The effect of chloride on general corrosion and crack initiation of low-alloy steels in oxygenated high-temperature water

Matthias Herbst (1), Dr. Armin Roth (1),
Dr. Martin Widera (2), Dr. Karin Küster (3), Dr. Frank Hüttner (3), Erika Nowak (4)

(1) AREVA NP GmbH, Paul-Gossen-Str. 100, 91052 Erlangen
(2) RWE Power AG, Huyssenallee 2, 45128 Essen
(3) Vattenfall Europe Nuclear Energy GmbH, Überseering 12, 22297 Hamburg
(4) E.ON Kernkraft GmbH, Tresckowstraße 5, 30457 Hannover

38th MPA-Seminar
October 1 and 2, 2012 in Stuttgart
Abstract

The effect of chloride on the general corrosion and its potential impact on EAC crack initiation of low-alloy steel (German reactor pressure vessel steel 22 NiMoCr 3 7) in oxygenated high-temperature water were investigated.

The general corrosion behavior was analyzed by exposure tests with either permanently increased chloride concentration levels or temporary chloride transients. The potential effect on EAC crack initiation was analyzed with pre-strained C-ring specimens and in SSRT (CERT) tests with slowly rising strain. Both kinds of tests were performed under simulated BWR conditions and with different chloride levels. The chloride concentrations of 5 to 50 ppb were chosen according to the action levels of the German water chemistry guideline for the reactor coolant of BWRs (VGB R401J, 2006).

In all exposure tests, none of the pre-strained C-ring specimens showed crack initiation during up to 1000 hours of exposure time with up to 50 ppb chloride. Investigations of the oxide layer thickness after immersion testing revealed a decrease with increasing chloride concentration. As shown by post-test chemical analysis of the oxide layer composition by TOF-SIMS, this effect is most likely primarily due to adsorption of chloride on the oxide layer surface, since only very limited penetration of chloride into the oxide was detected.

In contrast to the tests with C-ring specimens, where no crack initiation occurred, slightly accelerated crack initiation at lower elongation levels was observed at increasing chloride concentrations in SSRT tests under simulated BWR conditions using actively loaded specimens. In addition, SSRT specimens that were cyclically loaded at the oxide fracture elongation level were used to generate a continuous, exposure of bare metal to the environment by repeated fracture of the oxide. This loading pattern did not cause crack initiation at all chloride concentrations applied (up to 50 ppb).

From these results, it may be concluded that at least up to 50 ppb there is no immediate, significant effect of increased chloride concentration on the EAC susceptibility of low-alloy steel components with smooth, uncracked surfaces.

1 Introduction

Low-alloy steels are widely used as a structural material for pressure boundary components in both, Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs). The worldwide operating experience with low-alloy steels is very good so far, since no cracking incidents with a major contribution of stress corrosion cracking (SCC) to the total crack advance in properly manufactured and heat treated LAS primary pressure components have occurred in service [1-3].

Low-alloy steel components are generally not directly in contact with the primary medium because they are protected against erosion and corrosion through the application of austenitic cladding. However, depending on the design and reactor type, unclad pipes made of LAS may be in contact with the primary coolant in BWRs. Furthermore, cladding discontinuities on internal surfaces of the reactor pressure vessel, causing a direct contact of LAS with primary coolant, are postulated in safety assessments.

Following different contradictory laboratory results that have been published in the late 1980’s [4], a number of different laboratory testing programs using advanced testing methods have been performed during the last decades. These investigations have shown that LAS is not generally susceptible to SCC under nominal operating conditions of both, BWR and PWR conditions [5-8].

Within the frame of these laboratory programs experiments were performed at different levels of anionic impurities. The anionic impurities that were added to the high-temperature water during these experiments were chloride and sulfate [9, 10].
In the experiments with increased sulfate concentrations, no enhanced crack growth rates were observed, although the sulfate concentrations were increased up to an electrical conductivity of 1400 µS/cm. In contrast to the results obtained at increased sulfate concentrations, tests with increased chloride concentrations showed a drastic effect of small amounts of chloride contaminations on the crack growth rate. Tests with periodic partial unloading and a chloride concentration of 50 ppb revealed an onset of fast crack growth after an incubation period of approx. 3 hours (see Figure 1 A). Further experiments at different chloride levels and varying water chemistry conditions showed that the effect of chloride on the crack growth rate decreased at lower corrosion potentials and that there was virtually no effect of increased chloride concentrations under hydrogenated water chemistry conditions (see Figure 1 B) [11].

