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A corrosion management and applications engineering magazine from Outokumpu Stainless

Dear Reader

There is no reason to pretend anything else, I missed the target last year and what was intended to become No 4 will instead be No 1 this year.

This means that also the first issue of Acom for 2006 will follow the same track as those of last year; it will cover duplex stainless steel, emphasising the newcomer LDX 2101®. As mentioned in previous issues, this grade has created a lot of interest amongst our customers, not least illustrated by a number of papers at the latest Stainless Steel World conference in Maastricht in early November. Three of the papers covering oil & gas applications, flow-lines and umbilical tubing, are presented in this Acom.

Non-treated natural gas can be corrosive to mild steel and conventional duplex grades have for many years been used for pipelines transporting the gas to a processing plant. However, less costly options have been looked for and one such has been "super-martensitic" stainless steel, i.e. martensitic grades with 13% of chromium, low carbon and some nickel and molybdenum. But the story told shows that such grades were not yet fully optimised prior to the installations and several failures have been reported also at the Stainless Steel World conference (papers No 5019 and 5045 by Makhmari & Behlani and by Woollin respectively).

Fortunately also remedies were proposed, illustrated by two of the papers in Acom. Alternatives to LDX 2101 were tested with good results, but the chemical compositions indicate a cost advantage of LDX 2101 by the lower contents of nickel and molybdenum.

The third paper describes another interesting application for LDX 2101, umbilical tubing for deep-water oil & gas developments.

Enjoy the reading and a Happy New Year!

Yours sincerely
Jan Olsson

Technical editor of Acom

Lean Duplex Grades as Longitudinally Welded Pipes for Linepipes in the Oil and Gas Business

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Abstract

Since some years lower alloyed austenitic-ferritic stainless steel grades have been developed, which are summarized in the "Lean Duplex"- family of alloys. Lean Duplex materials have been used so far mainly as plate material for construction of containers and vessels in the pulp and paper business as well as in architecture and construction.

As they are lower alloyed in nickel and molybdenum compared to standard duplex grades, lean duplex grades can offer economical interesting advantages combined with a higher degree of technical liability compared to supermartensitic stainless steels.

Aim of the present study was to figure out, if lean duplex grades are able to close the gap between supermartensitic steels and standard duplex stainless steels with regards to weldability, structural stability, mechanical properties as well as corrosion behaviour in typical media for the oil and gas industry.

Due to the fact, that there are different grades of "lean" duplex stainless steels commercially available, which significantly differ one from the other in terms of chemical compostion, the investigation covered three grades.

Plasma/TIG-, Laser- and Electronbeam-welding have been used for the industrial production of the longitudinal welded pipes made of Uranus 35N, Al 2003and LDX 2101. The complete characterization of these welds has been carried out according to the Shell and PDO specifications SIEP 97-5763, SP-1095, and SP-1189.

The results have proven the suitability of longitudinally welded pipes made from lean duplex grades for linepipes for sweet and slightly sour service.

Introduction

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As they are lower alloyed in nickel and molybdenum compared to standard duplex grades, lean duplex grades can offer economical interesting advantages combined with a higher degree of technical liability compared to supermartensitic stainless steels. Aim of the present study was to figure out, if lean duplex grades are able to close the gap between supermartensitic steels and standard duplex stainless steels with regards to weldability, structural stability, mechanical properties as well as corrosion behaviour in typical media for the oil and gas industry.

Due to the fact, that there are different grades of "lean" duplex stainless steels, which significantly differ one from the other in terms of chemical composition, the investigation covered three different commercially available grades.

Plasma/TIG-, Laser- and Electronbeam-welding have been used for the industrial production of the longitudinal welded pipes made of Uranus 35N, Al 2003 and LDX 2101. The complete characterisation of these welds has been carried out according to the Shell and PDO specifications SIEP 97-5763, SP-1095, and SP-1189.

The results have proven the principal suitability of longitudinally welded pipes made from lean duplex grades for linepipes for sweet and slightly sour service.

Comparison of the Nominal Chemical Composition of Supermartensitic Grades with Lean Duplex Grades and Dupex Stainless Steel wt..-%

Table 1

	C	Mn	Si	P	S	Cr	Ni	Mo	Cu	N
12Cr-4.5Ni-1.5Mo 13%Cr Medium Grade	≤ 0.015	≤ 2.0	≤ 0.4	≤ 0.03	≤ 0.002	12.0	4.5	1.5	0.3	≤ 0.012
12Cr-6.5Ni-2.5Mo 13%Cr High Grade	≤ 0.015	≤ 2.0	≤ 0.4	≤ 0.03	≤ 0.002	12.0	6.5	2.5	0.3	≤ 0.012
LDX 2101 UNS S32101 1.4162	≤ 0.040	5.0	≤ 1.0	≤ 0.040	≤ 0.030	21.5	1.5	0.5	0.5	0.22
AL2003 UNS S32003 LEAN DUPLEX	≤ 0.030	≤ 2.0	≤ 1.0	≤ 0.030	≤ 0.020	21.0	3.5	1.75	–	0.17
Uranus 35N UNS S32304 LEAN DUPLEX	≤ 0.030	≤ 2.0	≤ 1.0	≤ 0.030	< 0.002	23.0	4.4	0.25	0.25	0.11
DSS UNS S31803	≤ 0.030	≤ 2.0	≤ 1.0	≤ 0.030	≤ 0.020	22	5.5	3.0	–	0.14

Comparison of the chemical composition and mechanical properties of lean duplex grades with supermartensitic and standard duplex stainless steels

The typical chemical composition of different commercially available lean duplex grades is listed in table 1. It is important to note that "lean duplex alloy" does not specify a certain defined chemical composition, but implies, that these materials are just lower alloyed compared to standard duplex stainless steels. With regards to the chromium content all lean duplex grades are comparable to standard duplex stainless steels with chromium content varying between 21.5% and 23%. Therefore lean duplex alloys provide a higher passivity compared to the always slow (and sometimes fast) corroding supermartensitic 13%Cr medium and high grades.

There are important differences between different commercially available lean duplex grades with regards to the nickel content (table 1). LDX 2101 (UNS S32101, EN 1.4162) is with 1.5% Ni on the lower alloyed end of the lean duplex grades. This material takes the austenite stability out of the high manganese content of 5% in addition to 0.22% nitrogen. It appears, as if this alloy is not specifically designed for localised corrosion resistance, as it is showing 0.5% molybdenum only.

AL2003 (UNS S32003) is showing a two percent higher nickel content than LDX 2101 and is coming with 1.75% molybdenum much closer to the composition of standard duplex stainless steels with 5.5% nickel and 3% molybdenum. Manganese is below 2% and comparable to standard duplex stainless steels.

Uranus 35N (UNS S32304) as another type of the lean duplex family of alloys is with 4.4% higher in Nickel than Al2003. In contrast to the even higher chromium content of 23% in standard duplex stainless steels, this alloy is showing a very low molybdenum content of 0.25%.

Compared to the supermartensitic 13%Cr medium and high grades, LDX 2101 and Al2003 are lower alloyed in nickel by 1 to 3%, lower alloyed in molybdenum by 0.75% to 2% and higher alloyed in chromium by 8% to 10%. As nickel and molybdenum are the price dominating elements in stainless steels, a lower price can be expected compared

Comparison of typical mechanical properties of Supermartensitic Grades with Lean Duplex Grades and Dupex Stainless Steel Table2

	$R_{p0.2}$ MPa	R_m MPa	A_{50} %
12Cr-4.5Ni-1.5Mo 13%Cr Medium Grade	> 620	> 830	15
12Cr-6.5Ni-2.5Mo 13%Cr High Grade	> 600	> 820	15
LDX 2101 UNS S32101 1.4162 LEAN DUPLEX	> 450	> 665	30
AL2003 UNS S32003 LEAN DUPLEX	> 450	> 620	25
Uranus 35N UNS S32304 LEAN DUPLEX	> 450	> 620	25
DSS UNS S31803 1.4462	> 480	> 660	25

to supermartensitic stainless steels and standard duplex stainless steels combined with a corrosion resistance of standard austenitic stainless steels.

Table 2 is giving an overview about typical mechanical properties of supermartensitic 13%Cr medium and high grades compared with lean duplex grades and standard duplex stainless steel. Regarding the mechanical values it is to state, that all the three lean duplex have comparable yield, tensile strength and elongation values. Therefore differences in alloy design may have an impact on corrosion resistance, structural stability or weldability, but no impact on the mechanical properties as shown in table 2. $R_{p0.2}$ of supermartensitic 13%Cr medium and high grades exceeds the yield strength of the lean duplex stainless steel by 150 to 170 MPa, which are with 450MPa only 30 MPa below typical values as known from standard duplex stainless steels. The tensile strengths of the lean duplex stainless steels differ in the same order of magnitude from those of supermartensitic and standard duplex stainless steels. The elongation with 25% of lean and standard duplex stainless steels is far above the 15% as achievable in supermartensitic stainless steels.

Laboratory and industrial weldments of lean duplex stainless steels

Comparative welding trials of lean duplex stainless steels and industrial welding of lean duplex pipes in a fully automatic welding line with integrated heat treatment and calibration facilities have been carried out. Therefore sheet and strip material with a wall thickness of 4.8 mm, 6.7 mm, 14 mm, 16 mm and 20 mm has been used. The heat analysis of the material as well as the matrix of the different welding methods applied are given in tables 3 and 4. Longitudinal and girth welds have been produced by using the TIG-process, the combined Plasma-TIG process, the Laser-process as well as the Electronbeam-welding process. In cases, where filler wire was used, Thermanit 22/09 as overmatching filler wire was the filler of choice. The effect of temperature and annealing time during the subsequent heat treatment has been investigated. All welds have been metallographically fully characterized and all relevant mechanical properties including hardness and charpy impact values have been determined. In cooperation with the DN Institute in Clausthal and the ISSV in Hamburg, the corrosion behaviour tested in ASTM G48A was completed by sour service corrosion testing and SSRT testing.

Chemical composition according to the certificates in wt-% Table 3

Material	heat	C	Si	Mn	P	S	Cr	Ni	Mo	N	PREN*
Uranus 35N	F4111	0.026	0.42	1.32	0.03	0.0024	23.36	4.38	0.28	0.115	27.7
LDX 2101	831678	0.035	0.73	5.04	0.017	0.001	21.56	1.52	0,30	0.220	29.2
LDX 2101	813292	0.032	0.68	4.84	0.017	0.004	21.86	1.47	0.27	0.239	29.9
AL2003	813394	0.016	0.61	0.43	0.021	0.001	21.6	3.3	1.80	0.16	32.3

**%Cr+3.3%M+30%N*

Industrial welds at Lean Duplex materials

Table 4

Material	Semi-finished product	Finished product	Welding procedure	
LDX 2101 UNS S32101 1.4162	Strip 4.8 mm	Pipe Ø219.1 x 4.8 mm	Longitudinal weld	Plasma/TIG
				Laser
			Girth weld	TIG-Orbital
				Plasma
				WIG-Hand
	Sheet 6.7 mm	Welding sample W. th. 6.7 mm	Longitudinal weld	TIG
AL2003 UNS S32003	Strip 4.8 mm	Pipe Ø219.1 x 4.8 mm	Longitudinal weld	Plasma/WIG
				Laserstrahlschweißen
			Girth weld	WIG-Orbital
				Plasma
				WIG-Hand
	Sheet 14.0 mm	Pipe Ø168.3 x 14.0 mm	Longitudinal weld	Electron beam weld with TIG-cosmetic layers
	Sheet 16.0 mm	Pipe Ø219.1 x 16.0 mm		Electron beam weld with TIG-cosmetic layers

Results and Discussion

Fig. 1 is showing the beneficial effect of the post weld heat treatment on the tensile properties of welded AL2003 and LDX 2101. Samples have been prepared transverse to the rolling direction. Because of the solution anneal at 1075°C followed by rapid cooling in water, yield and tensile strengths of both alloys are lowered by approx. 60 MPa. Parallel to this the elongation is increased by 10 to 15%.

