

SULPHIDE STRESS CORROSION CRACKING OF 1.4418 WELDED PLATES

Abstract

Stainless steel 1.4418 is a promising martensitic steel which combines high mechanical properties with good corrosion resistance due to a higher content of Cr and Mo compared with lower alloyed martensitic steel such as 1.4313. Its content of Mo suggests also a high resistance to stress corrosion cracking in sulphur and chloride enriched environment comparable with supermartensitic steel specifically developed for oil and gas industry and available only as pipes. A recent increase in its availability also as plate materials opens its field of applications in areas where corrosion together with high mechanical strength are required.

In the present work welded and seamless samples made of 1.4418 bent under constant tensile stress were tested in a moisture saturated environment in presence of chloride and sulphuric acid at room temperature, 80°C and 100°C for 6 months. No cracks or signs of corrosion were found on the samples suggesting the suitability of this material in particularly aggressive environments.

Keywords

Sulphide stress corrosion cracking, martensitic stainless steel, 1.4418

1. Introduction

Supermartensitic stainless steels (Super 13Cr, HP13Cr, UHP15Cr) were developed in the field of gas and oil industry as an alternative to duplex steels. Their reduced amount of alloying elements compared with duplex steels combined with their good resistance in CO₂ containing environment with low levels of H₂S makes them very attractive steels with a reasonable price. In recent years new supermartensitic steels start being available on the market, however, always limited to the gas and oil industry. [1] The general trend is to reduce the carbon content whereas the chrome, nickel and molybdenum contents are increased. The modification in the chemical composition aims to increase the corrosion resistance of these steels maintaining a good weldability. [2] HP13Cr and UHP15Cr are two examples of supermartensitic steels developed by JFE Steel as improved version of API-13Cr. [3]

The corrosive conditions in which supermartensitic steels operate are not limited to the gas and oil industry but they are also typical of other application fields, like sludge drying plants. Unfortunately, supermartensitic steels are still not included in European standards and they can be purchased only as pipes. The present work investigates the possibility of using a European standardized material similar to supermartensitic steels in corrosive environment containing chloride and sulphates.

¹ ANDRITZ AG, Stattegger Strasse 10, 8045 Graz

² IWS, Graz University of Technology, Institute for Materials Science and Welding

2. Material

Based on the chemical composition of UHP15Cr it was possible to identify the closest European martensitic stainless steels in EN10088-2 as 1.4313 and 1.4418. Table 1 compares the chemical composition of steels UHP15Cr, 1.4418 and 1.4313.

Table 1: chemical composition of JFE-UHP-15CR-125 (Datasheet JFE), 1.4418 and 1.4313 according to EN10088-2

		C% max	Si% max	Mn% max	P% max	S% max	Cr%	Mo%	Ni%	Other %
JFE-UHP-15CR-125		0,04	0,5	0,6	0,02	0,005	14-16	1,8-2,5	6-7	
X4CrNiMo16-5-1	1.4418	0,06	0,7	1,5	0,04	0,015	15-17	0,8-1,5	4-6	N>0,02
X3CrNiMo13-4	1.4313	0,05	0,7	1,5	0,04	0,015	12-14	0,3-0,7	3,5-4,5	N>0,02

From Table 1 it can be seen that both European steels 1.4418 and 1.4313 present a higher content of manganese and a lower content of chromium and nickel than the supermartensitic steel UHP15Cr. Considering the percentage of the remaining elements, martensitic stainless steel 1.4418 is more similar to UHP15Cr than 1.4313 even if the content of molybdenum and nickel is located slightly lower than the range specified for UHP15. The main problem in using 1.4418 is its availability as it is generally delivered only as bars and rods. However, because of its promising characteristic and wide applicability recently it can also be purchased as plate material.

Martensitic stainless steel 1.4313 suffers from Sulphide Stress Corrosion Cracking (SSCC) in environment containing sulphide due to its low molybdenum content. Therefore based on its chemical composition martensitic stainless steel 1.4418 is expected to show a higher resistance to SSCC. In order to evaluate its stress corrosion resistance in an aggressive environment a SSCC test according to ISO 7539-3 was designed and performed on martensitic stainless steel 1.4418 samples.

