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High-Pressure SSC Testing of TMCP Large-Diameter Pipeline Steel

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ABSTRACT

In the recent years concerns have been raised on the validity of 1 bar H_2S testing to be representative of the full extension of SSC region 3 as currently defined in NACE MR0175 / ISO 15156-2.

Within this work SSC four-point bend tests have been performed on base material and weld specimens from TMCP-based large-diameter pipes at exposure conditions in the range of 1-12 bar H_2S partial pressure in the presence of different levels of CO_2 up to 24 bar. The results are discussed based on microstructure and hardness of the tested pipes. Metallographic evaluation of the specimens to distinguish between SSC, grooves or stress-induced pits has been performed based on a recently published micrographic evaluation criteria chart. For this evaluation method, several examples are presented and discussed to contribute to the collection of data as a basis for damage feature evaluation.

The results show that the tested TMCP-based large-diameter pipes are resistant to SSC at partial pressures of H_2S above 1 bar, based on material parameters and test conditions. It is recommended to further investigate how the limits of SSC resistance depend on the quantity of CO_2 present.

Key words: SSC, TMCP, High Pressure

INTRODUCTION

Pipeline steels exposed to hydrocarbon environments containing hydrogen sulfide (H_2S), which are referred to as sour environments, must be resistant to hydrogen-assisted damage such as Hydrogen Induced Cracking (HIC), Sulfide Stress Cracking (SSC) and Stress Oriented Hydrogen Induced Cracking (SOHIC). For resistance testing on small-scale specimens standardized test methods are widely accepted, such as NACE TM0316 for SSC, or have been recently developed, such as AMPP TM 02451 for SOHIC. (1,2) The test conditions and evaluation and acceptance criteria must be appropriate for the field service conditions, particularly for the application of TMCP steel to environments of high severity, i.e. high content of H_2S and CO_2 resulting in high H_2S partial pressure (pH_2S) and low pH.

The influence of local hard zones on the SSC initiation in TMCP steel has been investigated in detail following an in-service SSC failure, and hardness limits and hardness control of plate material have been discussed. (3,4) For projects with a severe environment, a 100 % hardness monitoring by non-destructive testing (NDT) methods can now be applied.(5,6)

In case of the environmental severity assessment the pH-H_2S partial pressure diagram from NACE MR0175/ISO 15156-2 (Figure 1) is widely accepted and used by the industry to select carbon and low alloy steel for sour service when appropriately manufactured following the guidance and requirements from the standard. (7) For qualification at the severest region 3 a partial pressure of 100 kPa (1 bar) H_2S in TM0177 test Solution A is required. However, concerns have been raised on the validity of the qualification approach for partial pressures above 1 bar together with the hardness criteria of 250 HV10 maximum. (8)

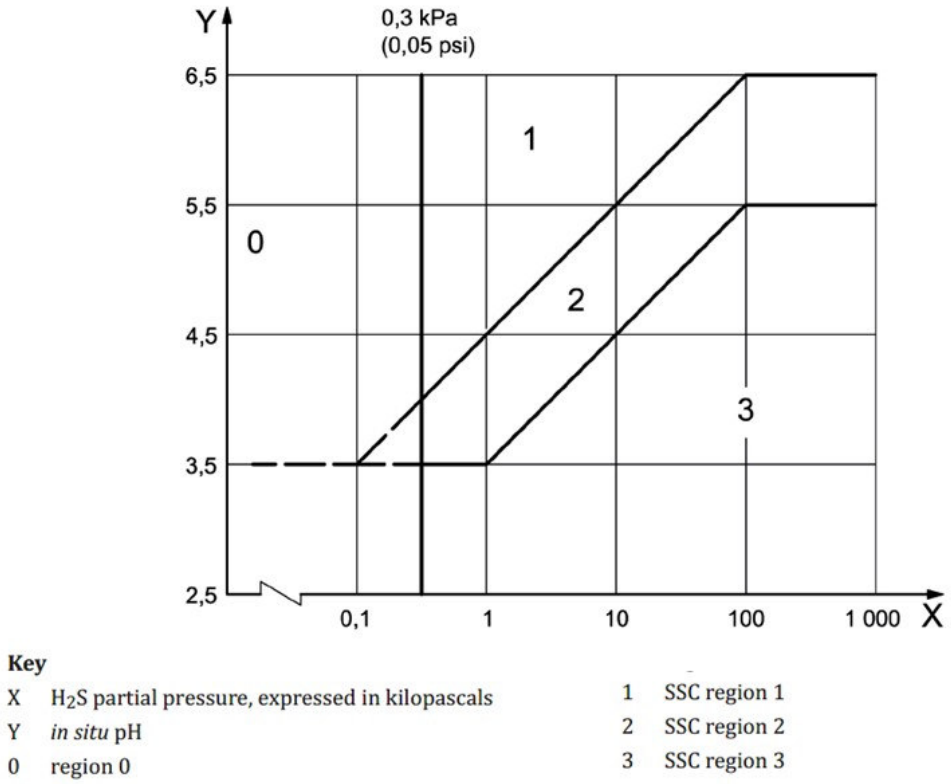

Figure 1: Regions of environmental severity with respect to the SSC of carbon and low-alloy steels (7)

Another observation in SSC testing at H_2S levels above 1 bar or in the presence of CO_2 is stress assisted grooving or pitting. (9,10) Under the combined influence of high specimen loads and severe environments stress induced pitting or grooving is likely to occur as a result of corrosive attack on the stressed specimen surface. Distinction between SSC cracks and pitting is essential, especially for determination of pass/fail criteria for SSC testing. Detailed advice on micrographic acceptance criteria has been proposed recently and is also discussed to be included in the next revision of NACE TM0316. The proposed flow chart is shown in Figure 2. (11)