Fig. 1 Welded LDX 2101 und AL2003, tensile tests at room temperature, transverse to the rolling direction

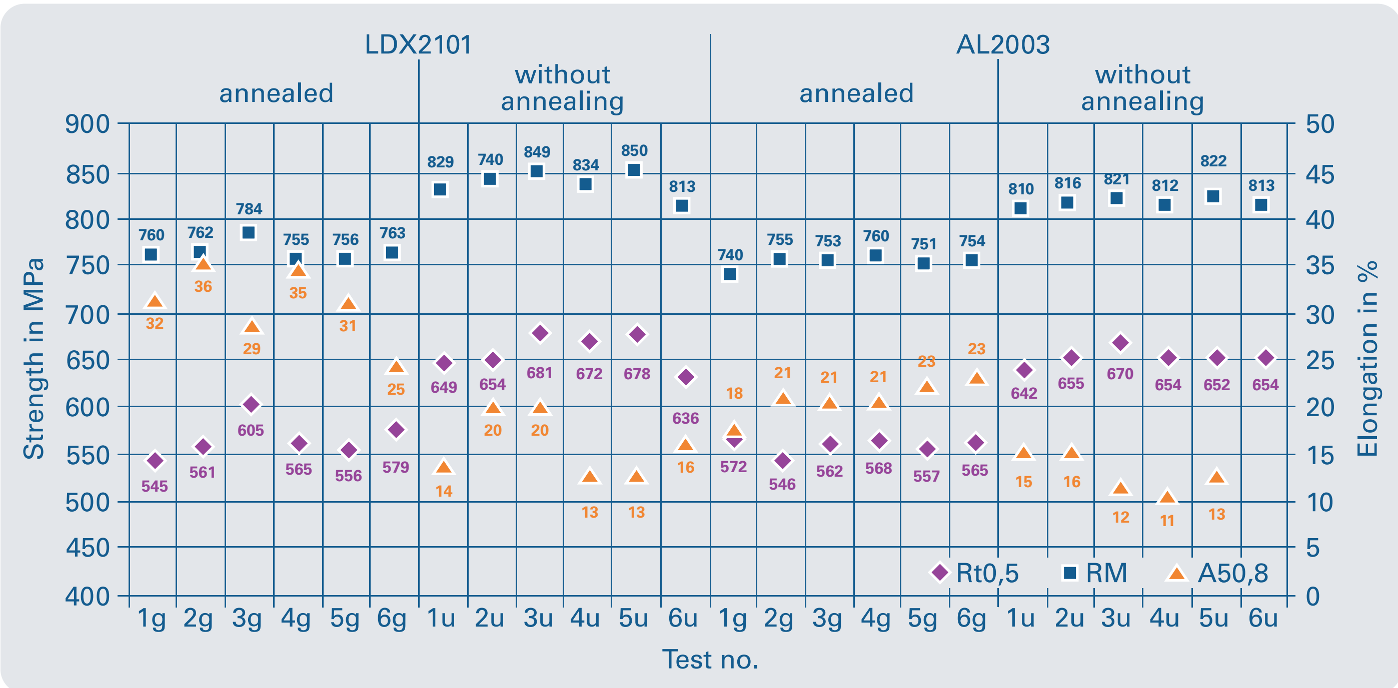


Fig. 2 to Fig. 5 show metallographic cross sections of Plasma/TIG-longitudinal welds of LDX 2101 and AL2003 welded with Thermanit 22/09 filler wire. The base metal, the heat affected zone and the weld show the typical binary austenitic-ferritic structure. The weld has been recrystallized during the in-line solution anneal. Especially in the weld of Al2003 the dendritic solidification structure is shown very clearly Fig. 5.

Fig. 2 LDX 2101 6g, metallographic cross section of the weld (elektro-lytically etched with NaOH)

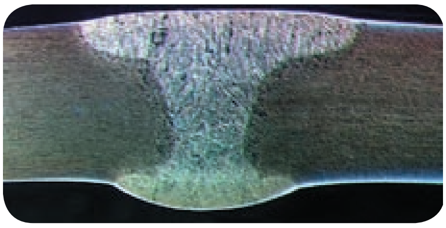


Fig. 3 LDX 2101 6g, metallographic cross section of the weld (electrolytically etched with NaOH)

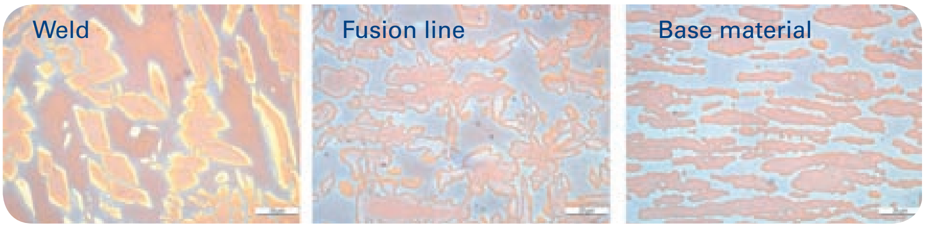


Fig. 4 AL2003 6g, metallographic cross section of the weld (electro-lytically etched with NaOH)

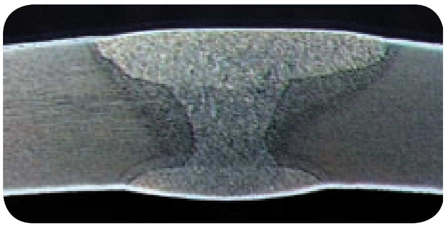
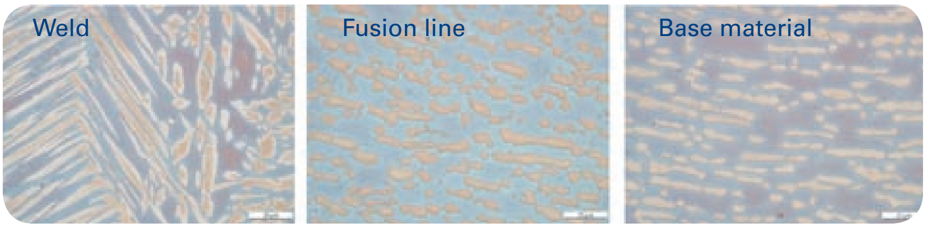


Fig. 5 AL2003 6g, metallographic cross section of the weld (electrolytically etched with NaOH)



Comparison of the results obtained with lean duplex grades and Shell specification SP-1095 for 13%Cr supermartensitic stainless steels -and SP 1189 for duplex stainless steels

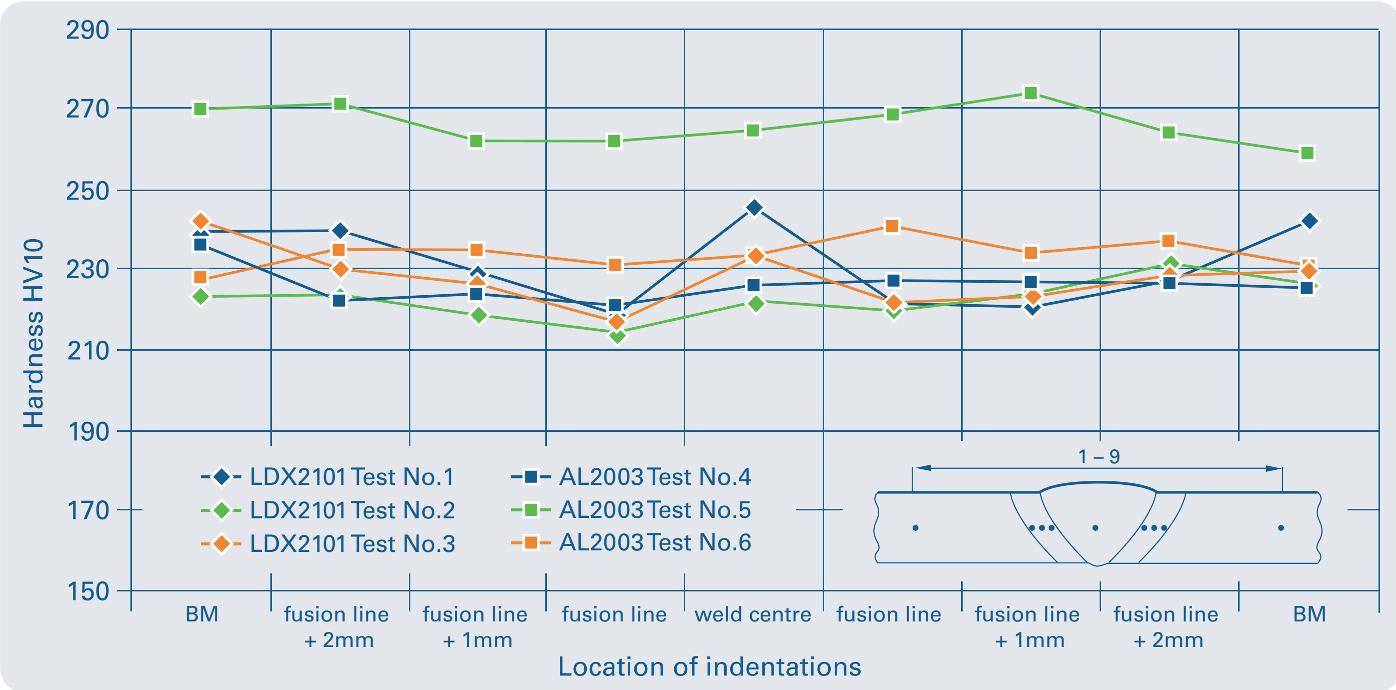
The summary of the results obtained with LDX 2101 and AL2003 according to SP-1095 and SP-1189 is given in table 5 and 6. In order to be able to evaluate the suitability of those alloys for flowlines in oil and gas applications, the comparison has been carried out between the requirements of existing specifications for line pipes made from supermartensitic stainless steels (SP-1095), standard duplex stainless steels (SP-1189) and the results obtained with LDX 2101 and AL2003. It becomes evident, that LDX 2101 and AL2003 are both promising candidates for the oil and gas business as their mechanical properties and corrosion behaviour can be positioned in between those of supermartensitic steels and standard duplex stainless steels.

SP-1095 specifies for supermartensitic steels yield strengths between 550 MPa and 700 MPa and SP-1189 specifies Rp0.2 > 448MPa for standard duplex steels. During tensile testing AL2003 and LDX 2101 show yield strength values, which are some MPa below the required values for 13Cr and fully in line with the requirements for standard duplex stainless steels.

For 13Cr supermartensitic steels no tensile values above room temperature are required, but AL2003 and LDX 2101 fit into the requirements of the duplex specification SP-1189 at 110°C and 200°C.

The maximum allowed hardness of 325 HV10 for 13Cr and 300 HV10 for standard duplex stainless steels never has been exceeded with both lean duplex grades, as can be

Fig. 6 HV10 of LDX 2101 and AL2003 girth welds



seen on the hardness values measured on girth welds on LDX 2101 and AL2003 in Fig.6. During guided bend tests no cracks had been observed neither in the root nor in the face. Charpy impact tests have been carried out using sub size specimens at –20°C. Charpy impact energies have been determined at the weld centre, the fusion line, the heat affected zone and the base material. The requirements of the minimum average and single charpy impact values according to SP-1095 and SP-1189 have been easily fulfilled by AL2003 and LDX 2101 in the heat treated condition.

In the welded and heat treated condition the amount of delta-ferrite should not exceed 60% as per SP-1189. This was easily met by LDX 2101. Al2003 was slightly exceeding 60% ferrite in the base metal, but this requirement now can be achieved because of some recent modifications on alloy chemistry.