A plate sample of 1.4418 with a thickness of 8mm was obtained from Nicromal for investigation purposes. Table 2 compares the chemical composition of the disc with the chemical composition of 1.4418 reported in EN10088-2.

Table 2: chemical composition of 1.4418 according to EN10088-2 compared to the chemical composition measured on the sample plate

		C% max	Si% max	Mn% max	P% max	S% max	Cr%	Mo%	Ni%	Al%	Cu%	al.%
X4CrNiMo16-5-1 1.4418	EN10088-2	0,06	0,7	1,5	0,04	0,015	15-17	0,8-1,5	4-6			N>0,02
Sample disc		0,04	0,28	0,79	0,018	0,001	15,5	0,81	5,11	0,02	0,17	

The plate meets the requirement of 1.4418 as plate material despite the molybdenum content is at the lowest value admissible according to EN10088-2. Molybdenum and chromium are the most important elements against corrosion, thus a low content of molybdenum can compromise the resistance to SSCC.

7 samples were cut with dimensions 150x20x8mm. The samples were divided into 3 groups depending on the testing temperature:

- room temperature (one sample labelled RT),
- 80°C (three samples: 1, 2 and 3) and
- 100°C (three samples: 4, 5 and 6).

Samples 2 and 5 were TIG welded, whereas samples 3 and 6 were MAG welded. Welding was performed as a bead on plate welding in the middle of the sample using AVESTA 248 SV as filler metal. All welding seams were performed in transversal direction. The welds were cleaned only by brushing. All samples were bent using a 3-point machine in order to introduce tensile stress on the external surface of each sample. After bending the samples were fixed using austenitic A4 screws to avoid the spring back to initial position and to maintain a constant stress condition. The samples presenting a transversal welding seam were bent with the weld facing the external of the bending and located at the maximum bending point where the tensile stress should be at its maximum. Fig.1 shows the plates made of 1.4418 after cutting and welding (a) and a side view of sample 2 (TIG welded) after bending (b).

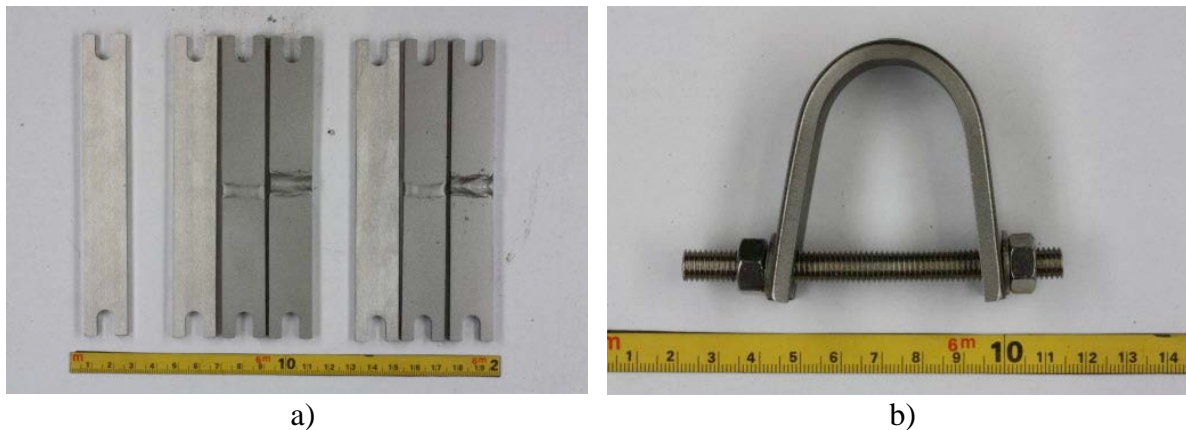









Fig.1: (a) 150x20x8mm samples of 1.4418 divided into three groups: from left to right the samples to be tested at room temperature, at 80°C and 100°C; (b) example of sample 2 with TIG weld after tensioning of the weld by bending

In Fig.1 a) the 3 groups of samples are shown. Only one sample without weld (RT) was tested at room temperature, whereas 3 samples were tested at 80°C and 3 samples at 100°C: each group was formed by a sample without weld, one sample with TIG welding seam and one sample with MAG welding seam. Fig. 1b) shows the side view of sample 2 after bending. The welding seam was placed in the most critical condition, i.e. the highest deformed area of the sample. Table 3 summarizes the different samples tested at room temperature, at 80°C and at 100°C.

