

STRESS CORROSION CRACKING OF STAINLESS STEELS IN HIGH PRESSURE ALKALINE ELECTROLYSERS

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ABSTRACT

Hydrogen-producing high-pressure electrolyzers operating with 40% potassium hydroxide solution and an applied oxygen pressure up to 30 barg have been developed. Austenitic stainless steels of type AISI316L are deemed resistant to stress corrosion cracking (SCC) in concentrated KOH solutions. However, SCC has on some occasions been observed on the oxygen side of the high-pressure electrolyzers, thereby representing a safety risk in the operation. Several materials have been tested for resistance to SCC using C-ring specimens in autoclaves under conditions similar to the high-pressure electrolyzers, and at temperatures up to 120°C. The tests confirmed the observed susceptibility of austenitic stainless steels to SCC in concentrated KOH solutions. Higher alloyed austenitic stainless steels also showed SCC. Duplex stainless steel and nickel based Alloy 28 showed good resistance to SCC in the given environment. Further tests are needed to define the optimum weld procedure.

1.0 NOMENCLATURE

HAZ Heat affected zone

KOH Potassium hydroxide

PTFE Polytetrafluoroethylene

SEM Scanning electron microscope

SCC Stress corrosion cracking

2.0 INTRODUCTION

Atmospheric electrolyzers have traditionally been constructed in and operated safely with austenitic stainless steel of type AISI 316 or similar. Newly developed high-pressure electrolyzers are operating at 70-80°C with 30-40% potassium hydroxide (KOH). The pressure range is 15-30 bar. The construction materials of the electrolyzers need to withstand the contained fluid over the lifetime of the equipment, without excessive corrosion or other failures. One critical failure mode of metallic materials is stress corrosion cracking (SCC) in concentrated KOH solutions. SCC acts to create cracks that can penetrate the steel wall and create leaks, and therefore represents a safety risk in the operation of the electrolyzers.

Stress corrosion cracking was unexpected in austenitic stainless steel AISI 316L, but has on some occasions been observed on the oxygen side of the high-pressure electrolyzers. The commonly referred to temperature limit for SCC occurring in austenitic stainless steels such as AISI 316L in high concentration caustics is approximately 100°C [1,2]. However, in the high-pressure electrolyzers, the steel equipment is operating under the combined influence of a high-temperature caustic solution and high oxygen pressure of 30–40 bar, which can reduce the temperature limit for the occurrence of SCC [3].

In order to explore the suitability of different stainless steels for use in high-pressure electrolyzers, the corrosion resistance of a range of *candidate material has been tested using C-ring specimens in autoclaves under conditions similar to the high-pressure electrolyzers, at temperatures up to 120°C.

3.0 STRESS CORROSION CRACKING

Stress corrosion cracking (SCC) is the term used to describe the service failure of engineering materials by slow, environmentally-induced crack propagation. The crack propagation is a result of the combined and synergistic interaction of mechanical tensile stresses and corrosion reactions. The tendency of SCC to occur is affected by the type of material and environment, the presence of tensile stresses and the interactions between these factors. Important factors are temperature, degree of aeration and concentration of ionic species. The structure of the material also affects the susceptibility to SCC.

The stresses needed for SCC to occur are below the yield stress of the material, and are always tensile stresses. The tensile stresses can be a result of externally applied loads or residual stresses from welding, machining etc, and are mainly static in nature.

SCC is peculiar to certain combinations of alloys and environments. A vast number of specific combinations can cause SCC, but no single environment will make all materials susceptible to SCC or vice versa. In general, SCC is observed in alloy/environment combinations that cause an oxide film formation on the metal surface. These films lead to a reduction in the general corrosion rate, making the alloy more resistant to general corrosion in that environment. SCC is a localised type of corrosion occurring in connection with local breakdown of the oxide layer.

4.0 EXPERIMENTAL

To explore the susceptibility of different alloys to SCC in concentrated KOH solutions, test specimens need to be influenced by the environmental conditions of the high-pressure electrolyzers (temperature, caustic solution and oxygen pressure), and tensile stresses need to be present in the material of the test specimens. To achieve the tensile stresses, C-ring test specimens were used.