The differences in alloy chemistry between LDX 2101 and Al2003 became very clearly during the localised corrosion test according to ASTM G48A. As LDX 2101 is of course not designed for high localised corrosion resistance and is a really "lean" alloyed duplex stainless steel with 21% Cr and 0.3% Mo only, the critical pitting temperature in $FeCl_3$-solution was far below the critical pitting temperature of AL2003 and standard duplex stainless steels. On the basis, that this study was carried out to prove if "lean duplex" materials may be a technically more reliable substitute of supermartensitic steels for an interesting price, the localised corrosion resistance of LDX 2101 compared to 13%Cr can be considered as sufficient. AL2003 was showing a critical pitting temperature of 22°C according to ASTM G48A. This appears as a very high value, caused by the relatively high amounts of chromium, molybdenum and nitrogen compared to LDX 2101.

From the results obtained during the industrial production of 8" pipes with 4.8mm wall thickness and the other weldments carried out acc. to table 4, it was concluded, that "lean duplex" grades as presented in table 1 are promising candidates for the oil and gas business in sweet and slightly sour services. This conclusion was confirmed by additional investigations regarding the behaviour of those materials during Electron Beam – and Laser - welding.

Plasma/TIG-welded pipes made from LDX 2101 tested acc. to specifications SP-1095 (13%Cr) und SP-1189 (Duplex) Table 5

Test (condition, method) and Property		Requirements acc to SP-1095	Results LDX 2101 (UNS S32101)		Requirements acc to SP-1189	
Chemical Properties	C [%] Mn [%] Si [%] P [%] S [%] Cr [%] Ni [%] Mo [%] N [%]	–	0.035 5.04 0.73 0.017 0.001 21.56 1.52 0.30 0.220		≤ 0.030 ≤ 2.00 ≤ 1.00 ≤ 0.030 ≤ 0.020 21.0 – 23.0 4.5 – 6.5 2.5 – 3.5 0.14 – 0.20	
	PREN Cr+3.3Mo+16N	–	26.1		≥ 34	
Tensile Test			longitudinal	transversal	minimum requirements	Enhanced properties
Base Material +20°C longitudinal / transversal	$R_{p0.2}$ [MPa] R_m [MPa] $A_{2''}$ [%] $R_{p0.2}/R_m$	550 - 700 ≥ 700 ≥ 20 ≤ 0.90	561 743 44 0.75	514 751 39 0.68	≥ 448 ≥ 620 ≥ 25 ≤ 0.90	≥ 480 680 – 880 ≥ 25 ≤ 0.90
Base Material +110°C longitudinal / transversal	$R_{p0.2}$ [MPa] R_m [MPa] $A_{2''}$ [%] $R_{p0.2}/R_m$	– – – –	485 648 36 0.75	448 662 32 0.68	– – – –	≥ 450 680 – 880 ≥ 25 ≤ 0.90
Base Material +200°C longitudinal / transversal	$R_{p0.2}$ [MPa]	–	420	419	–	≥ 310
All Weld Metal +20°C	$R_{p0.2}$ [MPa] R_m [MPa] $A_{2''}$ [%] $R_{p0.2}/R_m$	– – – –	545 704 37 0,77		≥ 448 ≥ 620 ≥ 25 ≤ 0.90	≥ 480 680 – 880 ≥ 25 ≤ 0.90
Transverse across Weld +20°C	R_m [MPa] $A_{2''}$ [%]	– –	763 25		≥ 620 –	680 – 880 ≥ 25
	Location of failure	base material	base material		–	–
Guided Bend Test	Face and root	no cracking	no cracking		no cracking	
Hardness Test	Base Material Weld / HAZ	≤ 325 HV10 ≤ 350 HV10	239 – 251 HV10 246 – 280 HV10		≤ 300 HV10 ≤ 300 HV10	
Charpy Impact Test at –20°C Specimen: ISO-V 10 x 3.3 mm	transverse	W | FL | FL+2 | BM	W | FL | FL+2 | FL+5 | BM		W | FL | FL+2 | FL+5 | BM	
	Average [J] Min. Single [J]	KV ≥ 14 KV ≥ 10	39 | 33 | 33 | 34 | 34 38 | 32 | 32 | 32 | 32		KV ≥ 24 KV ≥ 18	
	Individual Shear Area [%]	fibrous shear ≥ 50	100 | 100 | 100 | 100 | 100		fibrous shear ≥ 50	
Ferrite Content	BM and HAZ [%] Weld Metal [%]	–	51 – 54 48 – 51		40 – 60 30 – 60	
Corrosion Test	Visual Inspection	–	no pitting at +7.5°C		no pitting at +22°C	
ASTM G48A (24h)	Weight loss	–	0,050mg/cm² at +7.5°C		≤ 0,8 mg/cm² at +22°C	

Plasma/TIG-welded pipes made from Al2003 tested acc. to specifications SP-1095 (13%Cr) und SP-1189 (Duplex) Table 6

Test (condition, method) and Property		Requirements acc to SP-1095	Results AL2003 (UNS S32003)		Requirements acc to SP-1189	
Chemical Properties	C [%]	–	0.016		≤ 0.030	
	Mn [%]		0.43		≤ 2.00	
	Si [%]		0.61		≤ 1.00	
	P [%]		0.021		≤ 0.030	
	S [%]		0.001		≤ 0.020	
	Cr [%]		21.6		21.0 – 23.0	
	Ni [%]		3.3		4.5 – 6.5	
	Mo [%]		1.80		2.5 – 3.5	
	N [%]		0.16		0.14 – 0.20	
	PREN Cr+3.3Mo+16N	–	30.1		≥ 34	
Tensile Test			longitudinal	transversal	minimum requirements	Enhanced properties
Base Material +20°C longitudinal / transversal	$R_{p0.2}$ [MPa]	550 - 700	507	545	≥ 448	≥ 480
	R_m [MPa]	≥ 700	701	740	≥ 620	680 – 880
	$A_{2''}$ [%]	≥ 20	41	27	≥ 25	≥ 25
	$R_{p0.2}/R_m$	≤ 0.90	0.72	0.74	≤ 0.90	≤ 0.90
Base Material +110°C longitudinal / transversal	$R_{p0.2}$ [MPa]	–	444	472	–	≥ 450
	R_m [MPa]	–	641	655	–	680 – 880
	$A_{2''}$ [%]	–	33	28	–	≥ 25
	$R_{p0.2}/R_m$	–	0.72	0.72	–	≤ 0.90
Base Material +200°C longitudinal / transversal	$R_{p0.2}$ [MPa]	–	401	433	–	≥ 310
All Weld Metal +20°C	$R_{p0.2}$ [MPa]	–	485		≥ 448	≥ 480
	R_m [MPa]	–	674		≥ 620	680 – 880
	$A_{2''}$ [%]	–	39		≥ 25	≥ 25
	$R_{p0.2}/R_m$	–	0.72		≤ 0.90	≤ 0.90
Transverse across Weld +20°C	R_m [MPa]	–	754		≥ 620	680 – 880
	$A_{2''}$ [%]	–	23		–	≥ 25
	Location of failure	base material	base material		–	–
Guided Bend Test	Face and root	no cracking	no cracking		no cracking	
Hardness Test	Base Material	≤ 325 HV10	234 – 243 HV10		≤ 300 HV10	
	Weld / HAZ	≤ 350 HV10	237 – 252 HV10		≤ 300 HV10	
Ferrite Content	BM and HAZ [%]	–	60 – 64		40 – 60	
	Weld Metal [%]		53 – 61		30 – 60	
Corrosion Test ASTM G48A (24h)	Visual Inspection	–	no pitting at +25°C		no pitting at +22°C	
	Weight loss	–	0.037mg/cm² at +25°C		≤ 0.8 mg/cm² at +22°C	

Charpy Impact Test at –20°C Specimen: ISO-V 10 x 3,3 mm		Requirements acc to SP-1095 (W FL FL+2 BM)	Results W	Results FL	Results FL+2	Results FL+5	Results BM	Requirements acc to SP-1189 (W FL FL+2 FL+5 BM)
	transverse	W FL FL+2 BM	W	FL	FL+2	FL+5	BM	W FL FL+2 FL+5 BM
	Average [J]	KV ≥ 14	50	33	32	30	30	KV ≥ 24
	Min. Single [J]	KV ≥ 10	48	32	30	28	30	KV ≥ 18
	Individual Shear Area [%]	fibrous shear ≥ 50	100	100	100	100	100	fibrous shear ≥ 50

Summary and conclusion

Aim of the present study was to figure out, if lean duplex grades are able to close the gap between supermartensitic steels and standard duplex stainless steels with regards to weldability, structural stability, mechanical properties as well as corrosion behaviour in typical media for the oil and gas industry.

Plasma/TIG-, Laser- and Electronbeam-welding have been used for the industrial production of the longitudinal welded pipes made of Uranus 35N, Al 2003 and LDX 2101. The complete characterisation of these welds has been carried out according to the Shell and PDO specifications SIEP 97-5763, SP-1095, and SP-1189.

The results have proven the principal suitability of longitudinally welded pipes made from lean duplex grades for linepipes for sweet and slightly sour service.

Further investigations regarding the behaviour of longitudinally welded pipes in sour service and hydrogen loading during Slow Strain Rate Tests have completed this study and will be reported by Prof. Hoffmeister (ISSV) and Prof. Neubert (DN) elsewhere. It was proven that lean duplex stainless steels are not sensitive against hydrogen induced cracking in the base metal, whereas in the welded condition the hydrogen induced cracking resistance is not sufficient. Therefore further efforts on alloy development – especially with regards to the appropriate filler wires – is necessary.

Acknowledgements

The authors are grateful to the BMBF in Germany for the financial support of this work. Furthermore we like to say special thanks to John Dunn from Allegheny Ludlum for supplying the prematerial and the interesting discussions. We also thank Outukumpu and Industeel for supplying us with strip and sheet material. Finally we want to express our special thanks to Professor Hoffmeister from the ISSV in Hamburg and Professor Neubert from DN in Clausthal for the good cooperation and the SSRT-tests as well as the corrosion testing in sour service.

Effect of cathodic current densities and strain rates on SSRT fracture behaviour of Lean Duplex Stainless Steels and a 13%Cr Supermartensitic Stainless Steel in synthetic formation water

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Abstract:

The effect of hydrogen uptake on cracking of subsea flowlines has been frequently focussed on due to respective failures in particular, of partially cold deformed materials. Apart from specific sour service conditions hydrogen may be provided by inadequate cathodic protection. The present paper describes galvanostatic SSRT investigations in deaerated synthetic formation water of a high grade Supermartensitic 13%Cr Steel as compared to two Lean Duplex Stainless Steels. As a result, at constant strain rates, with increasing cathodic current densities the tensile ductilities of all investigated steels are reduced mainly within a range of between 0 and - 0,001 mA/mm^2. This is reflected by respective diffusible hydrogen contents determined at the broken test pieces after immersion in liquid nitrogen. The ductility reductions of the 13%Cr Supermartensitic Stainless Steel and the CrNiMo Lean Duplex Stainless Steel are nearly identical with a loss of around 50% of the fracture strain measured in the hydrogen free "dry" condition. The CrMnNi-alloyed Lean Duplex Stainless Steel shows a ductility drop of only 24% in the tangential and of 50% in the axial testing direction. With a constant current density of 0.0038 mA/mm^2 the fracture times for 50% ductility reduction of the Mn alloyed Lean Duplex Stainless Steels ranges considerably longer than the other steels. It is concluded that the application of Lean Duplex Stainless Steels with an appropriate chemical composition may be a resonable alternative for 13%Cr Supermartensitic Stainless Steels.

Introduction

Hydrogen assisted stress cracking of oil-and gas production equipment can be induced by hydrogen uptake in sour gas environments following local anodic acidification during pitting together with FeS-precipitation [1, 2] as well as from cathodic overprotection [3] in saltwaters. Regardless of the preceeding mechanism providing hydrogen ions and atoms, the susceptibility of structural materials to hydrogen embrittlement would be most favourably reflected by the ductility loss resulting from controlled galvanostatic hydrogen pick up during tensile testing. For this purpose constant load, constant strain and slow strain rate testing (SSRT) may be applied [4]. Out of these, the SSRT method provides quantitative material properties following final tearing. For consistent results, a crack relevant strain rate range has to be identified, secondary cracking should be reported and the tests should be monitored by continuous measurement of corrosion potentials [5].

