SUPERMARTENSITIC 13 %Cr LARGE DIAMETER SEAMLESS PIPES: MECHANICAL CORROSION AND WELDABILITY PROPERTIES

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Abstract - **The demand for weldable 13%Cr pipes with outside diameter such as 18", 20" and 24" has increased greatly. Considering such a requirement, Dalmine and NKK have developed a new production route for OD 20" pipes. Girth welded joints (GTAW) were produced. The mechanical properties of both base material and welded joints meet the target requirements.**

Corrosion qualification was aimed to determine the Sulfide Stress Cracking (SSC) resistance in slightly sour oil wells. Influence of chloride content (NaCl 5÷25%), H2S partial pressure (1÷10 kPa) and pH (3.5÷5), was assessed. CO_2 corrosion resistance was verified with static exposure tests at medium/high pressure of CO_2, high chloride (25% NaCl) and temperature up to 150°C.

Keywords – **13%Cr steels, flowline, Gas Tungsten Arc Welding (GTAW), toughness, Sulfide Stress Corrosion (SSC).**

I. INTRODUCTION

In the recent years oil & gas wells have been developed in increasingly severe corrosive environments characterized by high temperature, partial pressure of CO_2 and high concentration of chlorides and in some cases of H_2S (Nice *et al.*, 1997; Scoppio *et al.,* 1997).

A study by Nose and Asahi (2000) emphasize that flowline and gathering lines, which are used to transport oil and gas before any gas processing is performed and water is removed, should provide the same level of corrosion resistance of OCTG materials.

Possible solutions, as indicated by Amaya *et al.*, (1999) and Ogawa *et al.,* (1999), are the use of inhibitors or CRA duplex steels. These solutions are expensive. The oil companies (Kermani *et al.,*1995) have been looking for cheaper materials with satisfactory mechanical properties and corrosion resistance.

For these reasons low C martensitic stainless steels have been developed by steel manufacturers (Miyata *et al.,* 1997) and recently started to be used in fields, as flowlines as reported by Rogne *et al.*, 2000.

Satisfactory welding process have been developed by Woollin *et al.*, 1999; Gooch *et al.*, 2000; Rogne *et al.,* 1997.

The demand of weldable 13% Cr linepipe has increased rapidly. Seamless pipes seem to be a cost effective option, compared with longitudinally welded pipes, when high wall thickness is required.

Seamless pipe are typically available in outer diameter (OD) range up to 16" and wall thickness (WT) above 5 mm. Moreover, there is also an increasing demand of 13Cr weldable pipes for larger outer diameter such as 18", 20" and 24".

Considering such requirements, NKK Corporation and Dalmine SpA have developed together a production route for seamless pipes in 13 %Cr of OD larger than 16". Sample pipes with 20" OD were manufactured and weldability tests were carried out.

In this paper, the results of the production and the tests carried out to verify the mechanical and corrosion properties of base material and of welded joints are discussed.

II. PIPES PRODUCTION & CHARACTERISATION

II.1 Production of pipes

Two different mother pipes 406.4 mm OD x 16.8 mm WT and 406.4 mm OD x 23.5 mm WT, with a typical chemi stry of the steel for sour service applications, were manu-

TABLE 1
Typical chemical composition of weldable 13% Cr mother pipe (mass %).

C	Cr	Mo	Ni	N
0.01	12.3	2.1	5.8	0.01

TABLE 2
Test conditions and solution chemistry for SSC.

Solution	Gas		pH	NaCl [wt%]	Buffer CH_3COONa [%]
	pCO_2 [MPa]	pH_2S [KPa]			
Glass cell (Constant load)					
Solution 1	0.1	1	3.5	5	0.04
Solution 2	0.1	1	4.5	25	0.04
Solution 1	0.1	2	3.5	5	0.04
Solution 3	0.1	4	3.5	1	0.04
Solution 2	0.1	4	4.5	25	0.04
Solution 4	0.1	10	4.5	5	0.04
EFC sol.	0.1	4	4.5	16.5	0.04
Autoclave (FPBB)					
Solution 1	1	1	3.5	5	84mg/l $NaHCO_3$
Solution 2	1	1	4.5	25	84mg/l $NaHCO_3$

factured by NKK (Table 1).The size were as follows;

1) 406.4 mm OD x 16.8 mm WT

2) 406.4 mm OD x 23.5 mm WT

The mother pipes were rolled by the Expander mill in DALMINE works; size 1 for 508 mm ODx12.7mm wt and size 2 for 508 mm OD x 17.5 mm wt pipes, respectively.

The heat treatment of the pipes was a quenching and tempering.

II.2. Corrosion tests

Sulfide Stress Cracking

Modified NACE TM 0177-96 (method A) Tests were carried out at room temperature in chloride solutions at different concentrations (see Table 2). Buffered solutions of NaCl were utilized in order to obtain pH 3.5 and 4.5, respectively.

