



## Consequences of sigma phase on pitting corrosion resistance of duplex stainless steel

T. Mathiesen<sup>a</sup> <sup>1</sup>, J. V. Hansen<sup>1</sup>

<sup>1</sup>FORCE Technology, Department of Corrosion and Metallurgy, 2605 Brøndby, Denmark

**Abstract.** The recent examples of improperly heat treated duplex fittings for off-shore production facilities have raised the need for evaluating possible consequences on corrosion resistance and failure mode. In several cases the excessive sigma phase content was not realised before the systems had been in service for 1-2 years. As a basis, the presence of considerable amounts of sigma phase is unacceptable due to its detrimental influence on corrosion and mechanical properties. However, small amounts of sigma phase or sigma phase formed at certain temperature intervals might be without significance in some applications. The paper briefly reviews the available literature on the subject. Furthermore, the resistance against localised corrosion is examined using the ASTM G150 method for CPT determination on duplex specimens representing different levels of sigma phase. The obtained results are compared to other stainless steel types and correlated with typical service conditions found in off-shore production facilities.

### 1. Introduction

The recent examples of improperly heat treated duplex fittings for off-shore production facilities have raised the need for evaluating possible consequences on corrosion resistance and failure mode. The issue was realised quite late after a large number of components had been installed in projects all over the world. In some cases, the excessive sigma phase content was not realised before the systems had been in service for 1-2 years. Authorities announced warnings addressing the problem including PTIL and HSE [1,2]. Consequently, large scale efforts have been made to identify the substandard components by using on-site metallographic examination in order to locate and replace the affected components.

The presence of sigma phase in duplex stainless steel is usually unacceptable due to its detrimental influence on corrosion and mechanical properties. Of main concern is the reduced fracture toughness, which is related to the hardness and brittleness of the sigma phase in itself and possibly also to the precipitation hardening effect of the phases foreign to the ferritic-austenitic matrix. Similarly, the corrosion resistance is affected by the depletion of chromium and molybdenum at the interface adjacent to the formed sigma phase.

The effect on toughness due to sigma phase formation in thin-walled components has been dealt with separately elsewhere [3,4,13]. This paper focuses on the effect on pitting corrosion resistance in chloride-containing environment in order to obtain a basis for consequence assessment that can possibly support and optimise the strategies for replacing the affected components.

---

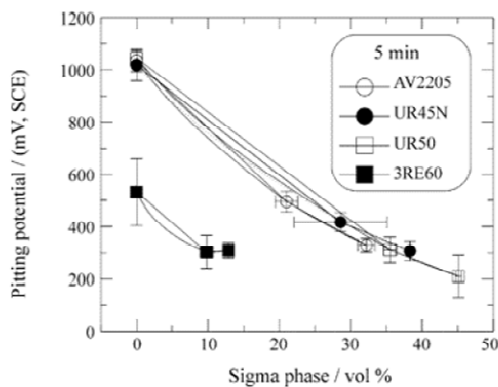
<sup>a</sup> e-mail: trm@force.dk

Numerous papers have been published about the impact on corrosion resistance, especially in relation to sigma phase formed during welding where the low-temperature heat-affected zone (LTHAZ) is of particular concern. Without doubt, even small amounts of sigma phase influence the resistance against most corrosion forms such as pitting [5-12], sulphide stress corrosion cracking [7], intergranular corrosion [13-15] and hydrogen embrittlement [14]. Consequently, the standard criterion is that no sigma phase is allowed in produced duplex materials. There is at least one known example of failure in a seawater system that could be ascribed to sigma phase presence. However, small amounts of sigma phase or sigma phase formed at certain temperature intervals might be without influence in some applications. Fitness for purpose studies have in some cases demonstrated that up to 2.5 % sigma phase in super duplex welds can be accepted without compromising the corrosion properties [5,7,10].

The available literature on corrosion related to sigma phase is much focussed on super duplex materials. For evaluating the consequence on pitting of 22Cr type duplex only limited data are available. A negative influence of sigma phase is always reported, but even when identical test methods are used, the determined value (pitting potential or CPT) could vary to a great extent as illustrated by the data in Figure 1 and Table 1.