As demonstrated in previous publications [6,7] crack relevant strain rates of the SSRT must be selected by testing at various strain rates and constant cathodic current densities supplying sufficient diffusible hydrogen to the test pieces. From such testing the time-strain-fracture limit (TSF) is established typical for materials subjected to the given mechanical and electrochemical conditions.

Evaluation of material susceptibility to hydrogen cracking thus requires two test series:

- Constant current loading applying various strain rates
- Constant strain rate testing with various cathodic currents.

With the background of recent failures [8] of a Supermartensitic Stainless Steel (SMSS) in the subsea environment the present investigation compares the mechanical behaviour of such a steel to that of two alternative "Lean" Duplex Stainless Steels (LDSS) which may provide a comparable economy.

Experimental Procedure

For the investigation the steels X6CrNiMo12 6 2 (SMSS), X3CrNiMo 22 3 2 (S32001) and X3CrNiMn22 2 5 (S32101), both LDSS, were selected according to table 1. Tensile subsize test pieces for SSRT with 3.0 mm testing diameter and 25.4 mm test length were machined in axial and tangential direction from the pipe materials. Prior to tangential test piece machining, the pipe plates were flattened and subsequently heat treated 630°C/30 min. (SMSS) respectively 1050°C/ H_2O (LDSS) for restoring the original material properties.

Properties of investigated materials Table 1

Heat treatments

material	plate thickness (mm)	heat treatment
X6 CrNiMo 12 6 2	20	630°C/30min/air
X3 CrNiMo 22 3 2	5	1070°C/water
X3 CrMnNi 22 5 2	5	1050°C/water

Chemical composition (%)

	C	Mn	P	S	Si	Cu	Ni	Cr	Mo	Al	N
X6 CrNiMo 12 6 2	.006	1.87	.021	.0009	.29	.47	6.49	11.6	2.33	.007	.009
X3 CrMnNi 22 5 2	.035	5.04	.017	.001	.73		1.52	21.56	.30		.22
X3 CrNiMo 22 3 2	.016	.43	.021	.001	.61		3.3	21.6	1.80	.16	

Mechanical properties (Mpa,%)

	Rm lg	Rm tg	$Rp_{0.2}$lg	$Rp_{0.2}$tg	A50 lg	A50 tg
X6 CrNiMo 12 6 2		883		735		46
X3 CrMnNi 22 5 2	764	725	560	564	40	33
X3 CrNiMo 22 3 2	720	767	550	550	37	31

Composition of synthetic formation water, mg/l Table 2

$SrCl_2$	$BaCl_2$	KCl	$CaCl_2$	$NaHCO_3$	NaCl
127	144	1048	942	1446	30145

The axial test pieces were tested in the as delivered state. For evaluation of test piece diameter effects such of 3.8 mm were also included for the SMSS. Some tests were additionally carried out at aerated conditions.

The synthetic formation water had the composition given in table 2. The tests were conducted in a sealed glass cell. Prior to start, the test solution was deaerated by argon to an oxygen level of below 0.01 mg/l and continuously purged during the test time. Testing temperature was 25°C. Corrosion potentials versus an Ag-AgCl reference electrode were continuously monitored.

For the slow strain rate tests two computer controlled 100 kN tensile testing machines provided strain rates down to 10^{-8} 1/s. The test pieces were partially masked to provide a defined nominal surface of 420 mm^2 for current charging. Following a test, one part of the broken test piece was immediately quenched in liquid nitrogen and subsequently subjected to diffusible hydrogen determination by the gas carrier method.
The following test series were carried out:

1. effect of current density on fracture strain at constant strain rate of 5.14E-06 1/s
2. effect of strain rates at constant current density of 0.0038 mA/mm2

Further evaluation was carried out by microscopic and SEM investigation of fractured test pieces.

Results and discussion

Test series 1

SMSS

At the constant strain rate of 5.14E-06 1/s increasing cathodic current densities provide increasing diffusible hydrogen contents up to 1.6 Nml/100g Fe to the X6CrNiMo 12 6 2, figure 1. The observed scatter of the results covers both the aerated and deaerated conditions as well as different test piece diameters. Figure 2 demonstrates the respective

Fig. 1 Effect of current density on diffusible hydrogen of X6CrNiMo12 6 2 at ε= 5.14E-06 1/s

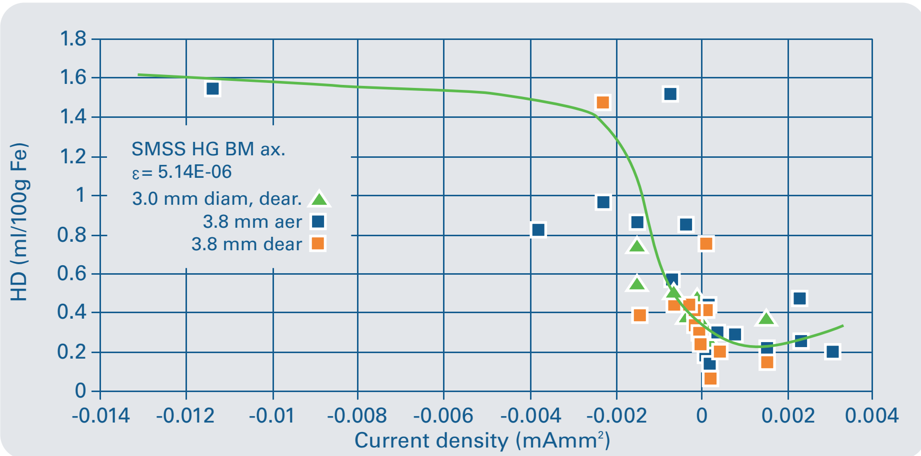
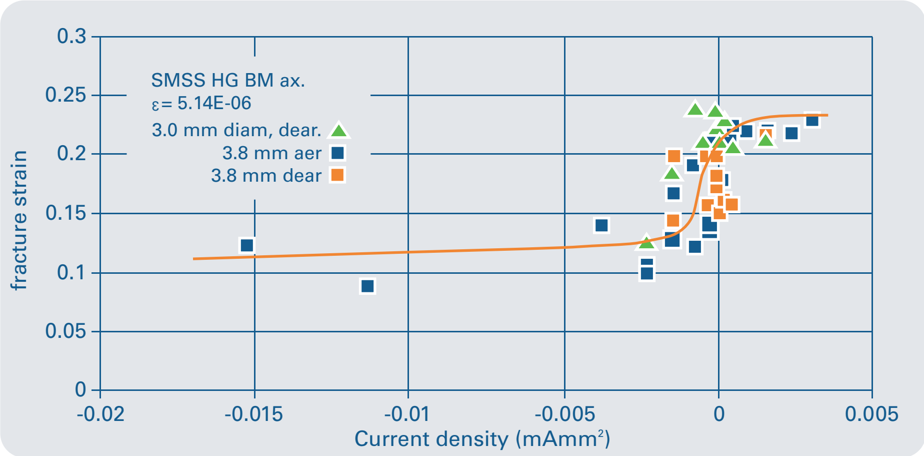
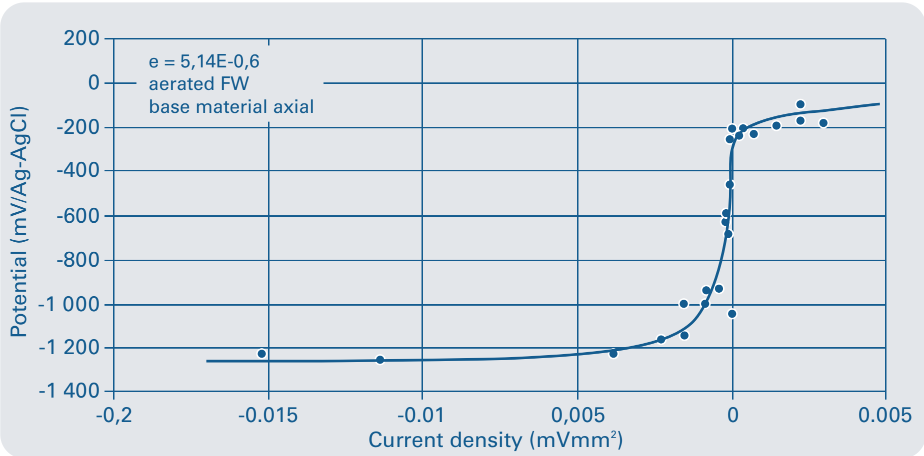


Fig. 2 Effect of current density on fracture strain and potentials of X6CrNiMo12 6 2 at ε = 5.14E-06 1/s





axial tensile ductility transition from anodic to cathodic conditions by reduction from a fracture strain of 0.25 to a plateau of about 0.1 at high cathodic current densities. At the same time the measured potentials drop from about -100 mV to -1200 mV. The SMSS thus looses about 60% of its original ductility in the axial to the pipe direction.

In figure 3 the effect of cathodic charging on ductility of the X6CrNiMo 12 6 2 is clearly visualized by reduced plastic necking and secondary cracking of the test pieces.

Fig. 3 X6CrNiMo 12 6 2 fracture at ε = 5.14E-06 1/s

LDSS

For the X3CrNiMo 22 3 2 figure 4 shows a similar hydrogen pick of the 3 mm diameter test pieces by increased cathodic loading up to 1.5 Nml/100g Fe. With an original axial fracture strain of 0.38 the ductility drops to 0.2 at higher cathodic current densities, while, the measured potentials drop from about 600 to -800 mV. This LDSS looses about 47% of its original ductility in the axial testing direction. The tangential testing direction reveals a fracture strain drop from 0.33 to 0.16 providing a respective ductility loss of 51%.

The reduction of ductility by cathodic currents is visible in figure 5 with reduced necking and increased secondary cracking at negative current densities.

In figure 6 the Mn-alloyed X3CrMnNi 22 5 2 picks hydrogen up to similar levels as compared to the other steels, i.e.1.5 Nml/100g Fe. Testing in axial direction demonstrates a 50% fracture strain drop from 0.6 to 0.3 with the potentials dropping from -200 to -750 mV at increased cathodic current densities. The tangential testing results are significantly lower and demonstrate a ductility loss of 29% represented by a respective drop from 0.37 to 0.26 of the fracture strains.

Again the effect of cathodic hydrogen charging on plastic deformation of the test pieces is visualized by figure 7.

It should be mentioned that the obtained diffusible hydrogen contents may not represent the levels originally present at the failure time of the test pieces. However, they reflect the qualitative effect of increased cathodic charging during the continuous straining process, which is in agreement to respective literature results [9].