Uniaxial constant load tests were carried out on smooth specimens. Subsize specimens were taken from the tube wall mid-thickness and prepared in accordance with the recommendations of NACE TM-0177-96, Method A (gauge diameter 3.8 mm). The specimens were stressed at 90% of the actual yield strength (AYS).

Tests in autoclave Specimens for four points bent beam (FPBB) corrosion tests were machined in the longitudinal direction of the pipe, transverse to the girth welds. Specimens in triplicate were taken both in proximity from the cap and from the root of the weld.

TABLE 3
Conditions for CO_2 general corrosion tests.

Condition	pCO_2 [MPa]	PH_2S [KPa]	pH	NaCl [%]	T [°C]
"Sweet"	1	-	3.5	25	100
"Slightly sour"	1	1	3.5	25	100

TABLE 4
Summary of the welding procedure.

Weld area	Welding process	Backing gas	Arc energy range [kJ/mm]	Interpass [°C]
Root/ 2nd pass	TIG	Ar	0.4-1.5	-
Hot pass	TIG	Ar	0.4-1.5	150
Fill/cap	TIG	Ar	0.4-1.7	150

The specimens were loaded to 100% of the Actual Yield Strength (AYS). In accordance with EFC (1996) Oil & Gas guideline, 0.2% proof stress was used as test stress to calculate the specimen deflection.

FPBB tests were performed at high pressure in autoclaves (1 MPa CO_2) and room temperature, with environments reproducing high salinity and slightly sour service conditions.

A buffering agent such as sodium bicarbonate was added to the autoclave solution although a quite large amount of CO_2 was present as well, as shown in Table 2.

CO_2 corrosion

CO_2 corrosion behavior was investigated by testing in Alloy UNS N06625 lined autoclaves at high temperature (100°C) and pressure (1 MPa) according to EFC. Test conditions are listed in Table 3. The exposure period in autoclave was 90 days.

Weight loss measurements were performed on flat coupons taken from the inner surface of the pipe. Specimens were cut longitudinally from the girth-welded pipe.

The average corrosion rate (mm/y) was calculated following the ASTM-G1 procedure.

Examination for localized corrosion evidence was performed using a stereo-microscope at 50X magnification.

II.3. Weldability Test

A seamless pipe ODxWT 508 x 17.5 mm was selected for the weldability test. A full girth weld was performed at TWI using a manual GTAW procedure in the 5G welding position, with a vertical up welding technique. The welding consumables consisted in a duplex filler wire 2.4 mm of thickness (LTN-4462) for the root run and a superduplex LTN-Zeron 100X TIG wire 3.2 mm thick for the hot pass and the capping runs.

In Table 4 is given a summary of the adopted welding

TABLE 5
Tensile properties of the pipes (OD x wt 508 x 17.50 mm and OD x wt 508 x 12.7 mm).

Pipe OdxWT Mm	Sample	YS [MPa]	UTS [MPa]	El 2"min [%]	YS/UTS
508 x 17.5	Long.	595	820	37.8	0. 73
		567	812	37.8	0.70
	Transv	614	852	23.0	0.71
508 x 12.7	Long.	613	845	30.7	0.73
		659	838	30.7	0.79

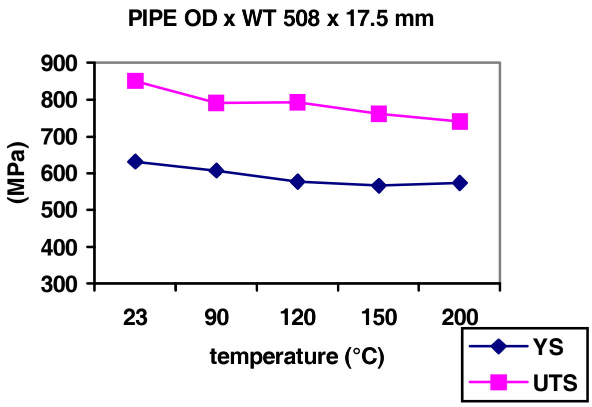

Figure 1 – Tensile properties of the pipes OD x WT 508 x 17.50 mm. (longitudinal round specimens).