Duplex welds for oil and gas installations are usually pre-qualified by using the ASTM G48 test for evaluating the pitting corrosion resistance in ferric chloride solution [16]. This test is an accelerated go/no-go test typically using a temperature criterion of 25 °C for 22Cr duplex steel and 35 or 40 °C for 25Cr duplex steel. Our experience with this technique is that materials occasionally fail the test on a questionable basis due to impractical issues related to e.g. cut faces [17]. Consequently, we have earlier proposed an improved protocol for this test together with DNV [18]. The ASTM G150 method for determining the CPT was applied as part of this study to obtain quantifiable data rapidly [19]. Moreover, this test can be restricted to the surface intended for exposure, and the measured CPT can be directly correlated with literature data. The test showed good agreement between the measured CPT and the results of the G48 exposure tests.

In the current study, the ASTM G150 method has been applied on 22Cr duplex steel representing different levels of sigma phase obtained by heat treatment at 750 and 850 °C. The results are compared to other stainless steel types and correlated with typical service conditions found in off-shore production facilities.



**Fig. 1.** Pitting potentials of duplex stainless steel obtained by polarisation in 3,5 % NaCl at RT [8]

**Table 1.** Pitting potentials of SAF2205 obtained by polarisation in 3,5 % NaCl at 25 °C [6]

Sigma phase vol.-%	E <sub>corr</sub> mV, SCE	E <sub>pit</sub> mV, SCE
0	461	1183
6	-150	151
21	-375	25

## 2. Experiments

### 2.1 Materials

The tested specimens were taken from the same 3 mm plate material of 22Cr duplex stainless steel, known as EN 1.4462 or UNS S31803. The chemical composition is shown in Table 2. The as-delivered material has a characteristic cold rolled microstructure with a volumetric ferrite content of 30.3 % when measured with a Fischer Feritescope.

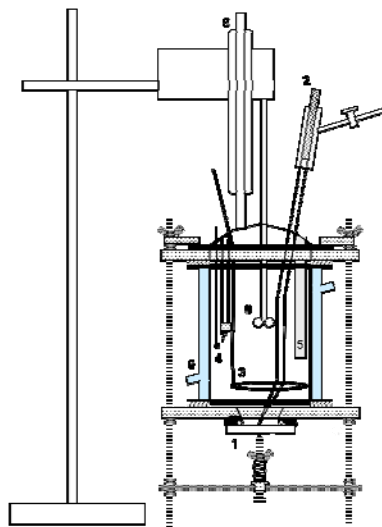
**Table 2.** Composition of the tested material type EN 1.4462 (wt%)

C	N	Si	Mn	P	S	Cr	Ni	Mo
0.021	0.167	1.49	0.025	0.025	0.001	21.90	5.80	2.99

Identical specimens measuring 50x100 mm were cut from the plate material. The specimens were heat treated at 750 or 850 °C for 5, 10, 20 or 60 minutes giving 8 levels of sigma phase formation. This treatment was followed by water quench. The amount of ferrite phase was determined as average values of 5 readings using the Feritescope. The difference between ferrite level in the reference material and the measured Feritescope result was calculated. This technique determines the total amount of transformed ferrite, which includes both secondary austenite and sigma phase. In addition, counting of sigma phase was performed in accordance with ASTM E562 on a selection of specimens. On this basis, the volumetric amount of sigma phase could be estimated.

### 2.2 ASTM G150 exposure

The test face of the specimen was wet ground to #320 in sequential steps. Subsequently, the specimen was left for at least 20 hours in air before exposure. The test set-up is illustrated in Figure 2. To avoid crevice corrosion, a flushed port cell with a specially formed flat gasket was used. The exposed surface area was 4.5 cm<sup>2</sup>.