4.1 Test specimens

C-ring specimens were cut from pipe sections. The outer diameters were approximately 30-35 mm and wall thicknesses were 2-4 mm. The C-ring test specimens were mounted on nickel alloy bolts and compressed to plastic deformation. Upon plastic deformation, the stresses reached the yield stress of the material. The deformation was maintained throughout the exposure. A C-ring test specimen mounted on the compression bolt is shown in Fig. 1. To avoid galvanic influence from the bolt and metal washers, heat-shrinkable polypropylene tubing covered the bolts and PTFE washers were used to isolate the metallic washers from contact with the test specimens.

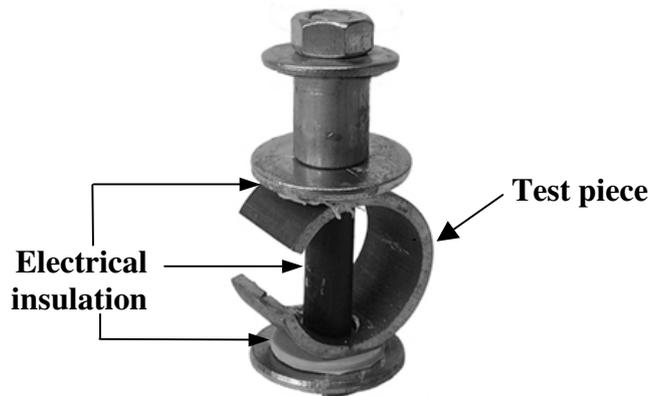


Figure 1. C-ring test specimen mounted with compression bolt and electrical insulation.

Weight loss test specimens were included in the tests for some of the materials. Square test specimens (37 x 22 mm) were prepared from 5 mm plates.

4.2 Autoclave exposure

The compressed test specimens were mounted in autoclaves by hanging from the top lid in PTFE threads. Each test specimen was fully submerged in the caustic solution. The autoclaves were heated to the predetermined temperature by hot plates with magnetic stirring to ensure a homogeneous temperature and oxygen concentration in the caustic solution throughout the exposure period. The temperatures were controlled by thermo elements (type K) placed directly in the caustic solutions in each autoclave. The test specimens were exposed for 3 months.

The exposure temperatures were actual operating temperatures of high-pressure electrolysers, with a safety margin of at least +10°K. Temperatures of 90, 100 and 120°C were used for the testing. The concentrations of the caustic solutions were 30 and 40 weight-% KOH, in accordance with the concentrations used in present and future high-pressure electrolysers.

Weight loss test specimens were exposed in the autoclave submerged in the caustic solutions by hanging from the lid in PTFE threads. Contact between individual test specimens was carefully avoided.

4.3 Inspection and analysis

The test pieces were removed from the autoclaves and dismantled from the compression bolt for inspection after the exposure. Each test specimen was rinsed and visually inspected in a light microscope for cracks in the tensioned surface. After the initial inspection, the C-ring test specimen was compressed to close the gap of the 'C' in order to open any cracks for easier identification.

Selected test specimens were cut, grinded and polished to find possible smaller cracks and to study the nature of identified cracks in an optical microscope. Some of the polished samples were etched to reveal the microstructure (grains) of the material. A scanning electron microscope was used to analyse the chemical composition of the different grains and phases of some test samples.

4.4 Materials and test conditions

The materials selected were austenitic stainless steels with increased nickel (Ni) and chromium (Cr) content compared to AISI 316L, and some duplex stainless steels. The materials with nominal compositions are given in Table 1. In the following, the test conditions are referred to by temperature only.

Table 1. Tested materials with nominal compositions.