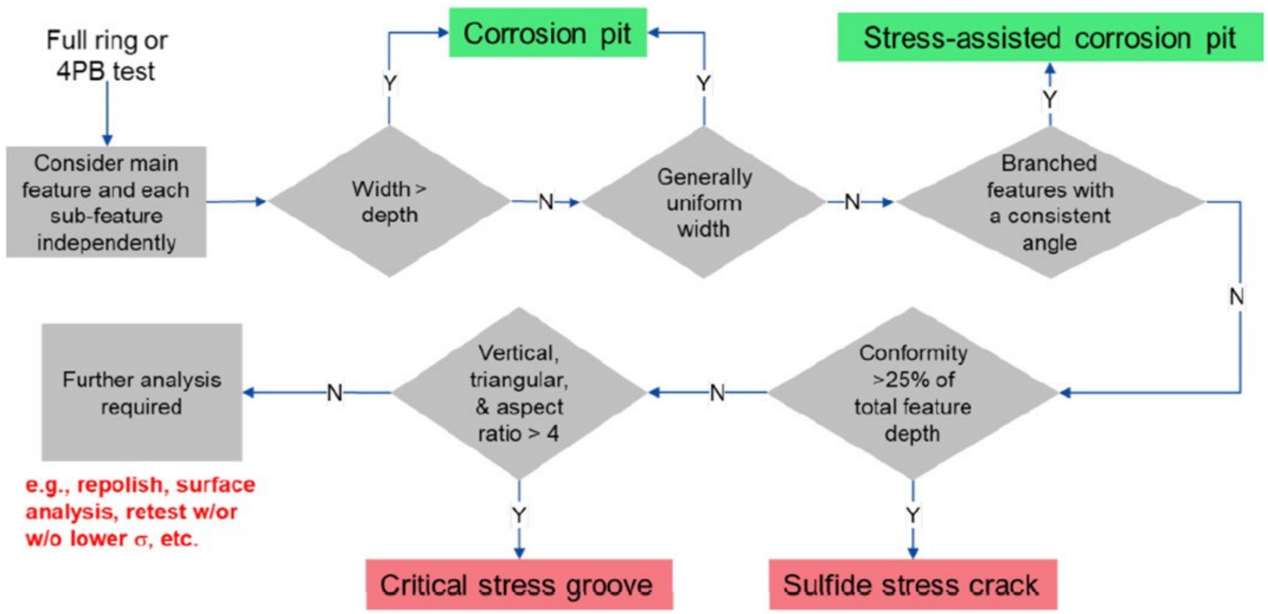

Figure 2: Acceptance criteria flow chart [11]

Within this work the performance of TMCP-based large-diameter pipe material at exposure conditions in the range of 100-1200 kPa (1-12 bar) H_2S partial pressure in the presence of different levels of CO_2 up to 2400 kPa (24 bar) has been investigated with regard to the above-mentioned requirements and evaluation criteria.

EXPERIMENTAL PROCEDURE

Investigated Material

SAWL large-diameter pipeline material of grade API[(1)] 5L X65 produced for sour service was investigated within this study. The pipe diameter was 812 mm (32”) and the wall thickness was either 28.8 mm or 25.4 mm. The steel was fully HIC resistant when tested according to NACE TM0284-2016 in test Solution A with Crack Lengths Ratio (CLR), Crack Thickness Ratio (CTR) and Crack Sensitivity Ratio (CSR) = 0 %. The microstructure of the steel was mainly bainitic and is shown in Figure 3 and the chemical analysis is shown in Table 1.

[(1)] American Petroleum Institute (API). 1220 L. St., N.W., Washington, DC 200005-4070

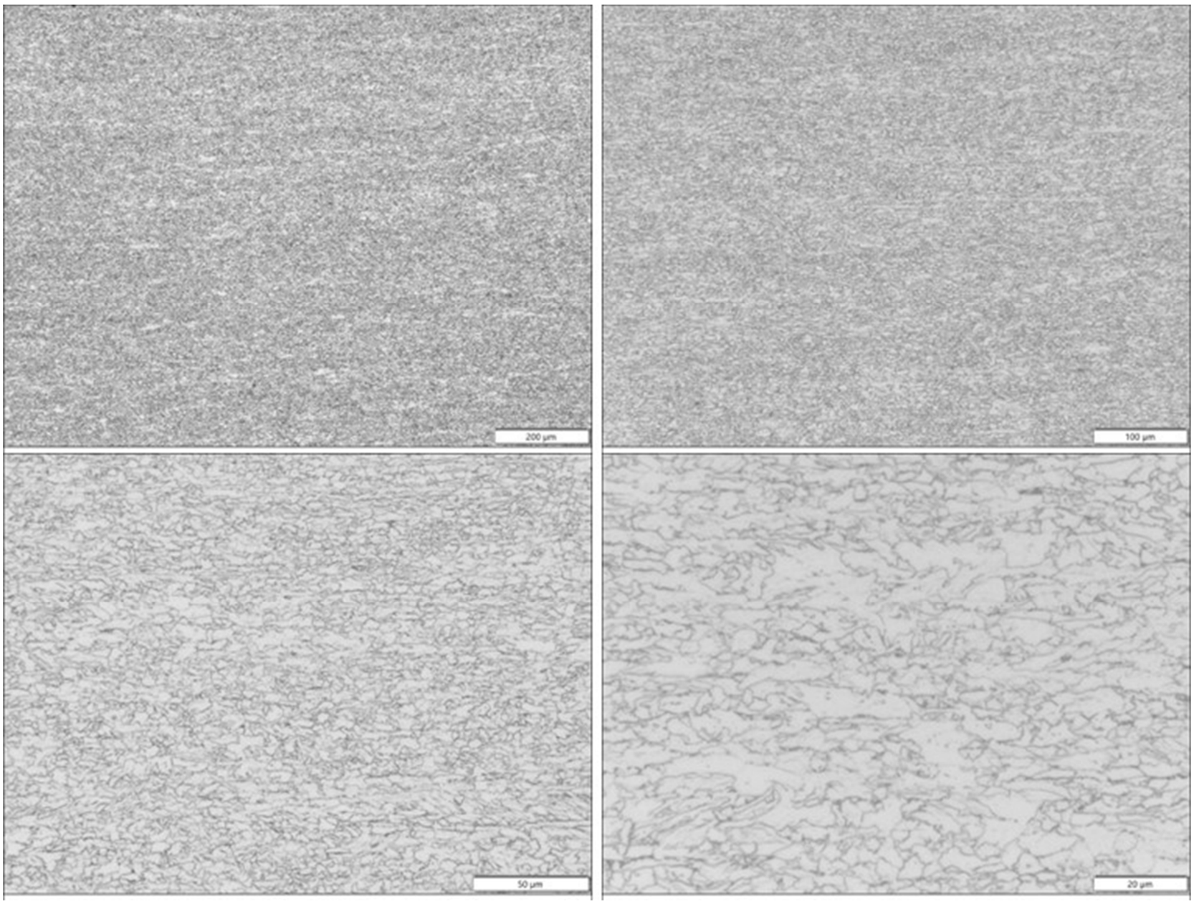

Figure 3: Microstructure of investigated X65 steel

Table 1:
Chemical analysis of investigated X65 steel

Chemical Analysis [Weight %]								
	C	Si	Mn	P	S	Ni	Nb + V + Ti	Others
Pipe	0.04	0.26	1.42	0.006	0.001	0.44	0.04	Cu, Cr