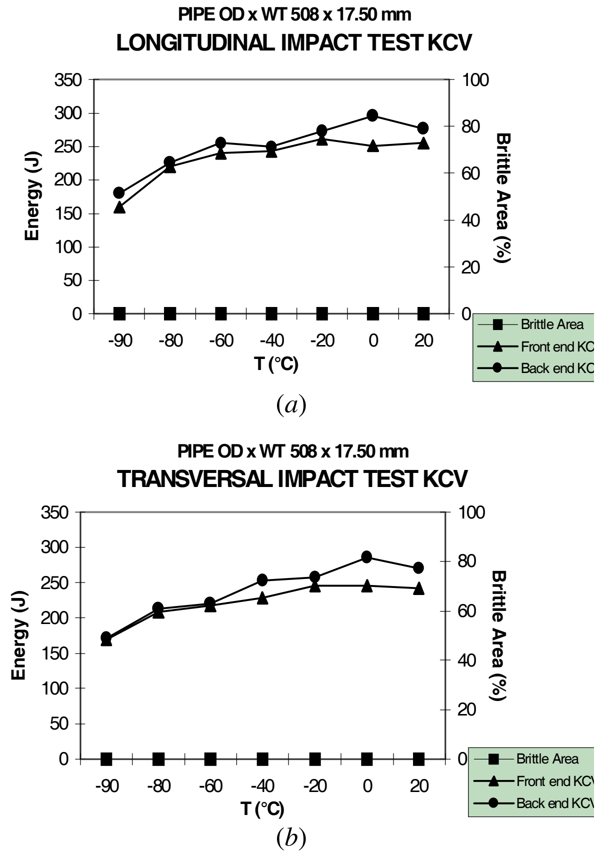

Figure 2 - Impact tests results. (*a*) longitudinal specimens, (*b*) transverse specimens.

procedure.

III. RESULTS & DISCUSSION

III.1. Mechanical Properties of Base Material

The tensile test results of the pipes OD x WT 508 x 17.5 mm and 508 x 12.7 mm are shown in the Table 5. The results are fully in compliance with the requirements of some oil companies specification. The most stringent is the Shell Specification SIEP 97-5763: YS min 550 MPa, UTS min 700 MPa, El min 20%, YS/UTS max 0.90.

Tensile properties at high temperature, measured on a pipe OD x WT 508 x 17.5 mm , show a de-rating from 20°C up to 200°C of about 9% of the initial value (Fig. 1). The hardness values (HV10) measured at 1.5 mm from the internal and external surfaces and in the midwall, are in the range 263-285 and 274-287 respectively for the pipes ODxWT 508 x 17.5 and 508 x 12.7 mm.

The impact values are showing practically the same values in the longitudinal and transverse direction. Toughness is fairly high (>160 J) and 100% of the shear area is measured even at –90°C (see Figs. 2 a, b for wt 17.5 mm).

III.2. SSC Corrosion Resistance of the Base Material

13%Cr base material presented a very good SSC resistance in all the tests performed: no cracks or signs of localized corrosion attack such as pits initiation were observed after 720 hours exposure in sour environment (Table 6).

Excellent SSC resistance was showed as well in autoclave tests. Four point bent beam tested in autoclave with 1 MPa CO_2 and 1 kPa H_2S partial pressure showed no failure after 720 h exposure time.

The entire specimen surfaces after autoclave exposure was very shiny. Mass loss determination of FPBB specimens were practically nil (≤0.004 mm/y).

III.3. Welded Joint Mechanical Properties

On completion the weld was examined visually and radiographically and the results were in accordance with the workmanship standards given in BS 4515.1996.
The weld passed all radiographic inspections gave an acceptable macro, micro and mechanical test results, as illustrated in Table 7.

TABLE 6
13%Cr 20" OD steel line pipe base material SSC tests.(TTR=time to rupture)

AYS [%]	pCO_2 [MPa]	pH_2S [kPa]	Solution	pH	TTR [hours]
Glass cell (Constant load)					
90	0.1	1	1	3.5	>720
90	0.1	1	2	4.5	>720
Autoclave (FPBB)					
100	1	1	1	3.5	>720
100	1	1	2	4.5	>720

TABLE 7
Properties of the welded joint

	Test methods	**Acceptance criteria**	**Results**
Hardness survey	HV_{10}	340 HV_{10} max	Max HV_{10} in HAZ= 327, Max HV_{10} in weld metal=297
Transverse weld tensile	Parallel length, 55 mm	Tensile strength ≥ 700 MPa	Max Stress 883 MPa
All weld metal tensile	-		Max Stress 853 MPa
Root bend *Face bend*	Former D. 45mm, Span 90mm, Width 22.5, Thickness 15 mm	No defects exceeding 3 mm	No defects
Charpy impact tests FL/WM	T=0-30°C	60 J Min	225-274 J (0°C) 205-250 J (-30°C)

III.4. SSC Corrosion Resistance of the Welded Joints

Corrosion tests (NACE TM 0177-96 method A and FPBB) were carried out on the girth weld in environments reproducing high salinity and slightly sour production operating conditions.