Table 3: overview of the samples prepared for the test at different temperature.

Temperature	No weld	TIG welded	MAG welded
-------------	---------	------------	------------

RT	<p>Sample RT</p> 		
80°C	<p>Sample 1</p> 	<p>Sample 2</p> 	<p>Sample 3</p> 
100°C	<p>Sample 4</p> 	<p>Sample 5</p> 	<p>Sample 6</p> 

As can be seen in Table 3 the surface of the samples was brushed after welding (no sand blasting) and the position of the welding seam is approximately in the area of the highest deformation of the samples facing the external environment. The TIG welding seams present higher surface quality than the MAG welding seam.

3. Experimental procedure

The experiment was designed to test the sulphide stress cracking (SSC) and stress corrosion cracking (SCC) resistance of martensitic stainless steel 1.4418 plates at different temperatures over a period of 6 months. For the experiment three desiccators were used: one desiccator was left at room temperature with water covering the base, whereas two desiccators presenting also water at the base were heated up to 80°C and 100°C respectively on a heating plate and connected to a condenser in order to have a constant moisture saturated environment: the evaporation of the water was hindered by using a condenser cooled with tap water at the top of the desiccator. In all desiccators a plastic support was used to isolate the samples from the water at the base. The samples were positioned lying on the supports and the area with the higher deformation was covered with sludge collected from a sludge drying plant. Table 4 shows the composition of the sludge.

Table 4: composition of the sludge used in the experiment

Parameter	Method	Unit	Result
Dry mass	DIN 38414-S2	%	94,5
Organic dry mass	DIN 38414-S3	%	69,4
Chloride, total amount	DIN 38405-D19 and DIN	mg/kg DM	2510,0

	51408-1		
Fluoride, total amount	DIN 38405-D19 and DIN 51408-1	mg/kg DM	131,0
Sulphur, total amount	DIN 51724-1	mg/kg DM	4700,0
Iron	DIN 38406-E1 - 1	mg/kg DM	30600,0
Acid insoluble substances	DIN 55920	% ash	20,2
Silicate	AAS	% ash	10,4

The sludge presents a considerable amount of chloride and sulphur. Fig.2 shows the three desiccators in the fume cupboard (a) and the samples lying on the plastic support and covered with sludge (b).



a)



b)

Fig.2: (a) setup of the experiment showing the equipment used for the test at room temperature, 80°C and 100°C; (b) disposition of the samples in the desiccator at 100°C

4. Results and discussion

At the end of the test after 6 months the pH of the sludge was measured showing a value of 5.5. A Sample of the water in the base of the desiccator at 100°C was collected and sent for chemical investigation. Table 5 shows the results of the chemical and physical analysis of the water sample.

Table 5: chemical and physical analysis of a sample of water collected from the desiccator at 100°C after test

Sample analysis of water after test at 100°C			
	standard	Unit	Test result
Conductivity	ÖNORM EN 27888	µS/cm	2730
pH (at 25°C)	DIN 38404 T5	-	5,31
Chlorides	ÖNORM EN ISO 10304 T1, T2	mg/l	107

Iron	ÖNORM EN ISO 11885	mg/l	20
Sulphates	ÖNORM EN ISO 10304 T2	mg/l	650
Sulphide	ÖNORM EN ISO 10304	mg/l	14

As can be seen in Table 5 results show considerable concentrations of chlorides and sulphates.

Fig.3 shows the samples tested at room temperature (a) at 80°C (b) and at 100°C (c) at the end of the 6 months test before cleaning.