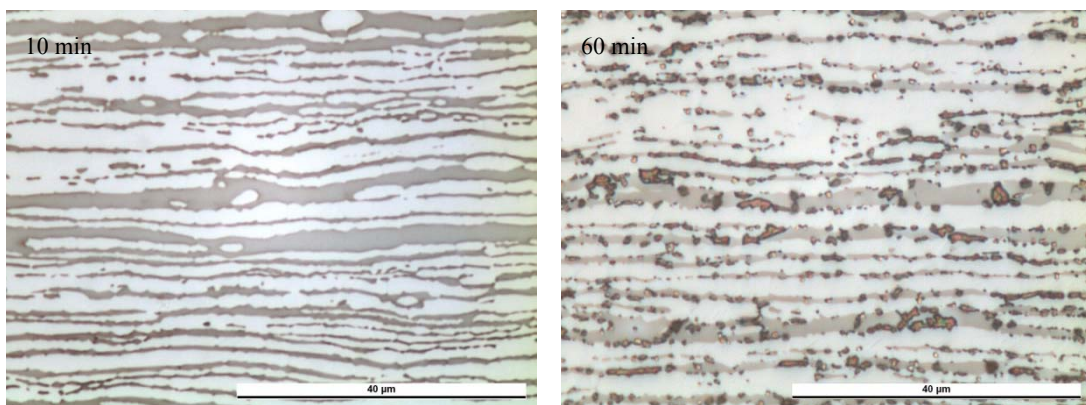
**Fig. 2.** Set-up for ASTM G150 testing: 1. Specimen with flush-port gasket. 2. SCE reference electrode 3. counter electrode 4. Temperature sensor 5. Heater 6. Stirrer 7. Nitrogen purge 8. Reflux. 9. Cooling jacket.

The critical pitting temperature (CPT) was obtained in double by performing a temperature ramp at fixed potential according to the ASTM G150 method. This implies polarisation to +700 mV SCE in a solution of 1 M NaCl. The temperature was raised from 0 °C at a rate of 1 °C/min. The test was ended at a higher current criterion (5 mA/cm<sup>2</sup>) than normal in order to develop a detectable amount of pitting. CPT was read at 10 µA/cm<sup>2</sup>.

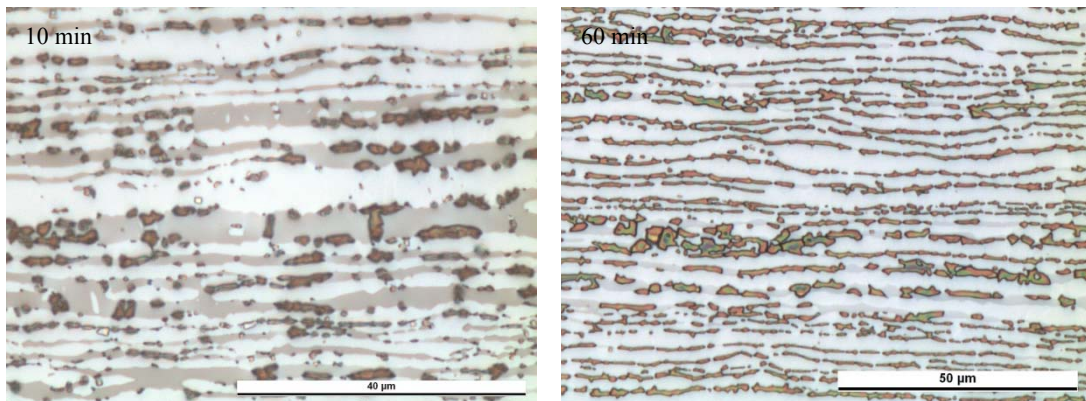
### 3. Results

#### 3.1 Microstructure

The performed heat treatments generated sigma phase contents between 0 and 26 % as can be seen in Table 3. From the micrographs in Figures 3 and 4 it appears that the sigma phase is formed mainly in the ferrite phase. The sigma phase appears as orange, sharp edged particles in the grey ferrite phase. Generally, treatment at 850 °C gives larger and coarser sigma phase precipitates that those observed at 750 °C. Due to the fine grained microstructure, the identification of sigma phase is difficult in the range of 1 to 2 % even at high magnification.



**Fig. 3.** Microstructure of EN 1.4462 stainless steel heat treated at 750 °C for 10 and 60 minutes. Electrolytically etched with NaOH.



**Fig. 4.** Microstructure of EN 1.4462 stainless steel heat treated at 850 °C for 10 and 60 minutes. Electrolytically etched with NaOH.