Alloy	Trade name	EN	UNS ASTM	%Cr	%Ni	%Mo	%Cu	%Mn	%Si
Alloy 904L	2RK65	1.4539	N08904	20	25	4.5	1.5	1.8	-
AISI 310L	2RE10	1.4335	S31002	24.5	20.5	0.1	-	1.8	-
AISI 316L	3RK60	1.4404	S31603	17	12	2.5	-	<2.0	<1.0
AISI 316Ti	5R75	1.4571	-	17	12	2.5	-	<2.0	<1.0
Alloy 28	Sanicro 28	1.4563	N08028	27	31	3.5	1.0	2.0	0.6
Duplex 2507	SAF 2507	1.4410	S32750	25	7	4	-	1.2	-
Duplex 2304	SAF 2304	1.4362	S32304	23	4.5	-	<0.6	<2.0	-
Duplex 2205	SAF 2205	1.4462	S32205	22	5	3.2	-	<2.0	<1.0
Duplex 2906	SAF 2906	-	S32906	29	6	2	-	-	-

Table 2. Test conditions.

Temperature, °C	Weight-% KOH solution	Oxygen pressure, barg
90	30	15
100	40	30
120	40	30

4.4.1 Standard duplex welds

Testing was performed with the duplex stainless steel 2205, and included general corrosion rate testing by weight loss samples and tests of resistance to SCC by tensioned C-ring test specimens. In addition, C-ring test specimens were prepared with welds in the stressed area at the back of the 'C'. The weld was specified as a standard weld for duplex 2205 material, and was performed according to the appropriate Norsk Hydro weld procedure using duplex filler material (Norweld LNT 4462 with 22.7% Cr and 8.5% Ni). The welds include some residual stresses, and the test specimens were exposed both with and without compression of the C-rings by the bolt arrangements. The test set-up is shown in Table 3, where all tests are performed in 40 weight-% KOH solutions with an applied O₂ pressure of 30 barg.

Table 3. Test set-up.

Temperature, °C	100	120
Number of weight loss test specimens	3	3
Number of tensioned test specimens without weld	3	3
Number of tensioned test specimens with weld	6	3
Number of non-tensioned test specimens with weld	6	0

4.4.2 Alternative welds

Based on the results from the standard duplex weld, additional tests were performed with alternative weld filler materials. Nickel base filler materials for Alloy 625 (Cromatig 625, 64.5% Ni and 22% Cr) and Alloy 600 (Inconel filler material 82, 67% Ni and 20% Cr) were used to prepare welded C-ring test specimens. In addition, welds with duplex filler material (Cromatig duplex, 22.5% Cr and 9% Ni) were included for further testing of standard welds.

5.0 RESULTS

5.1 Austenitic stainless steels

The results from SCC testing for the austenitic stainless steels are summarised in Table 4.

Table 4. Summary of results for austenitic stainless steels

Steel	Temp. °C	KOH wt-%	P(O ₂) barg	Number of test specimens	
				Cracked	Not cracked
AISI 316L	90	30	15	0	3
	100	30	15	3	0
AISI 316 Ti	90	30	15	1	3
Alloy 28	90	30	15	0	3
904L	100	40	30	3	0
	120	40	30	3	0
AISI 310L	100	40	30	3	0

AISI 316L showed no cracking at the lowest temperature (90°C), but one of the bolts holding the C-ring specimens tensioned, fractured during the exposure. The bolts were made of AISI 316L stainless steel (A4). The crack was identified as typical branched intergranular SCC. New bolts of nickel Alloy 625 were used for the further testing to avoid this problem. At the highest temperature (100°C), all three AISI 316L test specimens showed severe cracking. The main cracks fractured the test specimens over the cross-sections, and analysis of the crack surface revealed typical SCC cracking. In addition to the main crack, smaller cracks

were found close to the main crack upon microscopic analysis of a grinded and polished cross section. An example of such a crack is shown in Fig. 2.