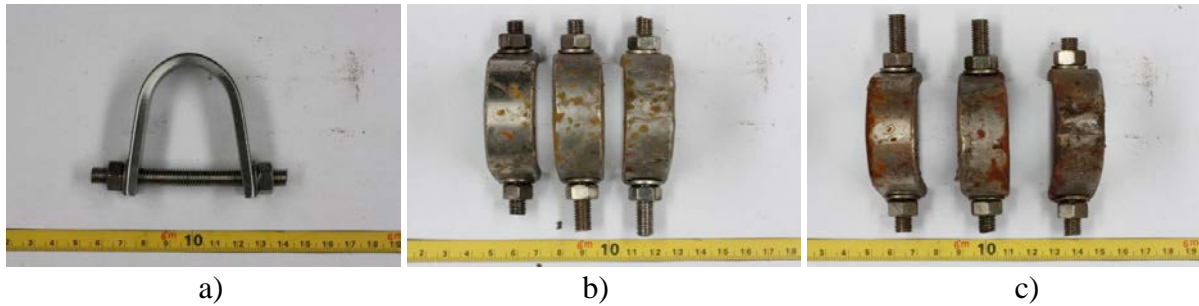


Fig.3: images of the samples at the end of the test before cleaning: (a) sample RT, (b) from left to right: samples 1, 2 and 3 tested at 80°C and (c) from left to right: samples 4, 5 and 6 tested at 100°C

As can be seen in Fig. 3a almost no rests of sludge were visible on the sample tested at room temperature. The surface of the sample under tension was visually compared with images of the same sample before the test and no difference was noticed. Samples tested at 80°C (Fig. 3b) and at 100°C (Fig. 3c) showed sludge strongly attached to the surface. In order to proceed with the visual analysis cleaning by means of brush and sonic bath was necessary. Fig.4 shows the samples tested at 80°C (a) and at 100°C (b) after cleaning.

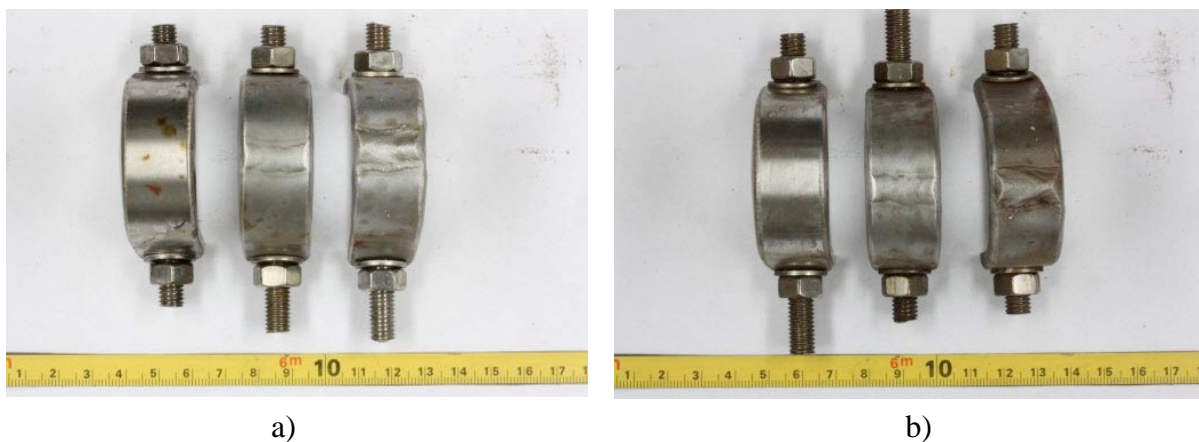


Fig.4: images after cleaning of (a) the samples tested at 80°C, from left to right samples 1, 2 and 3, and (b) the samples tested at 100°C, from left to right samples 4, 5 and 6.

After cleaning a first visual inspection was carried out on the samples side under tension. A naked eye analysis did not evidence any cracks or defects on the samples. A liquid penetrant test (PT) was performed on all samples with particular attention to the area with the higher deformation. Results confirmed the absence of surface cracks. All samples were further investigated by means of optical microscopy. Optical microscopy did not reveal any

defects on the surfaces of the samples with no welding seam (samples RT, 1 and 4) and the samples with a TIG welding seam (samples 2 and 5). During investigation of the samples with MAG welding seams (samples 3 and 6) small imperfections were noticed along the edge of the seam but were assessed as undercuts and not corrosion induced cracks.

Although no cracks were found during PT test or optical microscopy investigation, samples 5 and 6, tested in the most critical conditions (i.e. at 100°C) were cut transversal to the welding seam in order to examine the cross section of the welds. After cutting and embedding the cross sections were examined using light optical microscopy. The bulk material presents the typical microstructure of 1.4418. The heat affected zone was investigated with particular attention on the welding seam side.