Figure 1: A) Initiation of fast crack growth in a C(T)25 specimen during a phase of constant, static load between two PPU unloading during a 50 ppb chloride transient (T = 288 °C, DO = 8000 ppb) [9, 10]. B) Susceptibility area for onset of chloride induced SCC of low-alloy steels depending on chloride concentration and corrosion potential [11].

In addition to these experiments of further experimental work focused on the effect of chloride on the crack growth behaviour in the transition region between Alloy 182 and low-alloy steel [12, 13]. In these experiments no crack growth crossover from Alloy 182 weld metal into the low-alloy steel base material could be observed under normal operation conditions.

During all experiments in high-purity water and even with sulfate levels up to 30 ppb sulfate the cracks stopped at the fusion line between Alloy 182 and the low-alloy steel. In contrast to these results, prolonged crack growth across the fusion line and into the low-alloy steels was experienced in tests with addition of small amounts of chloride [14]. The observed behavior is in good agreement to the field experience, where SCC cracking also stops at the transition line between Alloy 182 and low-alloy steel under static loading conditions in chloride free environments [14]. For increased chloride contaminations and high stress intensity factors, however, crack growth crossing the fusion line and sustained crack growth into the low-alloy steel can not be fully ruled out.
Based on these laboratory results the question arose, how such chloride contaminated environmental conditions might affect the EAC-behavior of real plant components. Therefore, to systematically study the effect of increased chloride concentrations on the general corrosion and the SCC-behavior of low-alloy steel this project was launched.

2 Experimental work

All tests of this project were performed in once through refreshing autoclaves with full environmental control. The test environment was oxygenated high-temperature water (HTW) simulating BWR steady state operating conditions with an oxygen concentration of 400 ppb to ensure high corrosion potentials at the specimen location in the testing loop and thereby conservatism of the test results.

The environmental conditions that were adjusted at the inlet of the test loop were as follows:

- Electrical Conductivity (ECin) ≤ 0.1 μS/cm (before increase of Cl- conc.)
- Dissolved Oxygen (DO) 400 ppb
- Temperature (T) 288 °C
- Pressure ~ 95 bar

The performed tests were (1) exposure tests with continuously increased chloride concentrations or chloride transients and (2) Slow Strain Rate Tensile (SSRT) also known as Constant Extension Rate Tensile (CERT) tests at different chloride contamination levels.

Within the frame of the exposure tests firstly the effect of continuously increased chloride contamination levels with several testing durations up to 1000 hours, and secondly, the effect of a single, temporary 24-hour chloride transient (5, 20, and 50 ppb chloride, respectively) were investigated. In the transient tests, continued exposure in chloride-free HTW under specified conditions was applied for another 100, 200 and 500 hours following the chloride-transient in order to study any recovery effects (see Figure 2 A).

For the SSRT-tests, the testing procedure was applied as schematically shown in Figure 2 B. After the end of the pre-oxidation of the specimens, the chloride concentration was increased to the target chloride level 24 hours before straining was applied to the tensile specimens at a strain-rate of 10^-6 s^-1.

The material used in all experiments of this work is a typical German low-alloy steel RPV base material 22 NiMoCr 3 7. The chemical composition of this material is summarized in Table 1.

| Table 1: Chemical Composition (in wt.-%) of the tested low-alloy RPV steel. |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Alloy | C      | Si     | Mn     | P      | S      | Cr     | Mo     | Ni     | Cu     |
| 22NiMoCr3 7 | 0.22   | 0.20   | 0.91   | 0.008  | 0.007  | 0.42   | 0.53   | 0.88   | 0.04   |

180
Figure 2: Simplified testing procedure for A) exposure tests and B) SSRT tests.

In all tests, the applied chloride concentrations were chosen according to the action levels of the VGB water chemistry guideline (VGB R401J, 2006) see Table 2, [14].