### 3.2 Critical pitting temperature

Figure 5 shows two examples of the current and temperature curves obtained with the ASTM G150 technique. The start of the curve always shows a decreasing tendency before the stable, passive current is reached at typically  $1-2 \mu\text{A}/\text{cm}^2$ . The prescribed conditioning at +700 mV SCE for 1 minute prior to the temperature scan is apparently not enough to generate stable conditions.

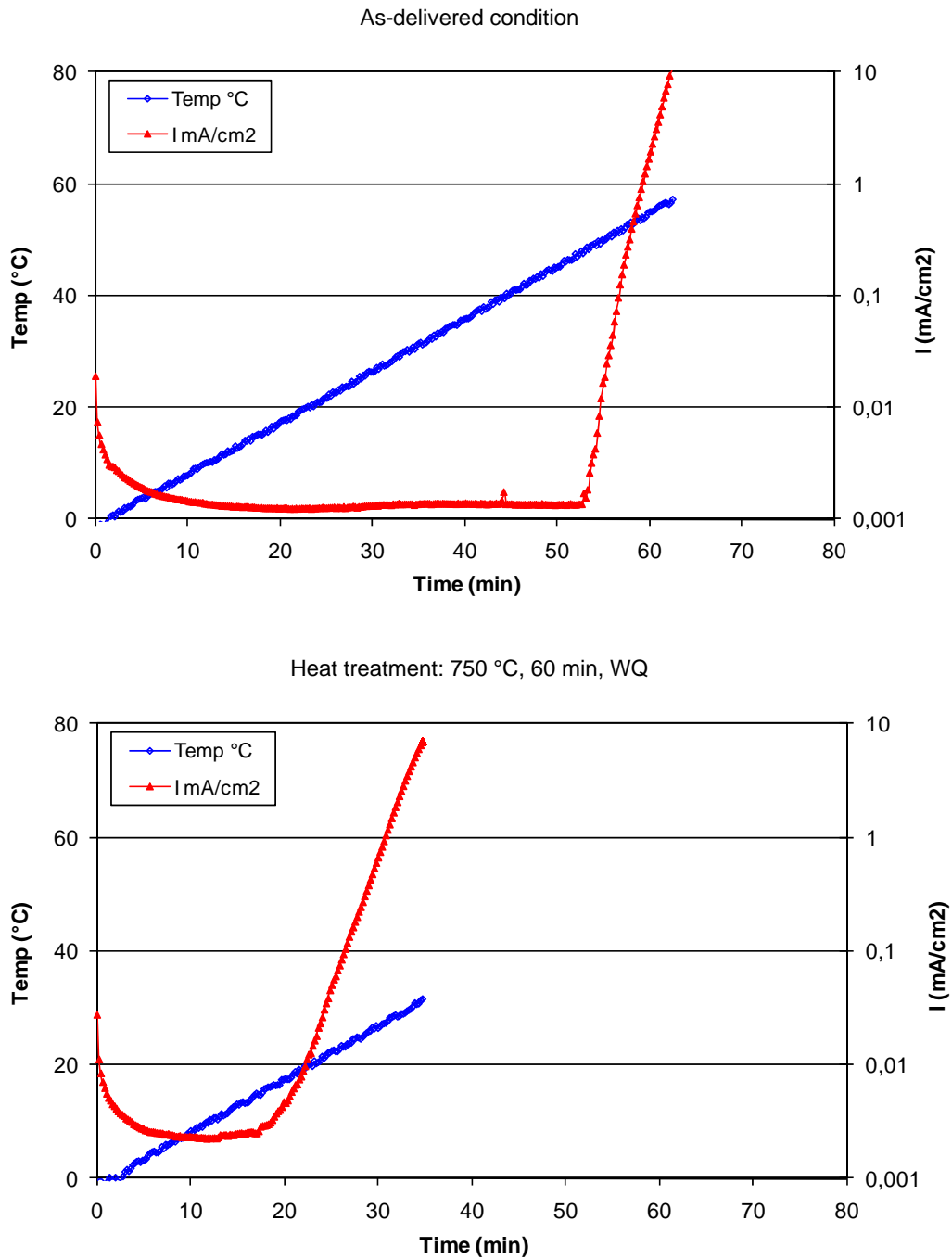
During the temperature scan, a distinct break in the current curve is observed when pitting initiates. Shortly after this point, the pitting temperature is read at  $10 \mu\text{A}/\text{cm}^2$ .