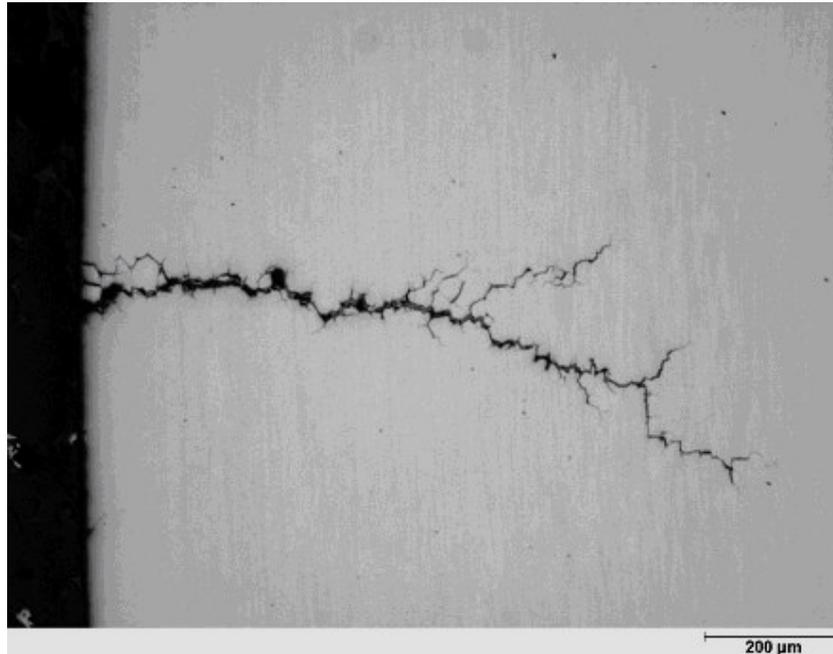


Figure 2. Cross section image of a stress corrosion crack in AISI 316L.

Two of the test specimens made of AISI 316Ti also showed cracking at 90°C. Examinations of the cracks identified them as typical SCC cracks, about 75–100 μm deep. Alloy 28 showed no cracking on any of the test specimens, either by microscopic inspection of the surface or of the grinded and polished cross sections. The test pieces of 904L all showed several smaller cracks in the tensioned areas of the test specimens exposed at both 100 and 120 °C. Examination of the grinded sample showed branched cracking with limited depth. The AISI 310L test specimens showed lots of small cracks all over the surface of the tensioned area of the C-ring, similar to those found in 904L.

5.2 Duplex stainless steels

The results from SCC testing with the duplex stainless steels in 40 weight-% KOH solution are summarised in Table 5. Cracking was observed in duplex 2507 at 100°C and duplex 2906 at 100°C, but no signs of cracking were identified in the duplex 2304 or duplex 2205 test specimens.

Table 5. Summary of results for duplex stainless steels (40 weight-% KOH, 30 barg O₂).

Steel	Temp. °C	Number of test specimens	
		Cracked	Not cracked
Duplex 2507	100	3	0
Duplex 2304	100	0	3
	120	0	3
Duplex 2906	120	2	0
Duplex 2205	100	0	3

All three Duplex 2507 specimens showed small cracks in the test at 100°C. Examination of the grinded surface revealed some small crack initiations or surface defects, but the grinded surface did not include any of the more developed cracks. At 100°C, some surface layer or surface deposits had developed in the duplex 2304 test specimens. No such surface deposits were found at 120°C, but local corrosion attacks were evident as shown in Fig. 3. No cracks were found during a microscopic examination of the surface and the grinded

cross section of any of the duplex 2304 test specimens exposed at 100 or 120°C. Neither were any cracks found in any of the duplex 2205 test specimens, and the exposed surfaces were smooth and clean and did not show occurrences of local corrosion. Examination of the grinded sample did not reveal any cracks.

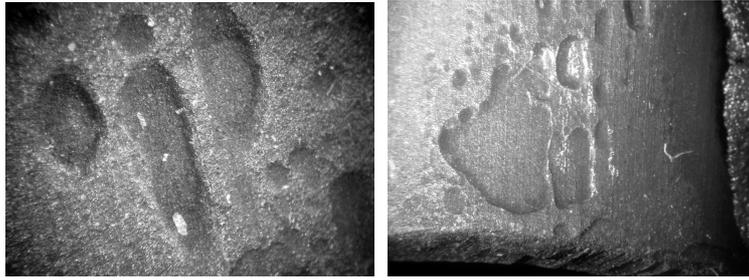


Figure 3. Local corrosion attacks on duplex 2304 exposed at 120°.