Fig. 4 Effect of cathodic charging on diffusible hydrogen, fracture strain and potential of X3CrNiMo 22 3 2 at ε = 5.14 E-06 1/s

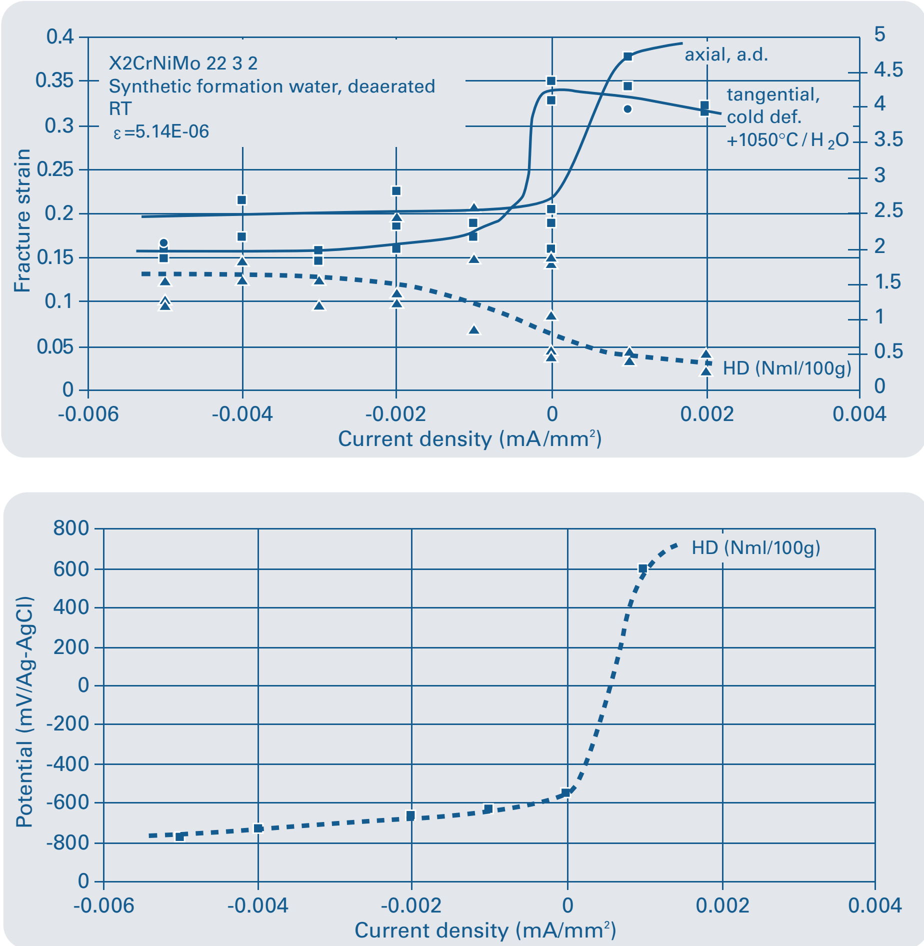
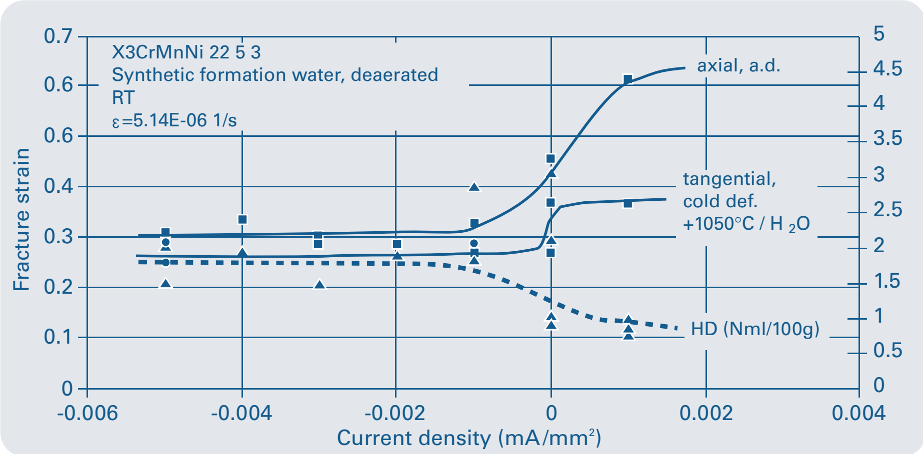


Fig. 5 X3CrNiMo 22 3 2 fracture at ε = 5.14E-06 1/s

Fig. 6 Effect of cathodic charging on diffusible hydrogen, fracture strain and potential of X3CrMnNi 22 5 2 at ε = 5.14 E-06 1/s



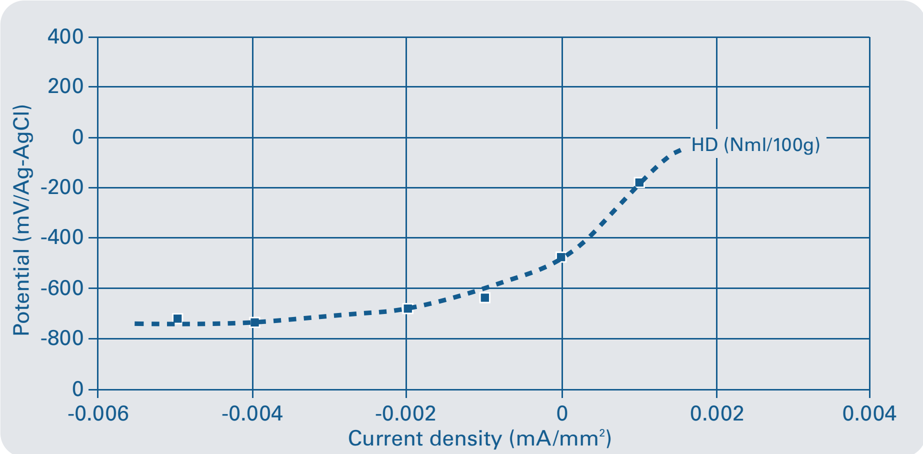


Fig. 7 X3CrMnNi 22 5 2 fracture at ε = 5.14E-06 1/s

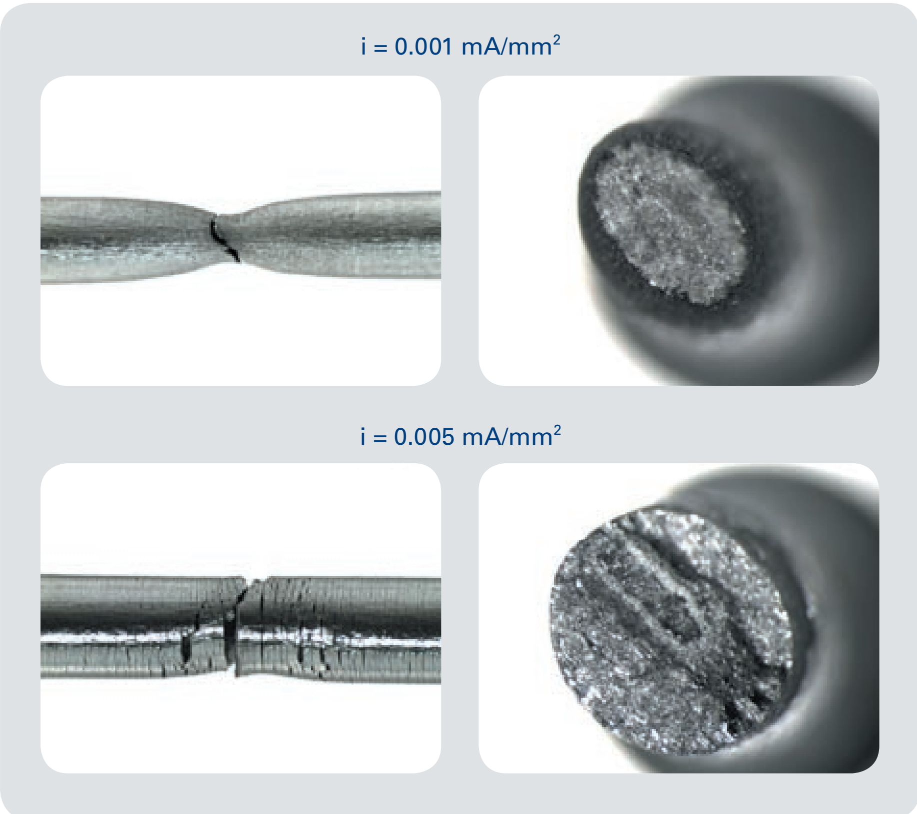
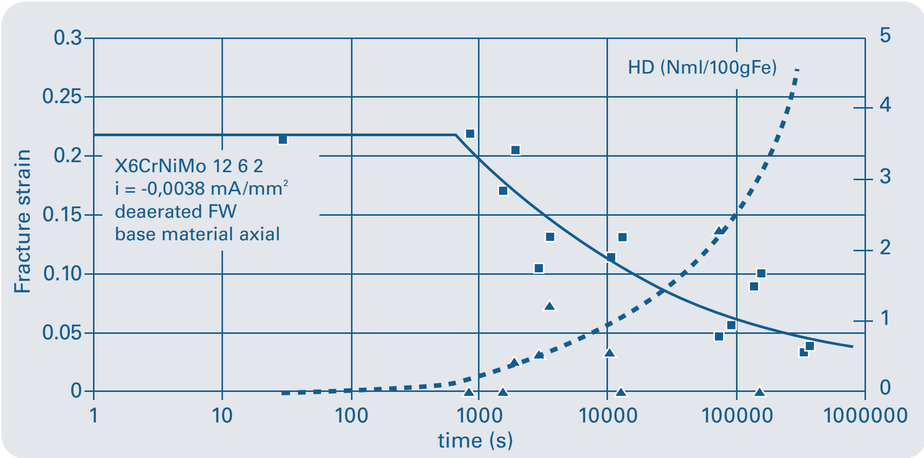


Fig. 8 TSF diagram for X 6CrNiMo 12 6 2 at i = - 0.0038 mA/mm² axial testing direction



Test series 2

SMSS

The SSRT at constant current density of - 0.0038 mA/mm² and variable strain rates provides the time-strain-failure (TSF) limit depending on hydrogen uptake of the tensile test pieces, figure 8. For the X6CrNiMo 12 6 2 the fracture times above 1000 s are clearly affiliated with significant reduction of fracture strains following from increasing hydrogen contents up to 30 Nml/100g Fe.

The failure limits are not significantly different for the axial and tangential testing direction, figure 9.

The embrittling effect of increasing exposure times to hydrogen charging at constant current density is also obvious from the fracture modes shown in figure 10. Increasing times provide less necking and more secondary cracks. Also by SEM observation, the change of fracture topography from ductile to brittle fracture surface is evident, figure 11.

Further microscopical investigation indicates no significant differences of the annealed martensitic microstructure between tangential and axial test directions in figure 12 for this steel.

Fig. 9 TSF diagram for X6CrNiMo 12 6 2 at i = - 0.0038 mA/mm² tangential testing direction