Table 3 compares the obtained CPT values. The presence of sigma phase seems to slightly impair the reproducibility of the test, Figure 6. Generally this method provides CPT values within 2-3 °C for stainless steels without intermetallic precipitates. However, the effect of sigma phase on CPT is evident. At sigma phase contents above 4 % there is a significant and rapid decrease in the measured CPT. Furthermore, it appears that the same amounts of sigma phase obtained at the two different temperatures affect the CPT differently. The effect is stronger for materials heat treated at the low temperature of 750 °C. This correlates well with the fact that diffusion takes place at slower rate causing steeper concentration gradients in the region up to the sigma phase precipitates.

**Table 3.** Sigma phase content and Critical Pitting Temperatures (CPT) determined by using ASTM G150 for duplex EN 1.4462 with different heat treatments

Heat treatment		Transformed Ferrite* Vol. frac., %	Sigma phase, Approx.** Vol. frac., %	Critical Pitting Temperature, °C		
Temperature	Time			n1	n2	Average
SA - as delivered		0	0	46	50	48
750 °C	5 min, WQ	4.3 ± 0.4	0	51	43	47
	10 min, WQ	5.6 ± 0.5	1	46	41	44
	20 min, WQ	10.1 ± 0.8	4	30	30	30
	60 min, WQ	16.3 ± 0.3	10	16	20	18
850 °C	5 min, WQ	5.7 ± 0.3	4	46	39	43
	10 min, WQ	16.3 ± 0.2	14	38	30	34
	20 min, WQ	22.1 ± 0.3	20	26	25	26
	60 min, WQ	27.5 ± 0.1	26	23	23	23

SA solution annealed, WQ water quenched. \*) Determined with Feritscope \*\*) Determined acc. to ASTM E562