Fig.5 shows light optical microscopy images of the heat affected zone in sample 5 (a) and sample 6 (b) and images of the welding seam surface taken from sample 5 (c) and sample 6 (d).

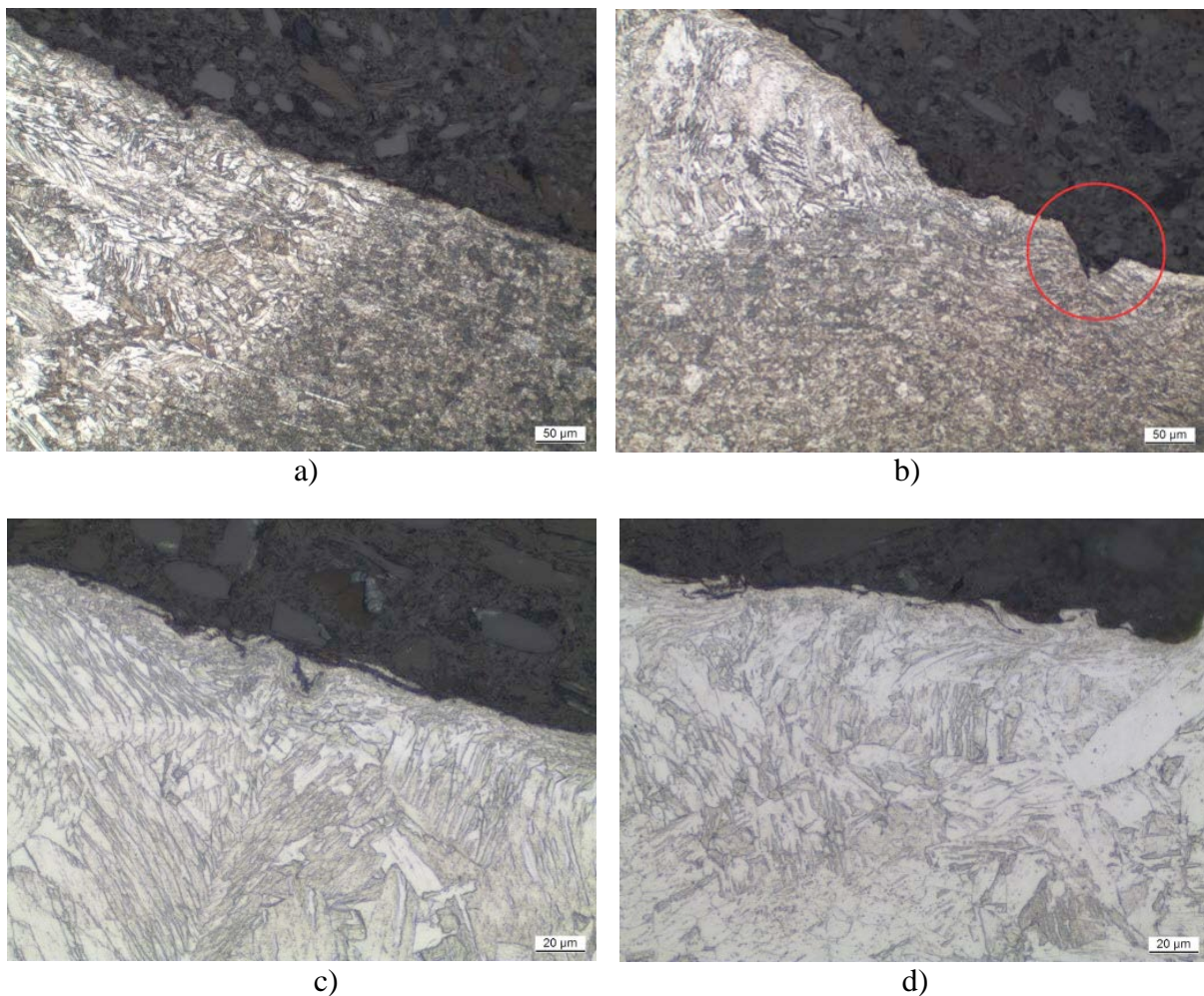


Fig.5: light optical microscopy images of the heat affected zone of (a) sample 5 and (b) sample 6, and of the welding seam surface on (c) sample 5 and (d) on sample 6.