SSC tests have been performed on several base metal specimens from eight different pipes and heats. The average surface hardness of the specimens referenced as LH (low hardness) is ~225 HV0.1 at 0.25 mm below the surface. The average surface hardness of specimens from one pipe referenced as EH (elevated hardness) is ~275 HV0.1 at 0.25 mm below the surface. In addition, transverse weld LH specimens have been tested. The typical hardness distribution is shown in Figure 4 for a LH and EH specimen and a typical weld specimen. Measurement has been performed over the complete stressed specimen area of 50 mm with

- HV0.1 measurement at 0.25 mm below the surface
- HV 0.1 measurement at 1 mm below the surface and
- HV10 measurement at 1 mm below the surface.

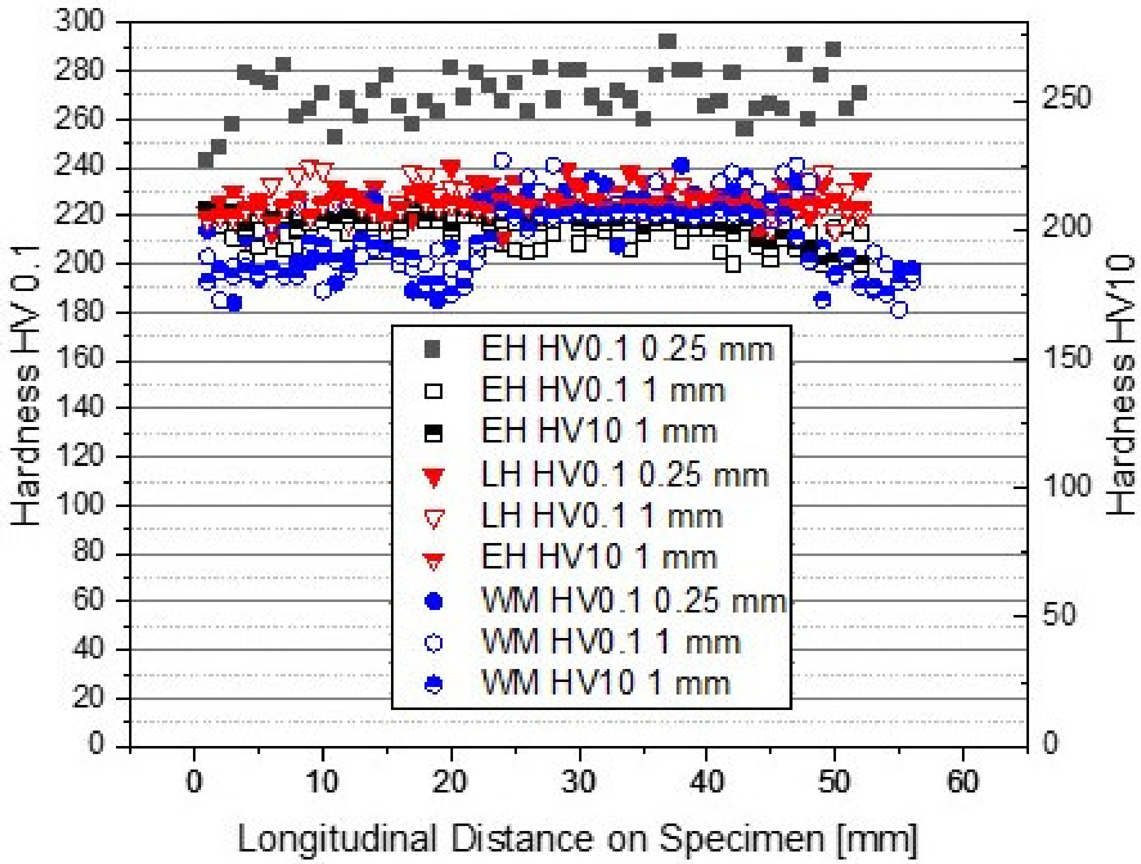

Figure 4: Hardness distribution in LH, EH and weld specimens

The actual yield strength (AYS) was determined on longitudinal round bar tensile specimens for each pipe and heat separately and was in the range between 481 MPa and 530 MPa for LH specimens and 508 MPa for EH specimens.

Flat test specimens, which fulfill the requirements of NACE TM0316-2023 with a length of 140 mm, a width of 15 mm and a thickness of 5 mm were machined. (1) Base material specimens were taken longitudinal to the pipe axis at 180° pipe circumference opposed to the seam weld as close as possible to pipe inside surface keeping the surface representing the pipe inside intact and unmachined. Weld specimens were machined transverse to the longitudinal weld as close as possible to the pipe inside, but with fully machined surfaces without the weld reinforcement. For each test condition a set of at least three specimens from different pipes and heats, including one EH specimen has been tested for the base material and longitudinal weld.

Test Procedure

SSC four-point bend tests have been performed in 6 different test conditions under ambient and elevated pressure at ambient temperature (25°C). The details are summarized in Table 2.

Table 2:
Test Conditions

Test condition	p H_2S [bar]	p CO_2 [bar]	Load AYS	Test solution	pH	Test duration
A	1.0	0.0	90%	TM0177 A	2.7-4.0	720 h
B	1.3	3.5	90%	TM0177 B	3.5	720 h
C	3.3	6.0	90%	TM0177 B	3.5	720 h
D	7.0	3.0	90%	TM0177 B	3.5	720 h
E	12.0	3.0	90%	TM0177 B	3.5	720 h
F	12.0	24.0	90%	TM0177 B	3.5	720 h

A load of 90 % of the actual AYS of each investigated pipe was applied to each test specimens. For load measuring and to check for any relaxation, strain gauges were utilized. Tests at ambient pressure (condition A) were performed in NACE TM0177-2016 test Solution A within the required pH ranges in glass vessels. Tests at elevated pressure (conditions B to F) were performed in autoclaves made of stainless steel with a maximum volume of 40l. The pH of the test solution TM0177 Solution B was adjusted with sodium hydroxide to 3.5 only before test start. The oxygen concentration was measured after transfer of de-aerated test solution into the autoclave and was far below 10 ppb. The autoclaves were pressurized to the designated H_2S and CO_2 partial pressures using H_2S and CO_2 as test gases by repeated intervals of pressurizing and monitoring until the pressure was constant. The pressure was monitored throughout the test, and if a pressure drop of more than 0.5 bar occurred, the test gas was re-plenished by immediate re-pressurization. At test end the autoclave was de-pressurized and purged with N_2 to remove any H_2S or CO_2 before opening.