5.3 Welded duplex 2205

The average general corrosion rate of duplex 2205 was found from weight loss test specimens to be 0.10 mm/year at 100°C and 0.57 mm/year at 120°C. No cracks were found in the test specimens exposed at 100°C or 120°C without weld, which verified the results from the previous tests. The metal surfaces were clean and even, with no signs of corrosion attacks. The welded, but not tensioned, specimens also showed no signs of cracking. However, microscopy inspection revealed some local corrosion attacks on the weld surface that were not found on the surface of the base duplex 2205 material. The depths of these attacks were about 50 μm , corresponding to a corrosion rate of approximately 0.2 mm/year. All of the welded C-ring test specimens that were tensioned by the compression bolts showed cracking of the welds exposed at 100°C. The cracking occurred in the middle of the welds. No cracks were found in the specimens exposed at 120°C. The reason for the latter can be attributed to the higher level of general and uniform corrosion at 120°C compared to 100°C. Stress corrosion cracking usually occurs by an anodic mechanism in passive or trans-passive states of the material, and will usually not occur in actively corroding states.

The test with standard duplex welds at 100°C was repeated in the test with alternative welds (Section 5.3.2) without observing any signs of cracking. Weld material from both tests was investigated by scanning electron microscopy. The aim was to reveal any possible differences in structure and phase compositions or to uncover possible grain boundary precipitations that could reveal possible differences in SCC susceptibility. X-ray mapping of the chemical composition of the surface area revealed no grain boundary precipitations on any of the welded test specimens. The grain structure and grain distribution varied through the inspected areas of both welds. However, in general, the two welds were quite similar, as illustrated in Fig. 4 where the microstructures are shown. The microstructures were sound and in accordance with expectations, with austenitic grains in a ferritic matrix.

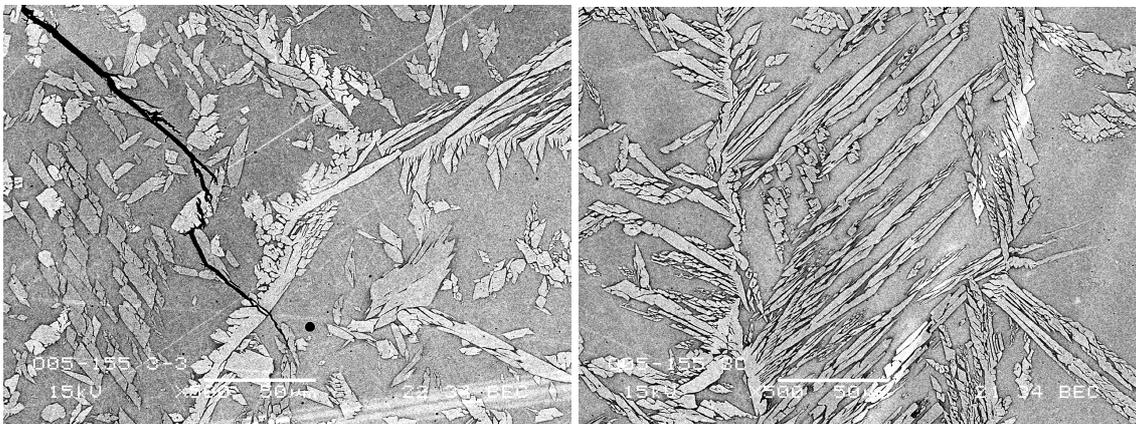


Figure 4. SEM images of duplex weld from the first tests (left, with crack) and from the repeated tests that did not show SCC (right). Light areas are austenite grains and darker areas are ferrite grains.