**Fig. 5.** Examples of obtained CPT curves using the ASTM G150 technique.

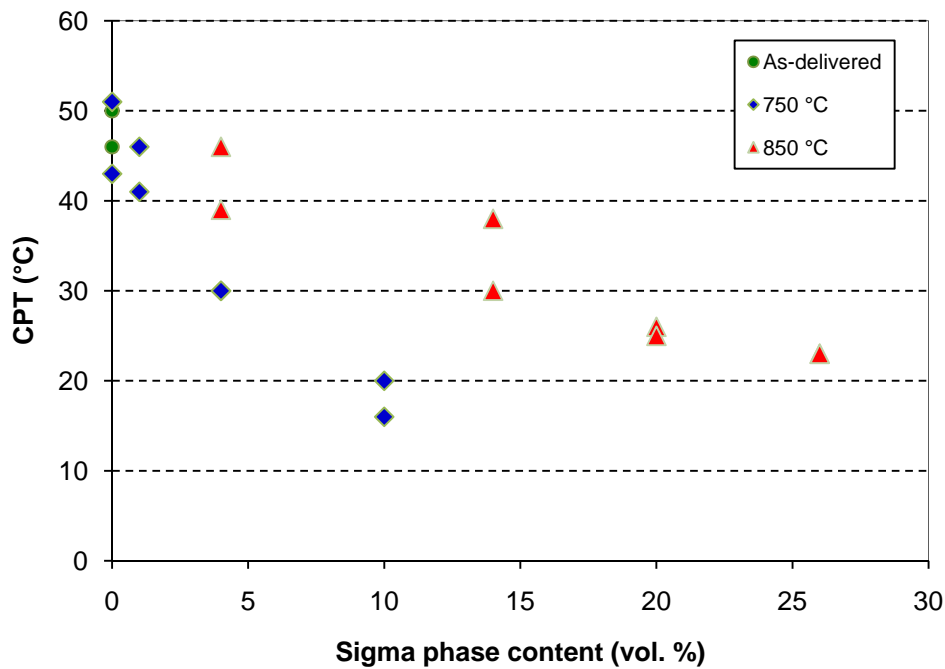


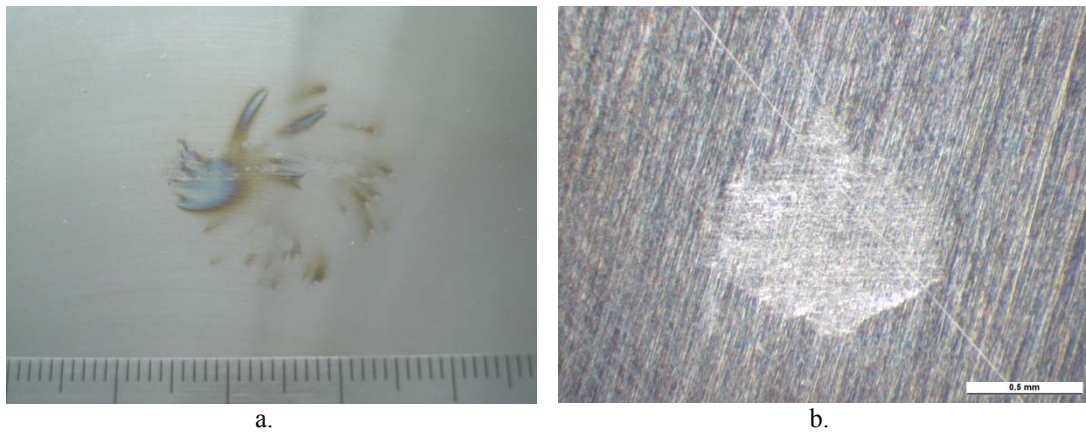
Fig. 6. Influence of sigma phase content on CPT of 1.4462 heat treated at 750 and 850 °C

### 3.3 Corrosion morphology

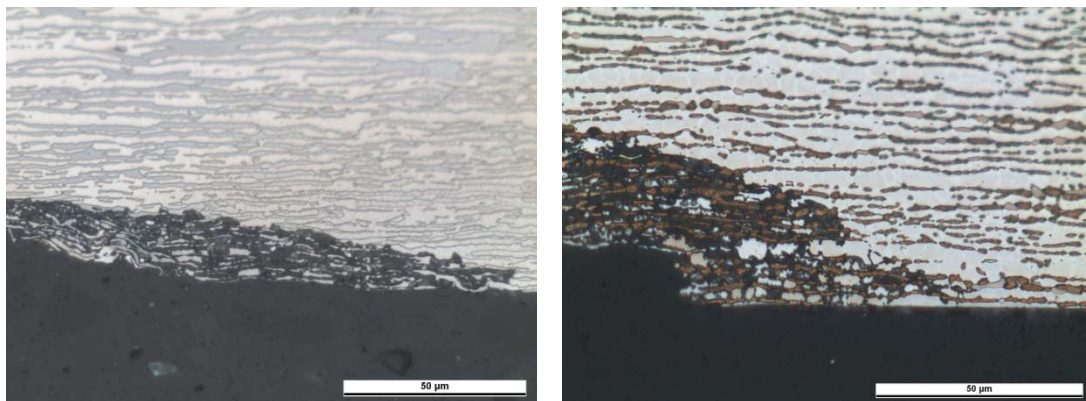
All exposed specimens were examined under a stereomicroscope at 10-50x magnification. Furthermore, the resulting form of corrosion was evaluated by making cross sections of selected specimens. The test results were discarded for a few specimens that showed crevice corrosion due to inadequate flushing through the flush port cell. As expected, this circumstance had a significant negative influence on the CPT.

Figure 7a shows an example of a successfully tested specimen, where pitting is restricted to the exposed area. Typically, 30-50 pits are generated within the exposed area of 4.5 cm<sup>2</sup>. At close hand it appears that the pits are covered by a thin metal film with signs of parallel bands from the cold rolling, Figure 7b.

Cross sections of pits in materials both with and without sigma show the same overall corrosion morphology. In both cases the pits are shallow (up to 50 µm deep) and fairly wide (up to 1 mm). At the corrosion front, the initial dissolution takes place in the austenite phase for solution annealed material. For the sensitised materials, both austenite and ferrite are dissolved, leaving the sigma phase unaffected.



**Fig. 7.** (a) Discoloured trails from pits on tested specimen within the exposed circle measuring  $\text{Ø}24$  mm. (b) Close-up of pit measuring 1 mm in diameter.