After test termination the specimens were evaluated for cracking by visual inspection with photo documentation and by wet magnetic particle inspection (MPI). For metallographic evaluation the specimens were sectioned at 1/3 and 2/3 width in longitudinal direction and evaluated for SSC cracks, pits and stress grooves over the complete tested length as per NACE TM0316.

RESULTS AND DISCUSSION

Evaluation methods for the SSC specimens must be capable of identifying SSC cracks that have initiated during the test Non-SSC related phenomena like small corrosion pits or HIC-blisters are usually also reported for information. Visual evaluation is the easiest and most convenient evaluation method for SSC specimens, as only a binocular with a magnification of 10x is necessary. Failed SSC specimens are often already separated into two parts, or the SSC cracks can clearly identified by naked eye. To detect surface-breaking cracks wet magnetic particle testing (MPI) can be applied additionally as an easy-to-provide technique. Additional metallographic sectioning has become more and more attractive, as it reduces the risk of “missing” a feature that could be identified as SSC. However, compared to visual examination and MPI, this is more time consuming and sufficient evaluation capacity (preparation, skilled technicians) is required. The highest challenge within evaluation is the distinction between “real” SSC cracks and all other corrosion- and stress-related phenomena, like pits or stress-assisted corrosion (SAC).

The results of visual evaluation, MPI and metallographic evaluation for the tested specimens are summarized in Table 3 for all tested conditions based on specimen location (base material or specimen containing a longitudinal weld) and test condition with partial pressure of H_2S and CO_2. Specimens are stated o.k. with no visible surface phenomena and no indications in MPI evaluation.

Table 3:
SSC Test Results

Test condition	Specimen Location	Evaluation		
		Visual	MPI	Metallographic
A	base material	o.k.	o.k.	Small pits
	weld	o.k.	o.k.	Small pits
B	base material	o.k.	o.k.	SAC / Pits
	weld	o.k.	o.k.	SAC / Pits
C	base material	o.k.	o.k.	SAC / Pits
	weld	o.k.	o.k.	SAC / Pits
D	base material	o.k.	o.k.	SAC / Pits
	weld	o.k.	o.k.	SAC / Pits
E	base material	EH: SSC; LH Blister	EH: SSC; LH Blister	EH: SSC; LH: HIC Blister
	weld	Blister	o.k.	HIC Blister (BM) / SAC / Pits
F	base material	o.k.	o.k.	SAC / Pits
	weld	o.k.	o.k.	SAC / Pits

Visual evaluation

Test condition A with a partial pressure of 100 kPa (1 bar) H_2S is the most common SSC test condition and also required for qualification for SSC region 3 of NACE MR0175/ISO 15156-2. All tested specimens showed no cracking in visual evaluation and MPI. Metallographic evaluation revealed only small corrosion pits, if any. Within test conditions B, C and D the H_2S partial pressure was increased together with an additional amount of CO_2. Up to test condition D, where 700 kPa (7 bar) H_2S and 300 kPa (3 bar) CO_2 was present, no visual cracking phenomena could be detected. Within metallographic evaluation typical stress-assisted corrosion pits (SAC) and grooves could be identified in the sections. The visual appearance of the stressed specimen surfaces for base metal specimens tested at condition D is shown in Figure 5 for a LH and EH specimen. The stress-assisted grooving is clearly visible.

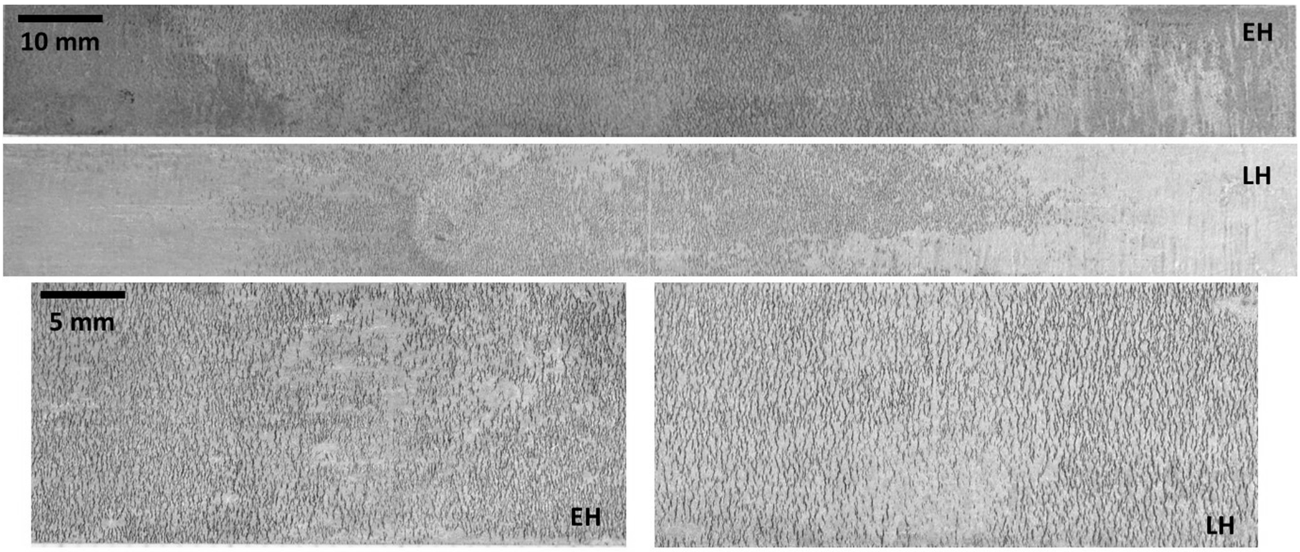

Figure 5: Visual appearance of base material specimens tested at condition D

Condition E had a higher H_2S partial pressure (1200 kPa, 12 bar), the pressure of CO_2 was kept at 300 kPa (3 bar). SSC cracking is clearly obvious for the base metal EH specimen (Figure 6), some LH specimens showed HIC blistering over the complete specimen surface, also outside of the test area between the inner rollers of the four-point bend jig. Weld specimens showed also some blister occurrence in the base material part and a suspicious groove, that can be assumed to be a crack at low magnification on the first view (Figure 7), however high magnification made clear that it was only a partly corroded stress groove feature. Further metallographic evaluation has also been made in this area.