Results from the constant load tests may be summarized as follows:

- In the environment 1 kPa pH_2S, 5% NaCl and pH 3.5 the welded 13%Cr 20"OD showed no susceptibility to SSC. If the critical H_2S content is increased from 1 to 4 kPa the steel presents still a good resistance to sulfide stress cracking, when the chloride concentration is 0.1%. If the pH is increased to 4.5 no cracks were observed with 4 kPa of H_2S.
  Comparison with previous results performed in similar conditions [3], showed a very good resistance to SSC of the girth welded 13%Cr joints, according to Figure 3.
- If the H_2S partial pressure is increased up to 10 kPa welded tensile specimens cracked, even if the solution pH was increased to 5.0 (Table 8).
- In the four point bent beam tests the 13% Cr girth weld passed the tests in all the examined conditions, even in presence of high salinity content (25% NaCl) and 1 kPa of H_2S.
- No cracks were observed on the specimens taken from the root or cap position (Table 9).

III.5. CO_2 Corrosion Resistance of the welded joints

The CO_2 corrosion resistance results of the girth welded coupons with comparison of conventional 13Cr API L80 are given in Table 10.

TABLE 8
13%Cr 20" OD girth welded joints test results: constant load. (TTR=time to rupture)

AYS [%]	**pH_2S [kPa]**	**Solution**	**pH**	**TTR [hours]**
90	1	1	3.50	>720
90	1	2	4.50	>720
90	2	1	3.50	>720
90	4	1	4.50	>720
90	4	3	3.50	>720
90	4	EFC	4.57	>720
90	10	1	4.48	127
90	10	1	5.00	59

TABLE 9
Four Point Bent Beam tests results on girth welded 13%Cr 20"OD line pipe. (n.d.= not determined)

Specimen Position	**pH_2S [KPa]**	**Solution**	**pH**	**SSC**	**Corr. Rate [mm/y]**
Root	1	1	3.5	No	≤0.004
Cap	1	1	“	No	≤0.004
Side bend	1	1	“	No	n.d.
Root	1	2	4.5	No	≤0.004
Cap	1	2	“	No	0.014
Side bend	1	2	“	No	n.d.

The corrosion rate of the 13% Cr girth welded is practically nil (0.002 mm/y) lower than that of conventional 13Cr API L80 more than 50 times. No preferential corrosion was observed in the "sweet environment" on the welded portion. A stable passive film was formed. CO_2 corrosion resistance depends on the stability of passive film, which consist of Cr oxides on the steel surface.

The threshold limit of 0.1 mm/y is respected also in the "sour environment", were a mass loss of 0.007 mm/y was determined.

In the "sour environment" rare pits were observed on the specimen surfaces of the 13%Cr welded coupons (Table 10), while the surface of conventional 13Cr steel was deeply corroded.

IV. CONCLUSIONS

20" seamless weldable 13% Cr pipes for linepipe application were successfully manufactured. The following conclusions can be drawn:

- Mechanical properties and corrosion resistance of the base material fully comply with the requirement of the API 5L X80 grade.
- Weldability by GTAW technology proved to be satisfactory in terms of soundness of the girth weld. The 20" 13%Cr stainless steel is suitable for welding

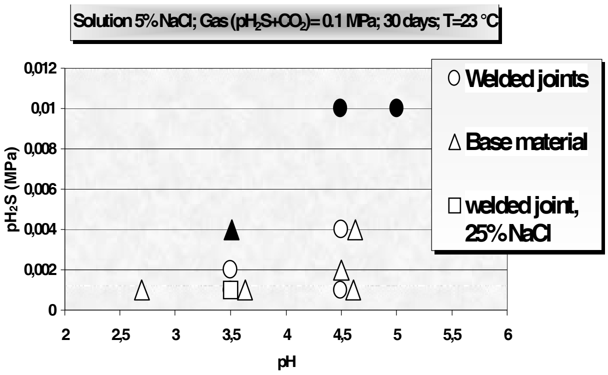

Figure 3 –SSC diagram (open symbol no SCC, closed symbol failure)

without PWHT.

- Mechanical properties in the girth weld were also good: worth to mention that low temperature toughness was as good as that showed by the metal base.
- SSC resistance of the welded joints was excellent in 5% NaCl solution with 0.004 MPa of H_2S partial pressure at pH 4.5.
- Resistance to general corrosion was also good confirming the suitability of weldable 13%Cr steel at elevated concentration of CO_2, even in slightly sour environment.

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TABLE 10

Autoclave exposure tests: mass loss determination and pitting susceptibility of girth welded 13%Cr 20"OD line pipe.

	Sweet		**Slightly sour**	
Steel	**Corr. Rate [mm/y]**	**Pitting**	**Corr. Rate [mm/y]**	**Pitting**
13Cr weldable 20" OD	0.002	None	0.007	rare pits
13%Cr API L80	0.100	corroded	0.110	corroded

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