**Fig. 8.** Cross section of pits in material (a) as-delivered material and (b) heat treated at 850 °C for 60 minutes.

#### 4. Discussion

The performed tests demonstrate that sigma phase formation in duplex stainless steel has a negative effect on the corrosion resistance given by the critical pitting temperature. This effect becomes evident at sigma phase levels above approximately 4 %. Moreover, for the same amount of sigma phase, the effect is stronger for materials heat treated at 750 °C in comparison to 850 °C. This observation is supported by data in published literature [13]. It can be ascribed to the fact that diffusion takes place at slower rate causing steeper concentration gradients in the region along the sigma phase precipitates. In addition, the formation of secondary austenite is expected to contribute to the inferior corrosion resistance.

The observed corrosion morphology is partly oriented along the longitudinal grains that originate from the cold rolling process. This circumstance results in pits that are wider and less deep (or spherical) than those observed for single phase materials such as austenitic stainless steel. While this might limit corrosion of the rolled surfaces, it makes the steel more susceptible to end-grain attack,

especially when sigma phase and secondary austenite is present, as both phases tends to favour selective corrosion along the phase boundaries.

The obtained CPTs for EN 1.4462 duplex stainless steel in Table 3 can be correlated with other stainless steel grades. Table 4 shows the results of previously examined materials tested with the same technique at FORCE Technology's laboratory. It appears that the severely sensitised duplex steel having up to 10 % sigma phase still provides a CPT at the same level of e.g. lean duplex or 316L. However, if pitting occurs in the sensitised materials, the consequence is more severe since the expected form of corrosion is to some degree intergranular. Consequently, the ranking based on CPT alone should be taken with certain reservations.

**Table 4.** Critical pitting temperatures (CPT) determined by using ASTM G150 for different alloys tested at FORCE Technology.

EN	Alternative name	PRE	Critical Pitting Temperature, °C			
			n1	n2	n3	Average
1.4404	316L (1)	24.1	17	18	19	18
1.4404	316L (2)	24.8	14	13		14
1.4162	Lean duplex	26.0	17	17		17
1.4462	Duplex (1)	34.4	46	50		48
1.4462	Duplex (1) w. 10%σ	34.4	16	20		18
1.4462	Duplex (2)	34.1	49	48	50	49
1.4539	904L	34.9	55	55	55	55
1.4547	254SMO	40.1	80	76	77	78

PRE = % Cr x 3.3 % Mo x 16 % N

EN 1.4462 duplex stainless steel is widely used in off-shore production facilities. The main argument for choosing duplex CRA rather than carbon steel is its high resistance against CO<sub>2</sub> corrosion. In comparison to common CRA grades like AISI 316L, duplex stainless steel also provides better resistance against stress corrosion cracking as well as higher tolerance against chloride containing media.

The reported studies on improperly heat treated duplex fittings have shown that materials could contain up to 10 % sigma phase. Apparently, the sigma phase formation could be ascribed to inappropriate packing of the fittings in the furnace during solution annealing. The exact temperature profile is not known, but sigma phase formation has most likely occurred due to extended holding in the temperature range from 750 to 900 °C.

When assuming the above conditions for the fittings, our results indicate that the CPT of the component could be 30 °C lower than that of correctly solution-annealed components. This circumstance has a potential high impact on components located in systems exposed to natural seawater such as cooling or firewater systems. Systems exposed to salty formation water or injection water are also in the risk zone, especially if the water contains traces of oxygen.

Systems located in the main process near the inlet separator are usually completely deaerated, but they typically operate at higher temperatures. In such systems the risk of pitting is usually smaller,

whereas CO<sub>2</sub> corrosion and sulphide-induced cracking should receive more attention together with external stress corrosion cracking. The presented CPT data cannot be applied for assessment of the latter corrosion forms, which require other testing methods.

Pitting might occur in the main process systems in connection with hydrostatic testing, acid jobs or during standstill periods with air access. During such periods, special attention should be made to avoid aggressive conditions if there is a suspicion that the system contains sigma phase-affected components. These efforts could involve nitrogen purging or treatment with chemicals such as oxygen scavengers or corrosion inhibitors.