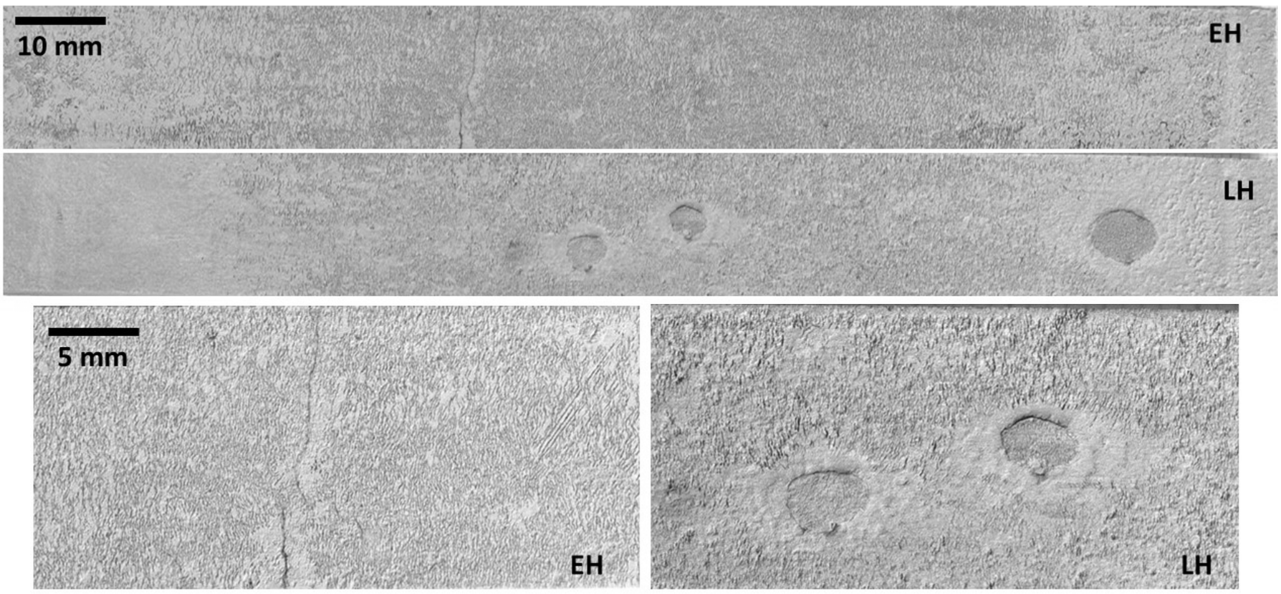

Figure 6: Visual appearance of base material specimens tested at condition E

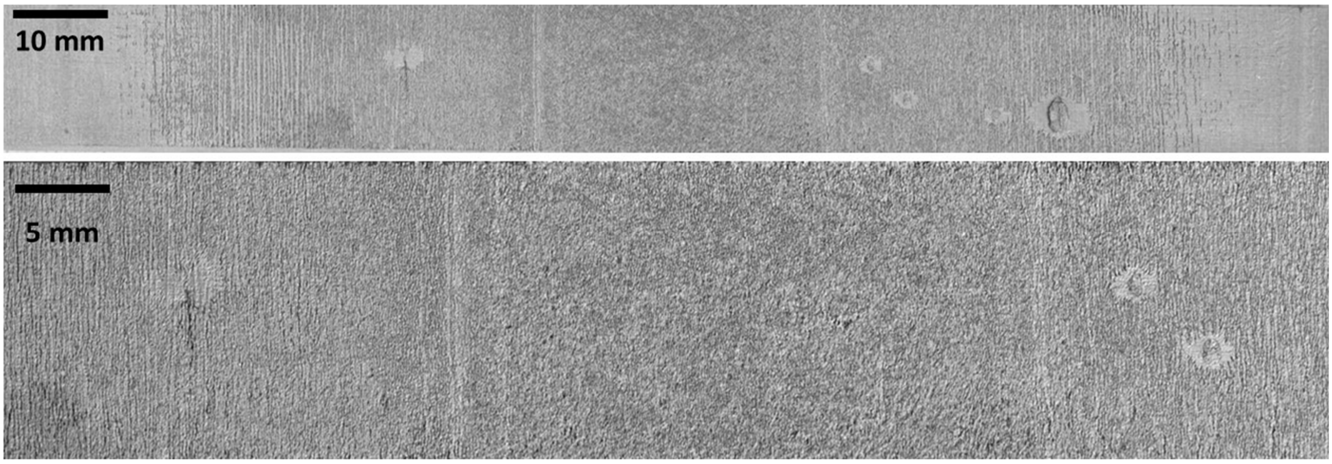

Figure 7: Visual appearance of weld specimen tested at condition E

Within test condition F the effect of a higher CO_2 amount on the test results has been investigated, as it was increased from 300 kPa (3 bar) to 2400 kPa (24 bar), the H_2S partial pressure was kept constant at 1200 kPa (12 bar). In contrast to condition E no cracking or severe blistering is visible at the same partial pressure of H_2S. The specimens show a fairly smooth surface with some grooving (Figure 8), likely as a result of more intense CO_2 corrosion due to the higher CO_2 level.