None of the duplex 2205 test specimens welded with Alloy 600 or Alloy 625 filler material showed any signs of SCC, either in the weld and heat affected zones (HAZ) or in the base material. However, some corrosion attacks were observed in the HAZ and fusion line as shown in Figure 5. The corrosion attacks were approximately 50–100 μm deep. The depth of the corrosion attacks corresponds to a corrosion rate of 0.2–0.4 mm/year when assuming a linear corrosion development over time. The nature of this corrosion has not been explored in detail.

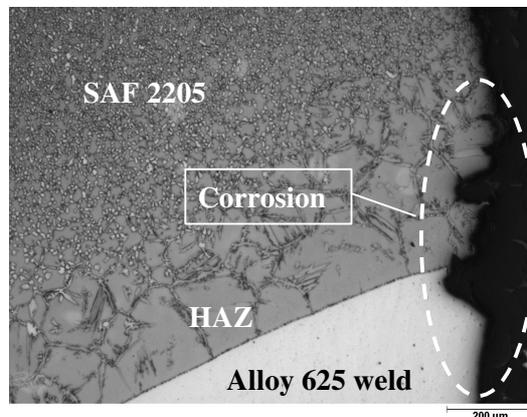


Figure 5. Duplex 2205 welded with Alloy 625 filler material showing local corrosion attacks in the transition zone between base material and weld.

6.0 DISCUSSION

Accelerated laboratory tests have confirmed that austenitic stainless steel AISI 316L and higher alloyed austenitic stainless steels are vulnerable to SCC in high-temperature parts of the oxygen part of high-pressure alkaline electrolyzers. The tests were conducted at 90 and 100°C, conditions that included a safety margin of 10–20°C in relation to typical operating temperatures of high-pressure electrolyzers.

While an absolute temperature limit for SCC in concentrated KOH solution with the presence of high oxygen pressure has not been fully established, it is expected that the operating temperatures of the high-pressure electrolyzers (80–85°C) are in the border area for susceptibility to SCC. AISI 316Ti was included in the tests as it is a commonly used alternative to AISI 316L. The two alloys were expected to have a similar susceptibility to SCC, as was confirmed by the test results. The higher alloyed austenitic stainless steels AISI 310L and 904L also showed susceptibility to SCC at 100°C, and are therefore not considered an applicable alternative to AISI 316L.

Alloy 28 showed good resistance to SCC in concentrated KOH solutions in test conditions.

Duplex stainless steels 2205 and 2304 showed no tendency of SCC in concentrated KOH solutions at 100°C. However, both duplex 2507 and 2906 did sustain SCC in the tests, even though these are higher alloyed materials. The reasons for this discrepancy have not been found. Tests on welded test specimens of duplex 2205 revealed SCC in the weld at 100°C, but the cracking did not recur in repeated tests.

Alternative welds using nickel base alloys as weld filler material did not sustain SCC in concentrated KOH solutions at 100°C. However, limited general corrosion attacks were found in the HAZ. Although unacceptable corrosion rates were observed at 100°C, it is very likely that only very low corrosion rates will occur at the operating temperatures of the high-pressure electrolyzers. Tests at lower temperatures will reveal this.

Overall, duplex 2205 is regarded the most suitable metallic material in the high-pressure electrolyzers operating at 75–85°C, based on the test results, availability and cost.

7.0 CONCLUSIONS

Use of stainless steel AISI 316L and equivalent alloys in high-pressure electrolysers should be avoided in high-temperature areas of the electrolysers, as tests have shown that these materials are susceptible to SCC in concentrated KOH solutions at temperatures below 100°C.

Duplex 2205 stainless steel is an alternative material, and was found to be resistant to SCC in concentrated KOH solutions under operating conditions. However, the weld of duplex 2205 has shown tendencies for SCC. Alternative weld procedures using nickel base filler material have been found to be resistant to SCC, but some local corrosion in the transition zones was found. The weld procedures therefore need some further qualifications.

8.0 ACKNOWLEDGEMENTS

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9.0 REFERENCES

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