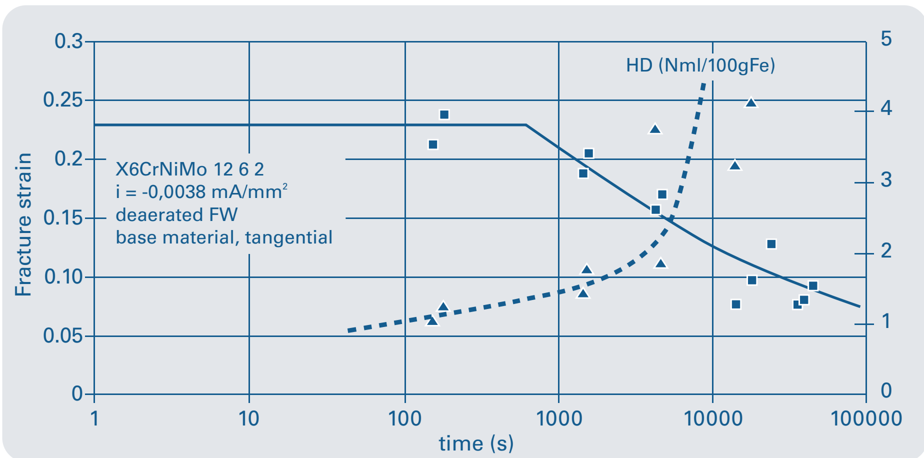


Fig. 10 X6CrNiMo 12 6 2 fracture at i = – 0.0038 mA/mm²

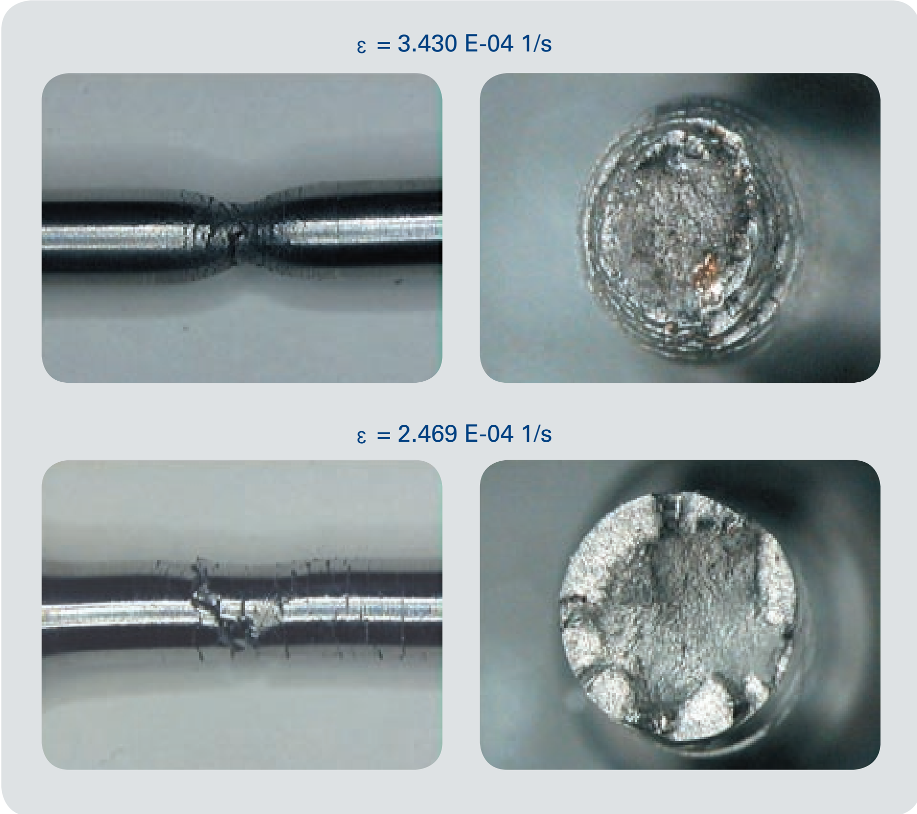


Fig. 11 X6CrNiMo 12 6 2 fracture at i = – 0.0038 mA/mm²

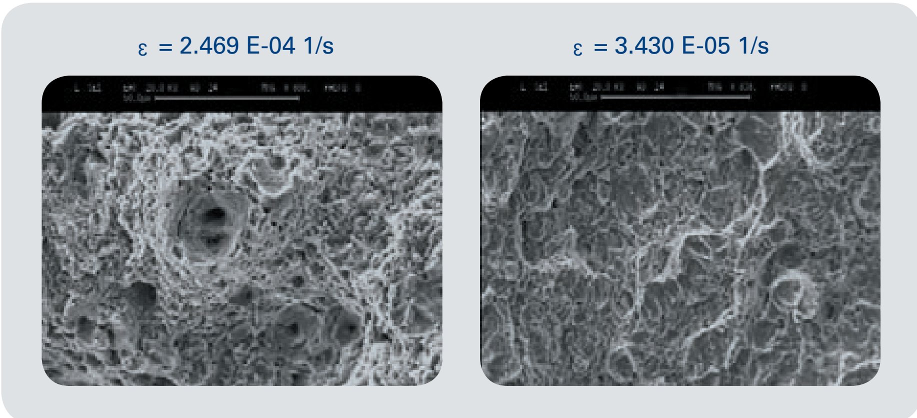


Fig. 12 Microstructure of X6CrNiMo 12 6 2 (500:1)

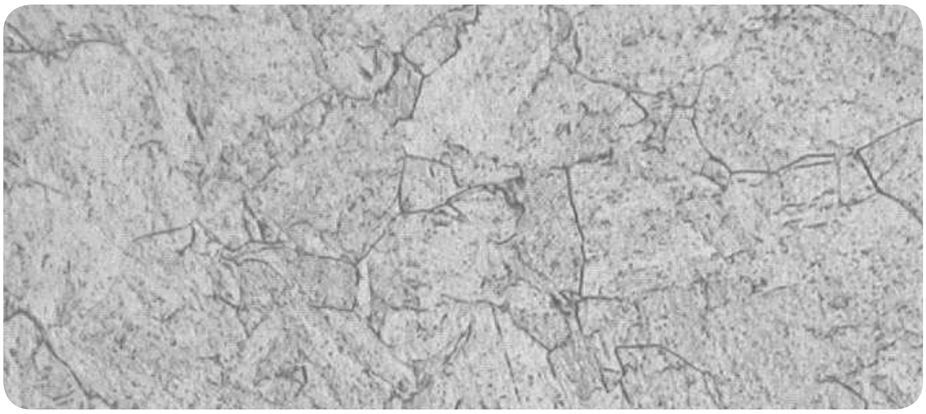
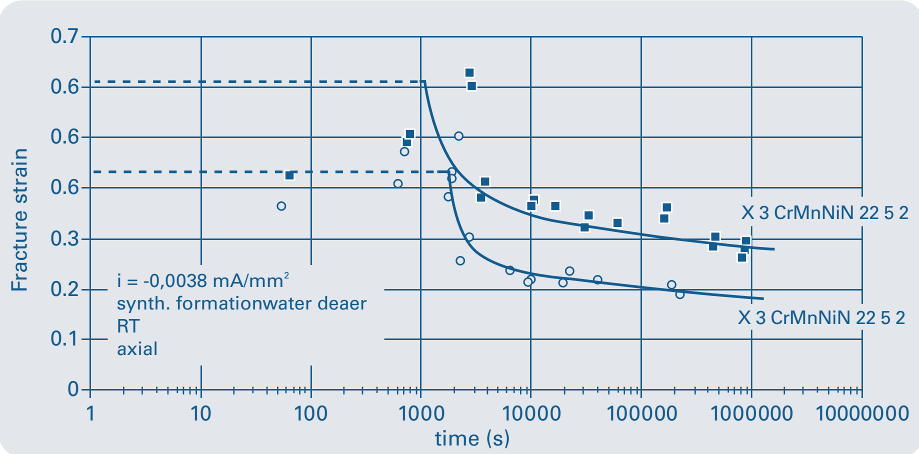


Fig. 13 Time-Strain-Fracture diagram of X3CrMnNi 22 5 2 and X3CrNiMo 22 3 2 axial, i = - 0.0038 mA/mm²



LDSS

The TSF failure limits of both lean duplex stainless steels in axial testing direction are shown together in figure 13. It is obvious that as in test series 1, the Mn-alloyed steel exhibits higher fracture strains also under embrittling conditions of the increased hydrogen contents following from longer exposition times to constant cathodic currents of -0.0038 mA/mm².

As compared to the supermartensitic stainless steel both duplex stainless steels maintain higher ductility in particular, at longer testing times while slowing down the hydrogen induced reduction of fracture strains. Thus, for fracture times of about 10^6 s (277.7 h) the X3CrMnNi 22 5 2 exhibits a fracture strain of 0.3, the X3CrNiMo 22 3 2 of 0.2 and X6CrNiMo 12 6 2 of 0.05 in the axial testing direction.

Figures 14 and 15 demonstrate the effect of increased cathodic charging times on fracture surfaces by transition from dimple shaped to the brittle fracture type.

The microscopic investigation in figure 16 demonstrates cracking of mainly the ferrite phase, but also of the austenite phase of both materials. It may be assumed

Fig. 14 X3CrMnNi 22 5 2 fracture at - 0.0038 mA/mm²

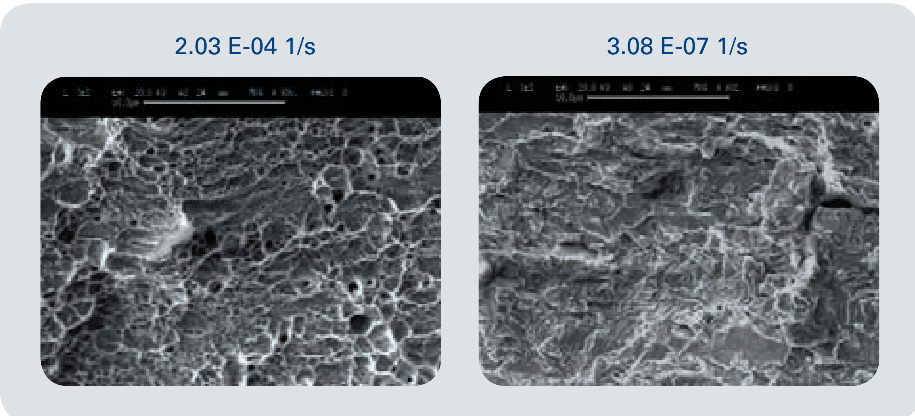


Fig. 15 X3CrNiMo 22 3 2 fracture at - 0.0038 mA/mm^2

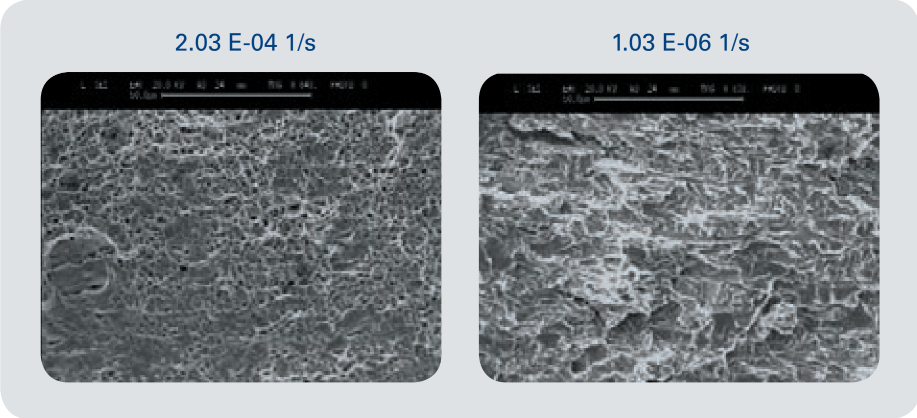


Fig. 16 Secondary cracks in δ and γ at - 0.0038 mA/mm^2 after axial testing

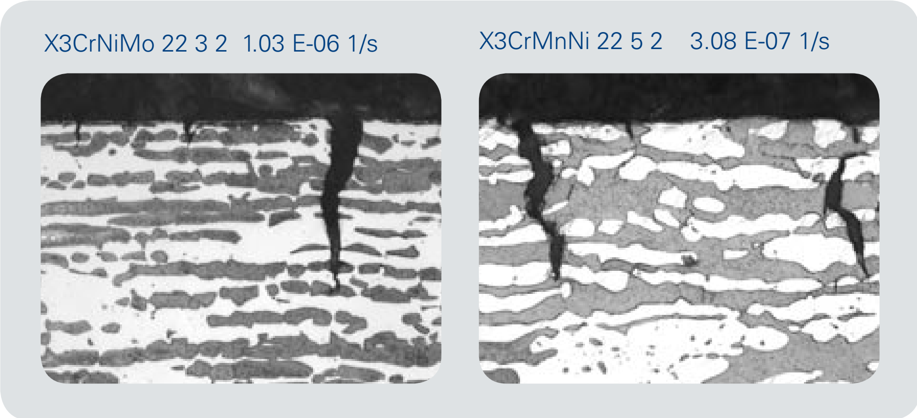
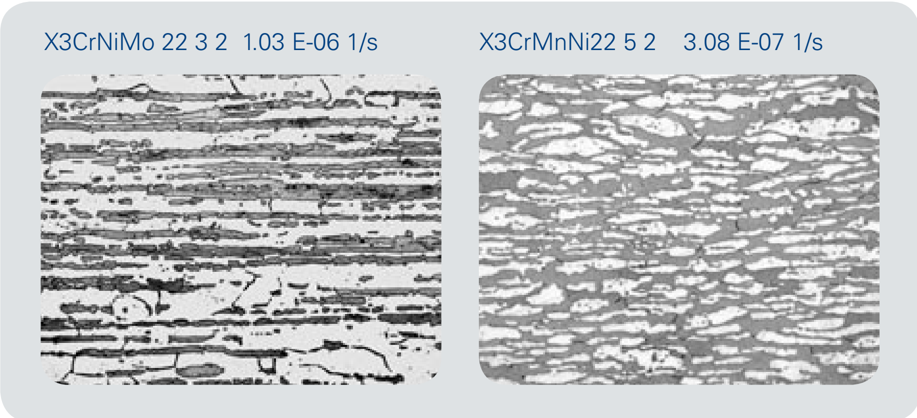


Fig. 17 Microstructures in axial direction



that at long exposition times the higher hydrogen solubility of the austenite would provide accumulation of diffusible hydrogen leading to final cracking at respective local microstrains in the austenite.