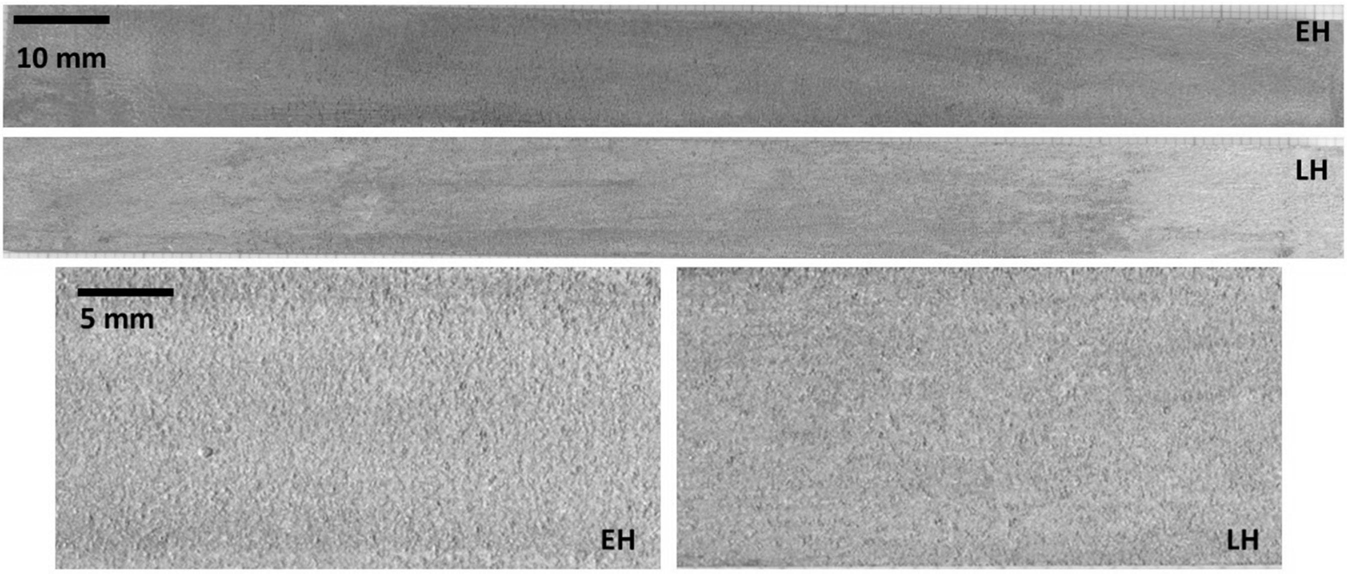

Figure 8: Visual appearance of base material specimens tested at condition F

Crack evaluation

SSC cracking and blistering for test condition E has been further investigated including hardness determination around the cracks. The EH specimen showed a clear SSC crack. Hardness (HV0.1) measurements around the complete crack structure have been performed and are shown in Figure 9a. At a sub-surface hardness level of 281 and 283 HV0.1 the crack start can be assumed. Around the crack depths of ~850 µm the hardness reduces to 212 HV0.1 in through thickness direction. LH specimens did not show any SSC cracking, but some HIC blisters. In Figure 9b and 9c the location of a HIC blister in the base material of a weld specimen is shown and the hardness is determined relatively low with 152-164 HV0.1. Also, the on the first view suspicious feature from Figure 7 has been evaluated, showing only wide pitting (> 100 µm) with SAC as secondary feature.

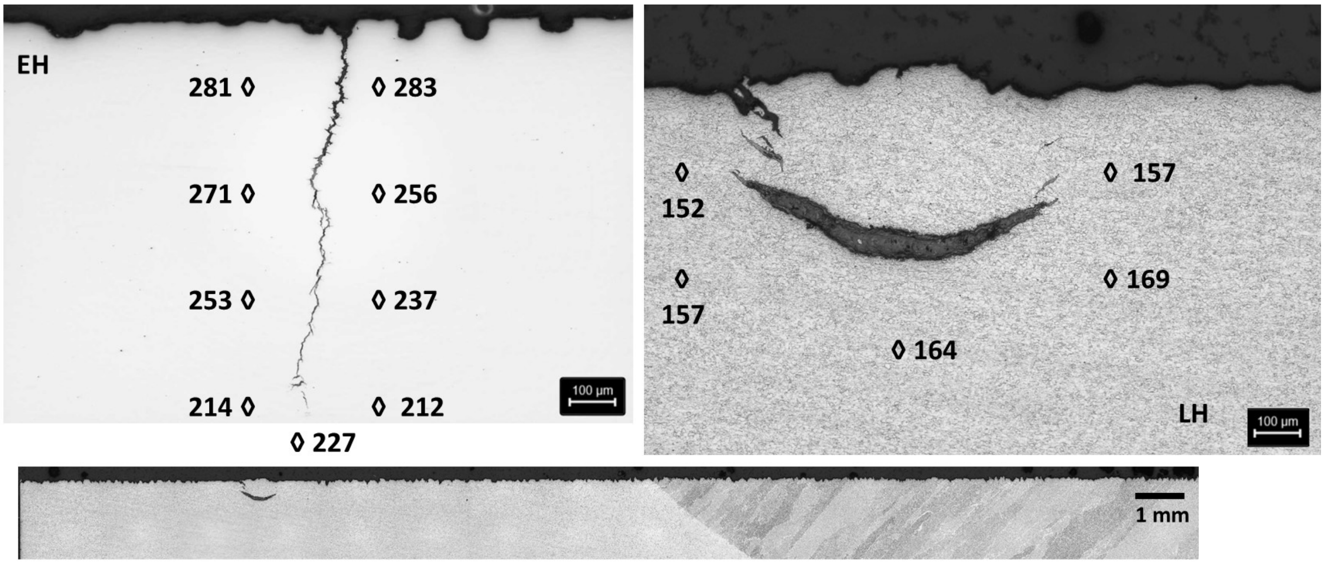

Figure 9: Metallographic evaluation and hardness determination of EH base material specimen (a, top left) and LH weld specimen (b, top right and bottom) tested at condition E