Our study confirms that the presence of even small amounts of sigma phase affects the corrosion resistance considerably. Yet, we are not aware of any failures in fittings that have been ascribed to sigma phase in the base metal, even though apparently such components have been in service for several years. However, the issue should not be ignored although there might be a larger margin against failure than initially expected. Instead efforts should be carefully coordinated to identify and locate the affected components whenever there is a suspicion. This effort to replace components can be further optimised by examining the removed components and possibly performing corrosion tests to characterise the precise condition. As realised in our study, the detection of small amounts of sigma phase by metallographic methods is difficult even under ideal conditions in the laboratory and on-site metallurgy does not make things easier. Consequently, improved methods for identifying sigma phase-affected steel are desirable, e.g. based on on-site corrosion testing.

## 5. Conclusion

A series of 22Cr duplex specimens representing different levels of sigma phase were tested using the ASTM G150 method to determine the effect on CPT in chloride-containing media. The study intends to simulate the problems recently reported for thin-walled fittings in oil and gas installations. The following conclusions can be made:

- Even small amounts of sigma phase have a significant negative influence on the CPT.
- For the same amount of sigma phase, the effect is stronger for materials heat treated at 750 °C in comparison to 850 °C.
- The pits formed in the test are shallow and fairly wide due to the grain orientation from the cold rolling of the tested plate material.
- Exposure of cut faces or end-grains in service is more severe, since the resulting form of corrosion due to sigma phase (and secondary austenite) is related to phase boundaries.
- The measured CPT of EN 1.4462 with 1-4 % sigma phase is higher than that of e.g. lean duplex and 316L, but corrosion initiation is expected to be more critical for the duplex material due to the intergranular behaviour.
- The study underlines the need for identifying and replacing sensitised duplex components that unintentionally have been installed in a process. This effort can be optimised using a combination of on-site metallurgy and analysis and corrosion tests of removed components.
- Development of improved methods for identifying sigma phase by use of on-site corrosion testing is currently being considered to locate sensitised components with greater certainty.

## References

1. Petroleumstilsynet, Norway, [www.ptil.no](http://www.ptil.no)
2. Health and Safety Executive, [www.hse.gov.uk](http://www.hse.gov.uk)
3. S. Topolska, J. Labanowski, Journal of Achievements in Materials and Manufacturing Engineering, Vol. 36, No. 2 (2009)
4. M. Pohl, O. Storz, T. Glogowski, Microscopy and Microanalysis, Vol. 11, No. 2 (2005)
5. P.L. Bowden, J.L. Ward, Offshore Technology Conference, OTC 7316, 1983
6. J.H. Potgieter, British Corrosion Journal, Vol. 27, No. 3 (1992)
7. R. Francis, G. Byrne, G. Warburton, Proceedings of NACE Corrosion 1997, Paper 12, Houston, TX.
8. D.Y. Kobayashia, S. Woly nec, Materials Research, Vol. 2, No. 4 (1999)
9. C.J. Park, V. Shankar Rao, H.S. Kwon, Corrosion, Vol. 61, No. 1 (2007)
10. E. Angelini, B. De Benedetti, F. Rosalbino, Corrosion Science, Vol. 46, 1351–1367 (2006)
11. P. Kangas, K. Tersmeden, M. Nyström, Proceedings of Duplex America 2000, DA\_009
12. H.M Ezuber, Journal of ASTM International, Vol. 2, No. 5 (2005)
13. O. Storz, A. Ibach, M. Pohl, Proceedings of Duplex 2007.
14. K. Toshio, Transaction of JWRI, Vol. 34, No. 2 (2005)
15. R. Chaves, I. Costa, H.G. de Meloc, S. Woly nec, Electrochimica Acta, 51, 1842–1846 (2006)
16. ASTM G48-03, American Society for Testing and Materials (ASTM International), 2003.
17. T. Mathiesen, T.S. Nielsen, T. Haugen, B. Esplid, P. Hummelgaard, K. Vilpponen, Proceedings of 13. Scandinavian Corrosion Congress, Iceland 2004
18. T. Mathiesen, T.S. Nielsen, T. Haugen, B. Esplid, P. Hummelgaard, K. Vilpponen, Nordtest Project No. 1639-03, Technical report, December 2003.
19. ASTM G150-99, American Society for Testing and Materials (ASTM International), 1999.