In figure 17 the microstructural differences between the two LDSS are evident from more pronounced ferrite/austenite banding of the X3CrNiMo 22 3 2 as compared to the X3CrMnNi 22 5 2.

From figures 16 and 17 it may be tentatively assumed that the X3CrMnNi 22 5 2 provides a higher crack propagation resistance by thicker austenite precipitations in the less ductile ferrite phase. However, further microscopical crack evaluation will provide more insight with respect to crack propagation mechanisms.

Conclusions

From galvanostatic charging during SSRT at various cathodic current densities and strain rates of a Martensitic X6CrNiMo 12 6 2 and two Lean Duplex X3CrNiMo 22 3 2 and X3CrMnNi 22 5 2 the following conclusions are drawn:

- By increased cathodic charging and respective uptake of diffusible hydrogen the fracture strains of the steels exhibit a sudden transition from their original levels without hydrogen to a lower level at high hydrogen.
- There is a characteristic relative hydrogen induced loss of ductility typical for each material at constant strain testing.
- The martensitic X6CrNiMo 12 6 2 thus looses 60% of its genuine ductility, the lean duplex steels X3CrNiMo 22 3 2 and X3CrMnNi 22 5 2 47% and 50% respectively in the axial testing direction.
- The time-strain-fracture investigations (TSF) at constant cathodic current densities of - 0.0038 mA/mm^2 also show superior fracture strains of the lean duplex X3CrMnNi 22 5 2 as compared to the X3CrNiMo 22 3 2 and, in particular, the martensitic X6CrNiMo 12 6 2.
- Although, the martensitic X6CrNiMo 12 6 2 provides higher strength and thus better economy at first sight, its higher susceptibility to hydrogen supported cracking includes a higher operational risk for respective flow lines at inadequate cathodic protection with too high local current densities and under sour gas conditions leading to local acidification during pitting corrosion.

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The introduction of Alloy 2101 for use as zinc-clad umbilical tubing for deepwater subsea oil and gas developments

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Abstract

Alloy 2101 (UNS S32101) is a lean duplex (ferritic-austenitic) stainless steel that has been proposed as an optimum cost solution for the umbilical tubing used to provide hydraulic power and transport production chemicals from deepwater oil and gas production facilities to remote subsea tie-back developments. Alloy 2101 does not have the inherent resistance to pitting and crevice attack in seawater environments of higher cost materials, such as super-duplex stainless steel, and so needs to be protected by a layer of zinc-alloy cladding (UNS Z13001 special high grade zinc with controlled iron content). This paper presents a comparison of zinc-clad alloy 2101 with alloy 19D (UNS S32001), which is the present material of choice for zinc-clad lean duplex stainless steel umbilical tubing and highlights some of the operational concerns inherent in the introduction of a new material to deepwater service.

Alloy 2101 has a composition very similar to alloy 19D, except that the chromium and nitrogen contents are slightly higher. Based upon the increased chromium and nitrogen contents, alloy 2101 has slightly improved corrosion resistance, higher strength, and improved austenite reformation characteristics during welding. These improved material properties may allow zinc-clad alloy 2101 umbilical tubing to be used at deeper water depths and higher injection pressures than alloy 19D, so increasing the performance envelope over which zinc-clad lean duplex stainless steels can provide a viable economic and engineering alternative to seamless super-duplex tubing.

Introduction

Alloy 2101 (UNS S32101) is a lean duplex stainless steel (LDSS) and is being considered as an alternative material for subsea umbilical applications in conditions where alloy 19D LDSS is currently considered to be appropriate. Alloy 2101 offers certain advantages compared to alloy 19D, including increased corrosion resistance, higher strength, and improved austenite reformation during welding [1].

This paper considers some of the primary operational issues that need to be addressed prior to the roll-out of this material for umbilical tubing serving the deepwater oil and gas production industry. Due to the extreme cost and complexity of such systems it is necessary to ensure that alloy 2101 will meet or exceed a twenty-year design life in such applications. Work is presently underway to address these issues, particularly those related to the propensity for LDSS materials to suffer from crevice corrosion in seawater environments. In addition, a joint industry project (JIP) is also planned to gather data on LDSS performance in both simulated seawater and seabed environments and field testing at deepwater production facilities.

An Overview of Umbilical Usage in the Oil and Gas Industries

The first subsea well was installed in the Gulf of Mexico in 1961, largely as a proof of concept. By 1993 the number of subsea wells had expanded to more than 750, placed in locations Worldwide [2]. Since the early 1990's there has been a further increase in the use of such wells following the expansion of production into the deepwater basins of the World. As an example to highlight this, by the end of 2003 there were 81 deepwater projects operating in the Gulf of Mexico. By the end of 2004 this figure had risen to approximately 96, with a large number of these employing subsea wells and tie-backs [3].

In order to control and monitor subsea wells in deepwater it is standard practice to run bundled umbilicals from the host platform in order to provide hydraulic and electrical power, bleed pressure from the well annulus and enable communication with the well [4].

Furthermore, the harsh flow assurance conditions experienced in many deepwater tie-backs generate chemical injection requirements that may involve provision of chemicals such as low-dosage hydrate inhibitors, glycol, methanol, scale inhibitors, corrosion inhibitors, H_2S scavengers, paraffin inhibitors and asphaltene inhibitors, amongst others. These chemicals are transported through the umbilical bundle, which may also contain ancillary equipment such as gas-lift lines. Use has even been made of umbilicals for the placement of acid in wells prior to stimulation treatments [5].

Umbilicals have been described as 'the lifeline of subsea production systems' [6] due to the ubiquitous requirements for hydraulic well control and flow assurance through chemical injection. The nature of the exposure conditions faced by umbilicals in deep water means that high mechanical performance and resistance to internal corrosion, external corrosion and stress corrosion cracking (SCC) are all required [7, 8].

Early umbilicals were manufactured from thermoplastic hose, but the move into deep water necessitated a change to higher strength materials providing greater collapse resistance with internal compatibility with a host of new production chemicals. Furthermore, the umbilical tubing must be protected from external corrosion due to exposure to all the environments encountered by umbilicals, namely seawater and seabed mud, both shallow and deep, as well as the splash zone and marine atmosphere.

Corrosion control for umbilical systems has often involved the use of cathodic protection (CP), coatings, or materials with a specified pitting resistance equivalent (PRE). Effective protection current distribution from CP systems can present problems due to the complex geometries and possible shielding effects of typical bundled umbilical systems, whilst the use of high-alloy materials is expensive and can generate significant fabrication costs and quality assurance concerns.

Due to its high strength and good corrosion resistance, the umbilical material of choice for deepwater has become super-duplex stainless steel (SDSS). Cost and fabrication issues with super-duplex subsequently led to the development of a zinc-clad Cr-Mo steel umbilical using a 1.6mm thick zinc coating conforming to ASTM B-6 [9] Special High Grade with controlled iron content [6], but use of this material was ultimately limited by the internal corrosion resistance of the tubing and subsequent compatibility and cleanliness concerns with the transported fluids [10].

In order to provide a material with similar internal corrosion resistance and mechanical properties to SDSS, yet with a lower cost, a ZCLDSS (zinc clad lean duplex stainless steel) umbilical utilizing alloy 19D (UNS 32001) was developed [4, 6]. The decreased resistance to pitting and crevice corrosion of this steel with respect to SDSS is offset by the use of zinc cladding to provide local cathodic protection (CP) to control localized corrosion. The specifications for the cladding are presented in table 1.

Zinc is amphoteric and so experiences accelerated corrosion in the presence of both acidic and alkaline solutions. However, zinc is stable and has a relatively low corrosion rate in typical seawater compositions [11]. The zinc coating on alloy 19D and alloy 2101 umbilicals serves a primary role of being a barrier coating to protect the underlying tubing material from exposure to the environment. The secondary purpose of the zinc is to act as a local source of sacrificial CP for the tubing in cases where the zinc contains holidays or where it has been damaged during umbilical laying or in service. Under such

Zinc Cladding Composition Limits [9] Table 1

Grade	Zinc Feedstock (UNS Z13001 Special High Grade with Controlled Iron Content)
Lead (%)	0.003 maximum
Iron (%)	0.01 – 0.014
Cadmium (%)	0.003 maximum
Aluminium (%)	0.002 maximum
Copper (%)	0.002 maximum
Tin (%)	0.001 maximum
Total non-Zinc (%)	0.021 maximum
Zinc (%)	99.979 minimum

conditions the zinc preferentially corrodes and maintains the steel below its critical pitting potential.

Overview of Lean Duplex Stainless Steel Umbilicals

Lean duplex materials have been tested and applied as cost-effective alternatives to SDSS umbilicals [4, 6, 10]. In order to provide an economical alternative to traditional duplex and super-duplex materials the chromium and molybdenum content of this steel is reduced, whilst manganese is substituted for nickel.

This results in a duplex stainless steel that is not susceptible to intermetallic phase formation during the thermal exposure times associated with tubing manufacture and umbilical bundling [4]. However, as can be seen from table 2, decreased alloy cost and increased ease of fabrication come at the expense of corrosion resistance. The PRE of LDSS is of the order of that for 316 stainless steel (UNS S31603), rather than the levels of 40 and above for which stainless steels are considered to be immune from crevice attack in seawater. This requires the use of an additional corrosion control system for the outside surface of the umbilical tube. This may be through the provision of CP or the use of a coating system. A combined system, such as the use of an extruded zinc sacrificial coating, is most typically applied in this role.

Whilst it is the case that the PRE of lean duplex is not sufficient to protect the outer face of the tubing when it is placed into seawater in the absence of additional protection, it is sufficient to be compatible on the inner face with the production chemicals and fluids typically handled by SDSS umbilicals. This is because chemicals such as scale inhibitors and corrosion inhibitors are typically formulated for compatibility with 316 stainless steel, as this is the predominant material used for the construction of chemical storage and handling systems for use offshore. Hence, compatibility with materials having a similar or superior corrosion resistance, such as SDSS and alloy 2101, is often not a concern in practice.

Whilst some operators are willing to continue the use of SDSS for their umbilicals, some are looking to move towards alternatives. Issues seen with SDSS, including

PRE Values for Common Stainless Steel and High Nickel Materials [1, 10, 21] Table 2

UNS No.	Common Name	PRE_N (Duplex)	PRE_N (Austenitic)	PRE_W (Duplex)
S32750	2507	37.7 – 47.6	–	–
S39274	DP3W	–	–	38.6 – 46.8
S32760	Zeron 100	–	–	37.9 – 45.7
S32550	Ferralium 255	35.2 – 45.5	–	–
S32205	2205	34.1 – 37.8	–	–
S32404	Uranus 50	27.1 – 35.6	–	–
S32101	Alloy 2101	24.5 – 28.6	–	–
S32304	2304	22.5 – 29.7	–	–
S32001	Alloy 19D	20.3 – 26.2	–	–
N08031	Alloy 31	–	50.3 – 58.6	–
R20033	Alloy 33	–	43.2 – 59.6	–
S31603	316L	–	22.6 – 30.9	–
S30403	304L	–	18.0 – 23.0	–

manufacturing and material costs, weld failures, sigma phase control and the need for aggressive chemical cleaning of the inner face, have driven a move towards the use of alloy 19D umbilicals for many deepwater applications since delivery of alloy 19D tubing commenced in the summer of 2000 [10].