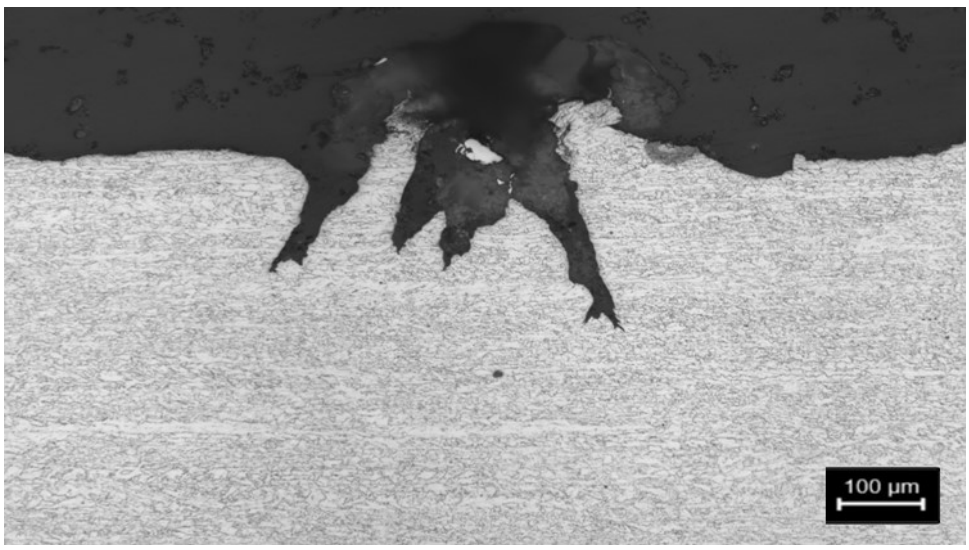

Figure 10: Metallographic evaluation of suspicious feature from Figure 7, base material part of weld specimen tested at condition E, identified as wide pit with SAC as secondary feature

Evaluation pits, grooves and SACs

Metallographic evaluation of unbroken SSC specimens is more frequently required to identify initiating SSC cracks that would possibly propagate into the steel within a longer exposure time. Most frequently the sections are taken in longitudinal direction at 1/3 and 2/3 of specimen width. The mechanism of stress groove initiation and the differentiation between critical SSC cracks and uncritical corrosion pits or grooves is of further interest and has been part of several publications in the past. [9,10,11]

For all test conditions with a partial pressure H_2S of 100 kPa (1 bar) or above in the presence of CO_2, the initiation of stress-induced pits and grooves has been observed. A representative view of a complete 50 mm long section through the test area of a specimen and detailed views are shown in Figure 11.

Figure 11: Longitudinal section of a specimen tested at condition A in different magnifications

About 200-250 individual pits or grooves are present in only one section, which in the worst case must be measured and evaluated individually. Within this test program the number of pits or grooves to evaluate would have added up to a few thousand.

Stress grooves seem to occur independent of microstructure. In Figure 12, similar pits and grooves can be identified in a weld specimen in base material, weld and heat-affected zone (HAZ). This could be interpreted as another indicator for preferred initiation of pits and grooves based on environment and applied stress, rather independent of possible SSC initiation in the steel.

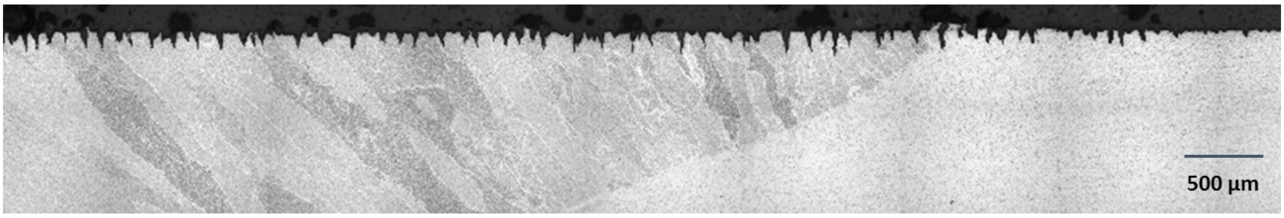

Figure 12: Section of a weld specimen tested at condition A

On the depth and form of pits and grooves over all six tested test conditions, no general correlation can be identified. Different forms as pits, deep pits, stress-assisted corrosion pits or stress grooves can be identified independent of test environment and specimen type (base metal LH/EH, weld) throughout the investigated range of material and test parameters. A higher partial pressure of H_2S does not initiate deeper grooving, as compared in Figure 13 for test conditions B and E, with B showing even slightly deeper, but less frequently appearing pits, although the H_2S level was lower. In general, the depths of nearly all non-SSC related phenomena were below 150-200 µm.

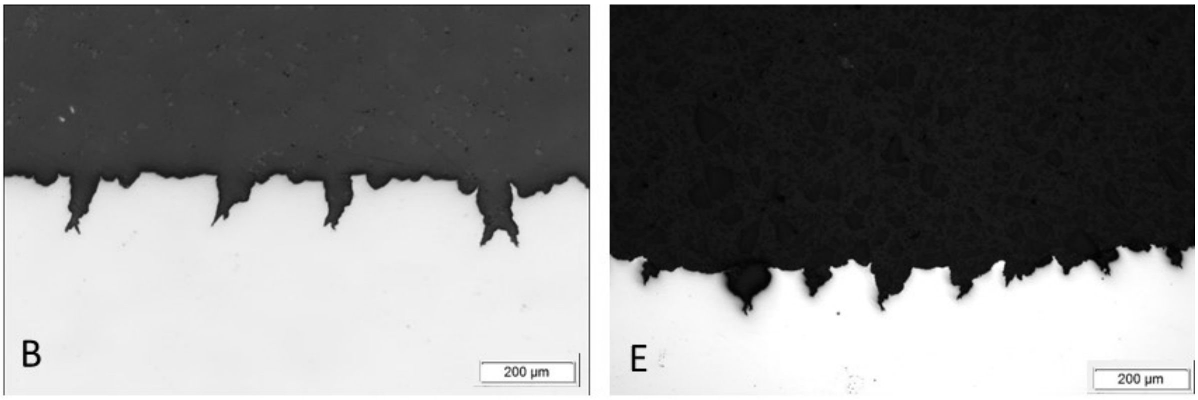

Figure 13: Comparison of corrosive attack in specimens tested at condition B and E

All known and different forms of pitting and stress grooving could be identified in the specimens. For evaluation the criteria from Corrosion paper 14845 (2020) have been applied. (11) Examples are shown in Figure 14 for

- stress grooves with measurement of the vertical, triangular and aspect ratio, which has to be below 4,
- measurements of conformity, which has to be max. 25 % of the total feature depth and
- identification of deep pits and stress-assisted corrosion pits (SACs).

None of the features could be identified as SSC. In cases, where the features were difficult to assess, re-polishing has been performed, which allowed a clearer distinction from other potential damage features.

