CPT and CCT values using test methods ASTM G150 and ASTM G48 Methods E and F [1]

Grade	304L	316L	LDX 2101 [®]	2205	254 SMO [®]	654 SMO [®]
CPT ASTM G150	< 10	20	17	52	87	> 90
CPT ASTM G48 F	10	20	15	40	65	> bp ¹⁾
CCT ASTM G48 F	< 0	< 0	< 0	20	35	60

¹⁾bp=102.5°C

Table 4. Summary of SCC testing of some stainless steel grades [2, 3]

Grade	304L	316L	LDX 2101 [®]	2205	254 SMO [®]	654 SMO [®]
Wick test	SCC	SCC	No cracks	(No cracks)	No cracks	—
40% CaCl ₂ , 100°C	SCC	SCC	No cracks	No cracks	—	—
25% NaCl, b.p. ¹⁾	—	SCC	No cracks	No cracks	—	—
DET ²⁾	< 10%	< 10%	—	30%	80%	100%

¹⁾b.p. = boiling point (107°C)

²⁾Drop evaporation test: results expressed as the threshold stress, % of R_{p0.2} at 200°C

Table 5. SSC testing of 13 Cr SMSS and LDX 2101[®][1]

Grade	pH ₂ S	Cl ⁻	CO ₂	Temp.	No. of specimens	
	[kPa]	[mg/l]			Tested	Cracked
13 Cr	1	100000	bal.	RT	6	6
LDX 2101 [®]	10	100000	bal.	RT	6	0

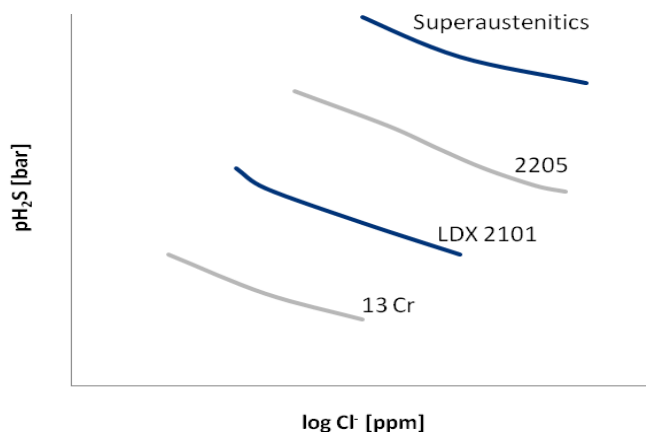


Figure 2. Schematic of limits of SSC resistance for some stainless steel grades.

Corrosion properties of 254 SMO[®] and 654 SMO[®]

Superaustenitic grades such as 254 SMO[®] and 654 SMO[®] have superior resistance to pitting corrosion compared to standard austenitic grades as shown in Table 3. The combination of high chloride content and the formation of biofilm or chlorination make natural seawater a very corrosive environment. Both 254 SMO[®] and 654 SMO[®] are candidates for sea water applications. 254 SMO[®] can be susceptible to crevice corrosion at temperatures above 30°C in chlorinated seawater, while the extreme corrosion resistance of 654 SMO[®] makes it an alternative to titanium and nickel-base alloys in many environments. For example, in loop tests in chlorinated (2ppm) seawater, performed at 45°C for 100 days, 654 SMO[®] flanges showed no signs of crevice corrosion [5]. When plate heat exchangers were tested in chlorinated seawater for 3 months, plates made of 654 SMO[®] did not suffer corrosion at 70°C, while plates in the Ni-base alloy N10276 suffered some crevice corrosion and transpassive attack at 45°C [6].

The superaustenitic grades also show excellent resistance to SCC and SSC as illustrated in Tables 4 and 6. Using severe evaporative conditions such as DET superaustenitic grades have a threshold level that can reach the yield strength. Table 6 shows results from SSC testing in NACE solution ((5% NaCl, pH 3, 1 bar pH₂S) of annealed and cold worked material at 25°C and 90°C. Under these conditions neither 254 SMO[®] nor 654 SMO[®] exhibit any cracking after 720 hours, even when cold worked up to 80%. As a comparison, extensive cracking was observed for 2205 material tested at 90°C at a lower H₂S level of 0.1bar. NACE MR0175 / ISO 15156-3 allows the use of both solution annealed and cold-worked 254 SMO[®] and 654 SMO[®] at any temperature up to 171°C in sour environments, if the partial pressure of hydrogen sulphide does not exceed 15 psi (1 bar), the chloride content does not exceed 5000 ppm and the hardness is not greater than HRB 95 for solution annealed material and HRC 35 for cold-worked material [7]. The superaustenitic stainless steels 254 SMO[®] and 654 SMO[®] are suitable for many oil and gas application where the very high corrosion resistance of these alloys is required. Successful applications include process piping, seawater piping, and condenser tubing.

Table 6. SSC testing of 4-PB specimens in NACE solution (5% NaCl, pH 3, 1 bar pH₂S) for 720 hours [4]

Grade	Cold work [%]	Stress [% of Y.S]	Temp. [°C]	Result
254 SMO [®]	0	100	90	No cracking
	40-80	90	25	No cracking
654 SMO [®]	0	100	90	No cracking
	0-80	100	25	No cracking

Conclusions

The lean duplex grade LDX 2101[®] combines excellent mechanical properties, with pitting corrosion resistance on par with standard austenitic stainless steel grades and superior resistance to stress corrosion cracking. The SSC resistance of LDX 2101[®] is significantly superior to that of 13Cr supermartensitic stainless steel.

The superaustenitic grades 254 SMO[®] and 654 SMO[®], show excellent corrosion resistance in a wide variety of media and find extensive use in seawater applications, demanding process fluids and sour service.

Both groups of stainless steels have an important place in the materials solutions for the oil and gas industry.

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