No corrosion cracks were found developing from the surface into the material across the grains or along the grain boundaries. As previously mentioned sample 6 shows an undercut in the transition area between the bulk material and the MAG welding seam (Fig. 5 b, indicated with a red circle). Although an undercut is generally considered having a negative influence

because it introduces notches in the samples, no corrosive attack could be detected in the notch.

4.1 Residual Stress measurements

Residual stresses were measured using the hole drilling and X-ray technique. While the X-ray technique returns residual stresses only near the surface, the hole drilling method can be used to determine the residual stresses up to a depth in the range of 1 to 2mm assuming a planar stress field. However, due to the plastic bending of the samples bending stresses up to yield strength can be expected which makes an exact determination using hole drilling difficult. In first place bending always leads to a stress gradient in thickness direction and secondly very high stresses can be expected due to the loading conditions. When stresses exceed approximately 70% of yield strength, an overestimation due to notch stresses can be expected as shown in Fig.6. [4]

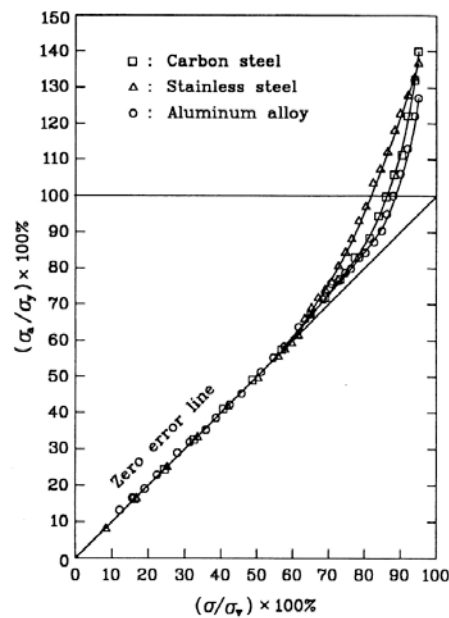


Fig.6: overestimation of the stresses measured on carbon steel, stainless steel and aluminium alloy when the stress exceeds approximately 70% of yield strength [4]

Fig.7 shows the residual stresses measured on samples RT, sample 1 (tested at 80°C) and sample 4 (tested at 100°C) up to a depth of 1mm. Typically a depth up to 1mm can be analysed when a hole with a diameter of 1.6mm is drilled.