Considering e.g., a number of several thousand features to be investigated within a short period of time, this procedure is time-consuming and requires unreasonably high capacity for metallographic evaluation. A methodology, which allows adequate evaluation of those features only that extend more than a well-defined limit in the through-thickness direction, would be beneficial. A lower limit would be supported by the fact that for all “ambiguous” features identified within this study, re-polishing revealed the absence of SSC. The results of this study suggest that features that extend less than 200 µm should be excluded from further metallographic evaluation for TMCP pipeline steels. Similar observations have been published for C110 steel. (9) Numerical calculations for different groove geometries have been performed in this publication as another useful tool.

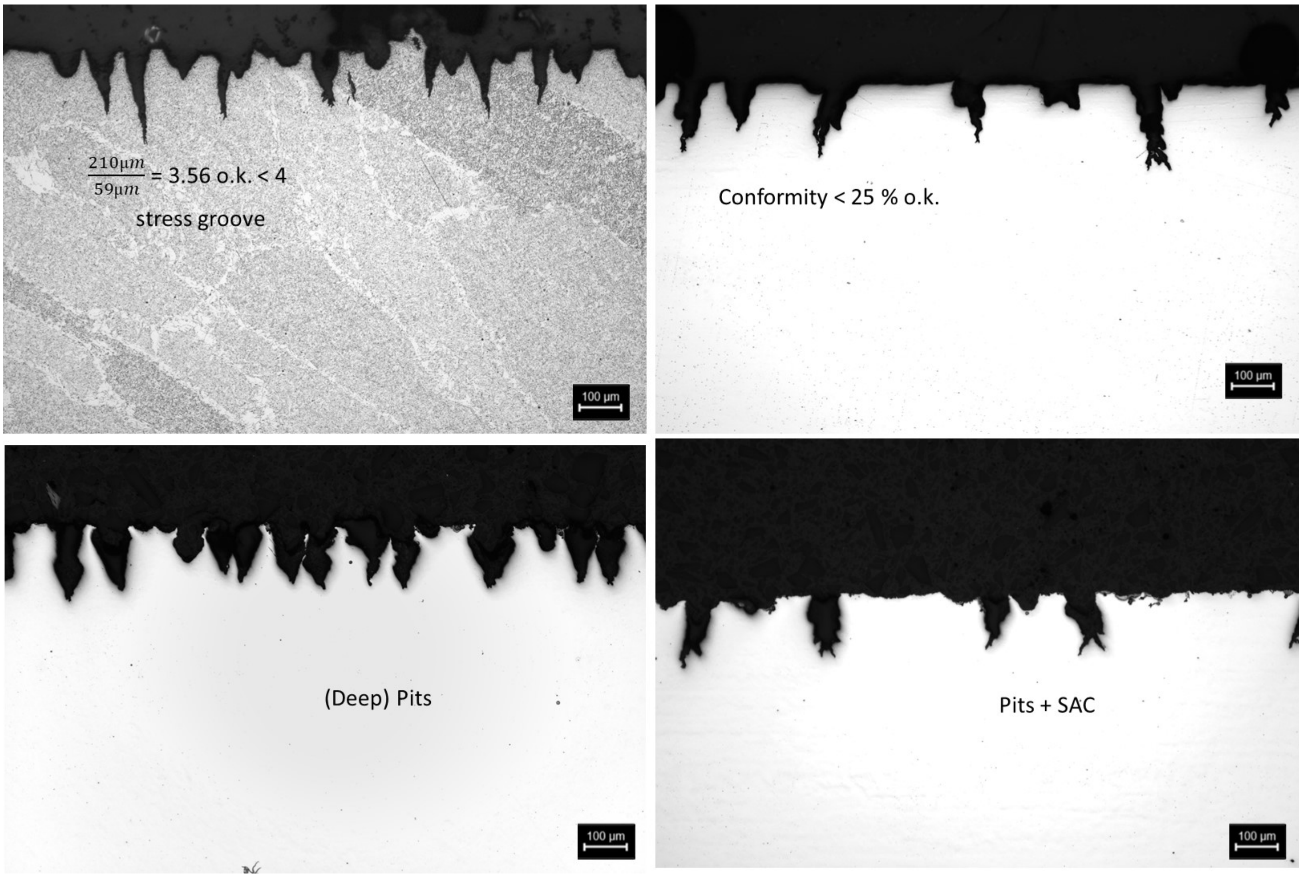

Figure 14: **Examples of feature evaluation in SSC specimens**

CONCLUSIONS

Within this study SSC tests have been performed at test conditions within NACE MR0175/ISO 15156-2 SSC region 3 with H_2S partial pressures up to 1200 kPa under different CO_2 levels on specimens with low sub-surface hardness (~225 HV0.1) and elevated sub-surface hardness (~275 HV0.1).

At all test conditions above a partial pressure of 100 kPa H_2S, a large number of different stress-assisted pits or stress grooves with a depth of 150-200 µm maximum were observed in base material as well as in weld metal. A relation between maximum or average depth of these features and H_2S-level could not be noticed. Extensive metallographic evaluation did not result in any feature being classified as SSC, similar to a previous study on X65 material, which showed that the groove depth is mostly related to the severity of the test environment. (9) It could be recommended that features that extend less than a particular limit (200 µm suggested) should be excluded from further metallographic evaluation. In EFC 16 already a threshold of 100 µm has been recommended in the past. (12)

A relationship between sub-surface hardness, H_2S and CO_2 partial pressure as individual test parameters can be observed. For the investigated steel, the sub-surface specimen hardness was essential only for the SSC performance at H_2S partial pressures above 700 kPa. Up to 700 kPa none of the tested specimens revealed SSC. At 1200 kPa only specimens with sub-surface hardness ≤ 250 HV0.1 passed. However, HIC-blistering was noticed as another effect when testing at such severe conditions. With increasing CO_2 partial pressure, the severity of the test environment was found to decrease, due to the anticipated effect of more intense CO_2 corrosion. A higher partial pressure of CO_2 is apparently enhancing the SSC resistivity under an identical H_2S partial pressure. Ultimately, it is not clear whether this change in resistance is due to differentiation in the corrosion mechanism or to lower H_2S fugacity in the 12 bar H_2S / 24 bar CO_2 condition compared to the 12 bar H_2S / 3 bar CO_2 condition. The level of CO_2 should therefore be considered as relevant and should be close to field conditions when SSC testing at elevated pressure is intended. This might also be of relevance for the ongoing discussion about improvement of the NACE MR0175/ISO 15156 severity diagram.

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