Alloy 2101 and Alloy 19D: A Comparison

Alloy 2101 is a LDSS that was recently introduced by Outokumpu. It has a composition very similar to alloy 19D, except that the chromium and nitrogen contents are slightly higher (see table 3 for material composition ranges and table 4 for typical variations between heats). Zinc-clad alloy 2101 tubing offers several advantages in comparison to alloy 19D when used for subsea umbilical service.

Based upon the increased chromium and nitrogen contents, alloy 2101 will have higher strength, improved austenite reformation during welding [1], and marginally greater corrosion resistance. It is reasonable to anticipate that zinc-clad alloy 2101 tubing will be compatible with subsea umbilical applications where zinc-clad alloy 19D is currently used. The alloy has already been included in various ASTM specifications including ASTM A240 (plate, sheet and strip) [12], A276 (bars and shapes) [13], A479 (bars and shapes) [14], A789 [15] (seamless and seam welded tubing) and A790 (seamless and welded pipe) [16].

The higher strength of alloy 2101 with respect to alloy 19D has significant operational implications for LDSS umbilicals as it will extend their existing operating envelope. This will allow the consideration of LDSS tubing for use in conjunction with the higher pressure ranges typical of modern deepwater developments for which SDSS materials are presently the only viable alternative.

Improved austenite reformation characteristics in comparison to alloy 19D will facilitate tubing manufacture with alloy 2101 and allow a greater level of control of the weld characteristics. As problems with duplex and super-duplex steels have predominantly been associated with a loss of phase control in and around the weld and heat affected zone (HAZ), increased metallurgical stability is a significant asset for the material.

Lean Duplex Stainless Steel Composition Ranges [12] Table 3

	Weight Percent									
Material	C	Mn	P	S	Si	Cr	Ni	Mo	N	Cu
Alloy 19D	0.030	4.0-6.0	0.040	0.030	1.00	19.5-21.5	1.00-3.00	0.60	0.05-0.17	1.00
Alloy 2101	0.04	4.0-6.0	0.040	0.030	1.00	21.0-22.0	1.35-1.70	0.10-0.80	0.20-0.25	0.10-0.80

Composition of Heats for Which Data was Submitted to ASTM and UNS Table 4

Heat Number	Weight Percent C	Mn	P	S	Si	Cr	Ni	Mo	N	Cu	PRE_N**
804030	0.024	5.07	0.017	0.000	0.69	21.36	1.49	0.30	0.232	0.32	26.1
813292	0.033	5.03	0.017	0.000	0.69	21.76	1.54	0.27	0.214	0.30	26.1
813293	0.029	5.00	0.015	0.000	0.65	21.59	1.54	0.30	0.234	0.32	26.3
Mean	0.029	5.03	0.016	0.000	0.68	21.57	1.52	0.29	0.227	0.31	26.2
Minimum	0.024	5.00	0.015	0.000	0.65	21.36	1.49	0.27	0.214	0.30	26.1
Maximum	0.033	5.07	0.017	0.000	0.69	21.76	1.54	0.30	0.234	0.32	26.3

As umbilicals face a dynamic service environment, often being deployed from floating production platforms for design lives in excess of twenty years, the ability of the welded tube to resist fatigue is a critical issue. Limited rotational fatigue testing of zinc-clad alloy 19D and alloy 2101 tubing samples has been completed to evaluate any difference in behaviour between the two materials. The results of this testing have demonstrated improved performance for alloy 2101 compared to alloy 19D. In addition, alloy 2101 samples had only slightly lower fatigue performance than that for seamless SDSS tubing.

Operational Considerations

There are a number of operational considerations that must be considered prior to the introduction of alloy 2101 as an umbilical material. Aspects such as rotational fatigue performance and ease of defect-free manufacture are of importance, but detailed investigations of material durability must also be undertaken. For lean duplex stainless steels, including alloy 2101, this is particularly associated with localized corrosion of the exterior of the tubing as a result of consumption or damage to the zinc cladding used to provide protection from seawater-induced crevice corrosion.

Manufacturing Quality and Consistency:

A significant benefit of both the alloy 19D and alloy 2101 materials is that they can be formed into seam-welded tubing by cold working strip stock [12, 15]. Seam welding is a much faster process than individually welding lengths of seamless tube, as is typically required for conventional SDSS tubing. The continuous nature of the manufacturing process, as well as being faster, also facilitates good control of welding and heat treating procedures.

Strip splice welds join one end of strip coil to the next to enable continuous tubing production at the mill. Orbital welds are subsequently used to join mill coils of seam welded tubing to form longer coils for shipment [4]. However, these welds can be several thousands of feet apart, rather than at the approximately 15 to 30 metres (50 or 100 feet) required for seamless SDSS tubing.

Stress Corrosion Cracking:

Lean duplex materials have a further advantage over SDSS grades in their resistance to embrittlement phenomena. The sulphide stress corrosion cracking resistance of lean duplex grade UNS S32304 has been evaluated using the NACE TM01-77 [17] and EFC17 [18] testing procedures. Tests performed on longitudinally welded pipe confirmed the good SSC resistance of lean duplex in the environments used to qualify supermartensitic grades [19].

Such findings have been validated directly with alloy 19D umbilical tubing by the use of cathodic hydrogen charging tests [17]. Seam welded tubing samples with an autogenous orbital weld at the centre were used for this testing and were found to not crack after 30 days of exposure [20]. This is of importance in situations where tubing is exposed to the protection potentials generated by sacrificial cathodic protection systems, such as at subsea umbilical termination assemblies.

Corrosion:

Umbilical damage predominantly results from the laying process and is caused as the umbilical bundle is passed through the tensioners. These can occasionally scrape off the outer sheathing during layout, where the concern is that the zinc cladding may also be removed and allow direct exposure of seawater to the LDSS tubing below. Direct exposure of a significant proportion of tubing may impact the ability of the zinc to provide adequate cathodic protection to the exposed tubing for the anticipated design life of the system and has been found to be a significant source of concern to those oil and gas producers who have yet to utilize ZCLDSS umbilicals in their operations.

Calculations based on theoretical considerations and limited experimental testing suggests that such damage would need to remove greater than 15% of the zinc from a typical umbilical tube before any concerns arise regarding the achievement of a twenty-year system life. This assessment was made using a simplified method that assumes that the area of zinc coverage is not depleted as the coating corrodes and that there is no combined effect between adjacent tubes. The latter may increase the allowable bare area for individual tubes in open bundle forms, such as those used with roved systems. A further limitation that will need to be addressed in future testing is the ability of the zinc to provide sufficient current flow to protect large exposed steel areas in the tightly-packaged conditions encountered in sheathed umbilicals. However, one significant point of note is the fact that sheathed umbilicals will typically be more resistant to installation damage than roved systems and so will be less likely to have significant areas of zinc removed from the start of the design life.

It has also been noted that the bundling of ZCLDSS umbilicals in conjunction with SDSS tubing will potentially result in the decrease of zinc coating lifetime as a result of the current drain imparted by the unclad SDSS. Until further test data are gathered to allow a detailed assessment of this phenomenon, it is recommended that ZCLDSS tubing is not bundled with SDSS tubing in umbilical systems unless the SDSS is individually extruded with a polyethylene coating.

Corrosion at Elevated Temperature:

Whilst many umbilicals will face seawater conditions ranging from ambient sea level, which can be upwards of 27°C (80°F), to the low temperatures encountered on the deep seabed of around 4°C (39°F), there are instances where operating or exposure temperatures will be higher. Examples include areas in the splash zone heated by direct sunlight, umbilicals carrying recirculated fluids such as reclaimed glycol, umbilicals bundled around gas-lift injection lines, umbilicals hanging near hot production risers at the host platform, and tubing carrying well annulus fluid returns.

Past experience suggests that the anodic characteristics of the zinc cladding will be affected by exposure to high temperatures. As a result of this uncertainty a limited laboratory testing program has been undertaken to evaluate the performance of zinc-clad alloy 2101 and alloy 19D at exposure temperatures of up to 82°C (180°F). This was undertaken as a means of providing a basis from which to plan a more detailed evaluation of zinc behaviour in a future JIP.

The findings from these tests found that protection from corrosion was afforded to unclad alloy 2101 and alloy 19D tubing sections when these were galvanically coupled to zinc-clad tubing sections at an area ratio of 6:1 zinc-clad to unclad material at temperatures of 49°C (120°F), 60°C (140°F), 71°C (160°F) and 82°C (180°F) during an eight-week exposure testing program. This validates previous design guidance issued for ambient temperature exposure conditions and is supported by both visual assessment and potential measurement. The current densities drawn by the unclad tubing during exposure to ambient temperatures were found to be comparable to ZCLDSS test results published in other studies [6].

Significant current continued to be provided throughout the duration of the tests, showing that the zinc used to clad LDSS umbilical tubing shows no propensity for spontaneous passivation at temperatures of up to 180°F. Exposure to elevated temperatures also did not affect the subsequent behaviour of the samples following their return to ambient temperature conditions of (70°F). This implies that exposure to transient thermal phenomena, such as might be encountered following the use of an umbilical during annulus pressure maintenance of subsea wells, will not have any long-term impact on the performance of ZCLDSS tubing.

Calculation indicates that ZCLDSS tubing will be able to achieve a 20 year design life at exposure temperatures of up to 180°F under conditions where greater than 95% of the installed tubing is clad with zinc, as presented in table 5. This reflects a significantly more stringent control than that which must applied under ambient exposure conditions, where calculation indicates that only 85% of the tubing surface area needs to be clad to meet a 20 year design life. Even so, this represents a significantly greater rate of zinc damage than would be expected during a typical installation.

However, at the given time the findings of these calculations must be applied with

Zinc Lifetime Calculations

Table 5

Temperature (°F)	Estimated Zinc Life at 85% Original Zinc Cladding Coverage (Years)		Estimated Original Zinc Coverage for a 20 Year Design Life (% Total Area)	
	Alloy 19D	Alloy 2101	Alloy 19D	Alloy 2101
120	17	19	85	86
140	9	13	93	90
160	6	8	95	93
180	7	7	94	94

caution until such time as they are validated by additional work as part of the planned ZCLDSS JIP. A high apparent level of localized cladding consumption was detected on many of the alloy 2101 specimens in comparison to alloy 19D specimens that were also exposed as part of the study. At the present time the cause of this difference has not been elucidated, although initial assessment suggests that it is likely to be an issue related to zinc composition, rather than the alloy 2101 substrate.

Fatigue:

As noted previously, the rotational fatigue performance of alloy 2101 is slightly improved over alloy 19D and approaches that of SDSS. In order to gather more data on this aspect of alloy 2101 behaviour additional testing is planned for the near future. This will expand the limited testing undertaken to date and provide information on samples containing orbital welds with added filler metal.

Conclusions

The use of zinc-clad lean duplex stainless steels for subsea umbilical tubing has, with the introduction of alloy 19D, provided a viable lower cost alternative to super-duplex stainless steel materials for many deepwater applications. This has become particularly important in recent years as demand for oil and gas has risen and driven operators to exploit ever deeper and more remote subsea developments at a time of significant volatility in the metals market.

With the forthcoming introduction of alloy 2101 to this market, the operating pressures to which lean duplex materials can be taken will be increased beyond the present range of alloy 19D. This will provide a wider number of developments with the opportunity to explore alternative material selections to the super-duplex materials that have until now been the only option in many applications.

However, it is clear that significant work remains to evaluate the long-term durability of the zinc-cladding system and the fatigue behaviour of the material before alloy 2101 can be introduced in this role. A joint industry project is presently being developed that will enable these aspects to be investigated in detail in a program that will encompass laboratory testing and long-term exposure testing in deepwater production environments.

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