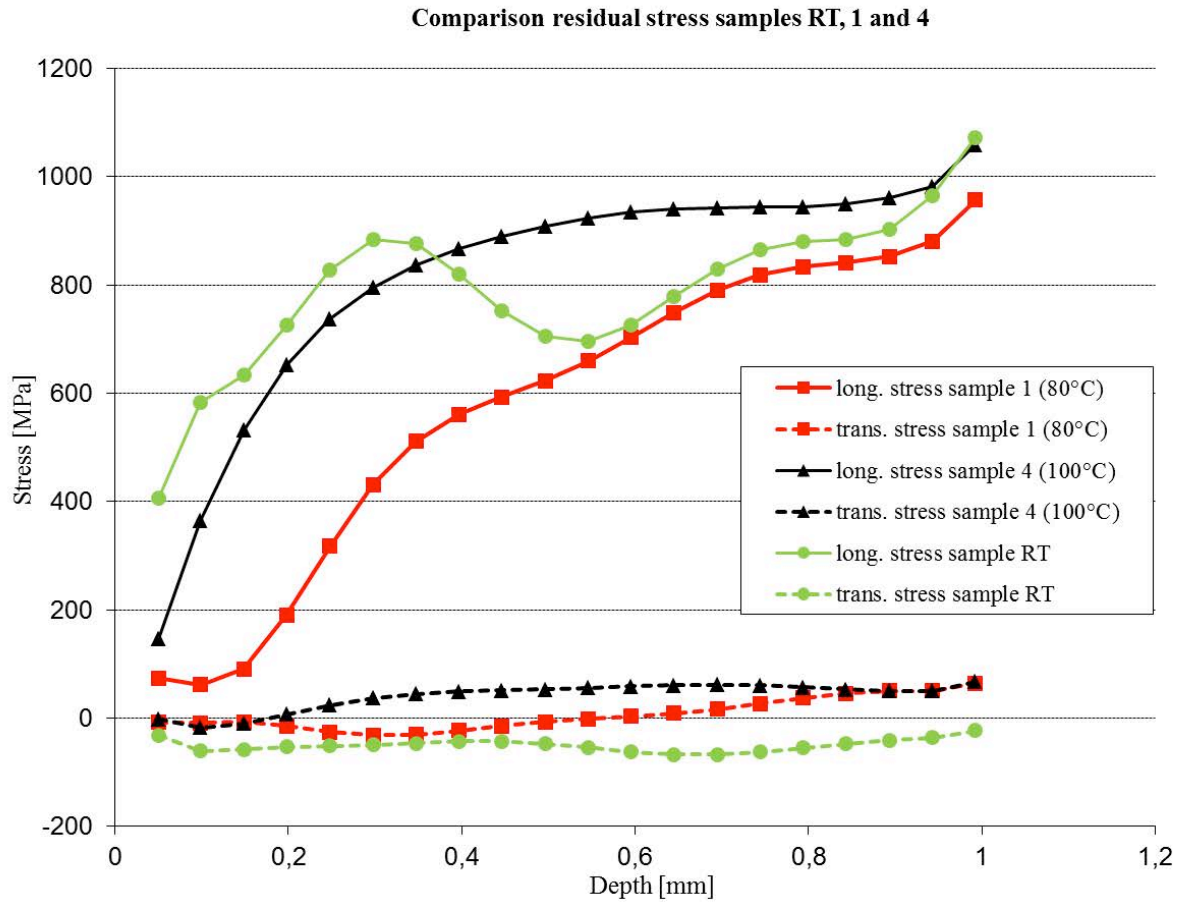


Fig.7: residual stresses measured on sample RT, sample 1 (tested at 80°C) and sample 4 (tested at 100°C)

Since corrosion starts at the surface, the stresses close to the surface are significant. As shown in Fig 7 stresses transverse to the sample bending direction are approximately 0MPa. Bending stresses longitudinal to the bending direction show a significant increase from the top surface with increasing depth. Very low stresses near the surface could be explained by the stress redistribution due to plastic deformation after bending and too low load.

Since the top surface cannot be measured by hole drilling method the measurement was complemented using the x-ray technique. Table 6 shows the results of the residual stress measurements using the x-ray technique.

Table 6: residual stress measurements performed at the surface of sample RT, sample 1 (tested at 80°C) and sample 4 (tested at 100°C)

Label	Stress [MPa]
Sample RT	74±36
Sample 1 (80°C)	294±37
Sample 4 (100°C)	99±32

Very low stresses in the range of 74 – 294 MPa at the surface were confirmed.

5. Conclusion

After six months in a sulphide/chloride corrosive environment at different temperatures (room temperature, 80°C and 100°C) the U-bent 1.4418 samples were visually assessed by means of penetration test and optical microscopy. Cross section of the TIG and MAG welded samples tested at 100°C were analysed in order to state the presence of sulphide stress corrosion cracking. No cracks or signs of corrosion were found either on the welded or the seamless samples. Residual stress measurement confirmed tensile stresses at the surface of the samples.

These preliminary results demonstrate the feasibility of using martensitic stainless steel 1.4418 in corrosion environment containing a significant amount of chloride and sulphur. However, the low value of longitudinal bending stress measured on the surface could have decreased the criticality of the experimental conditions. Further investigations on field are therefore encouraged to verify the positive results obtained in laboratory condition.

References

- [1] L. Scoppio, M. Barteri and G. Cumino, Sulphide Stress Cracking Resistance of Supermartensitic Stainless Steel for OCTG, Proceedings, NACE Corrosion (1997), paper n.23
- [2] K. Kondo, K. Ogawa, H. Amaya, M. Ueda, H. Ohtani, Development of Weldable Super 13Cr Martensitic Stainless Steel for Flowline, Proceeding of The Twelfth International Offshore and Polar Engineering Conference, Japan (2002), p.303
- [3] M. Kimura, T. Tamari, K. Shimamoto, High Cr Stainless Steel OCTG with High Strength and Superior Corrosion Resistance, JFE Technical Report (2006), p.7
- [4] Y. C. Lin, C. P. Chou, Error induced by local yielding around hole in hole drilling method for measuring residual stress of material, Materials Science and Technology 11 (1995), June, p. 600