According to these Action Levels, four different chloride concentrations were adjusted during the test runs:
- without chloride (reference testing conditions)
- 5 ppb chloride (Action Level 1),
- 20 ppb chloride (Action Level 2) and
- 50 ppb chloride (Action Level 3).

Table 2: Monitoring parameters, values and Action Levels for BWR plants according to VGB water chemistry guideline (VGB R401J, 2006) [15].

<table>
<thead>
<tr>
<th>Monitoring parameter</th>
<th>Regular operation</th>
<th>Action Level 1</th>
<th>Action Level 2</th>
<th>Action Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (at 25 °C / µS/cm)</td>
<td>&lt; 0.15</td>
<td>&gt; 0.25</td>
<td>&gt; 1</td>
<td>&gt; 5</td>
</tr>
<tr>
<td>Chloride / µg/kg</td>
<td>&lt; 2</td>
<td>&gt; 5</td>
<td>&gt; 20</td>
<td>&gt; 50</td>
</tr>
<tr>
<td>Sulfate / µg/kg</td>
<td>&lt; 5</td>
<td>&gt; 10</td>
<td>&gt; 40</td>
<td>&gt; 100</td>
</tr>
</tbody>
</table>
2.1 Experimental procedure

The exposure tests were performed in stainless steel autoclaves attached to a HTW-refreshing loop. During the experiments, all important environmental testing parameters (dissolved oxygen DO, electrical conductivity, temperature, pressure) were monitored and recorded. DO and conductivity were measured and recorded at the inlet and outlet position of the testing loop (see Figure 3). Continuous monitoring of the electrochemical corrosion potential (ECP) of the specimens and the redox potential was performed using an external high-temperature balanced Ag/AgCl HTW electrode. The target chloride concentration was adjusted by direct injection of a sodium chloride solution into the inlet of the stainless steel autoclaves. Accordingly, the injected chloride flow and the flow of the high purity water were calculated to meet the target chloride level in the autoclaves. The exchange rate of the solution in the autoclaves was adjusted to 2 exchanges per hour. All relevant ionic impurities were regularly analyzed during testing using Ion Chromatography. The used autoclave setup with four autoclaves in four parallel legs allowed running experiments at different chloride concentrations simultaneously in one single test run.

All crack initiation tests were performed in an 18 l stainless steel autoclave connected to an INSTRON Type screw-driven electromechanical tensile test machine (see Figure 4). The flow rate was adjusted to approximately 8 l/h resulting in an average exchange rate of approximately 0.5 per hour. This exchange rate is sufficient to maintain the desired chemistry conditions for the specimen under quasi-stagnant flow conditions. As for the exposure tests, the target chloride concentration was tuned by injection of a sodium chloride solution into the inlet of the autoclave. The chloride concentration was monitored by the change of the electrical conductivity at the outlet. In addition, the chloride concentration was periodically analyzed using water samples taken from the outlet of the testing loop.

For the exposure tests, two kinds of specimens were used, pre-strained C-ring specimens and unloaded coupon specimens. The C-ring specimens were used to gather information on the effect of increased chloride concentrations on the crack initiation susceptibility of passively strained specimens and the coupon specimens were used to study the general corrosion behavior of the investigated low-alloy steel. Before immersion testing was started, the C-ring specimens were strained to an initial stress of 500 MPa which is above the yield strength of the tested material at both, room temperature and testing temperature (see Figure 3 B).

Figure 3: A) Schematic view on the testing facility and B) Specimen setup used for the exposure tests with different chloride contamination levels.
In addition to the acquisition of the redox- and corrosion potential different electrochemical measurements, i.e., Electrochemical Impedance Spectroscopy (EIS) and Electrochemical Noise (EN) analysis were performed during the experiments. Using EIS, an alternating perturbation of current or potential with a small magnitude is applied to the investigated system. Accordingly, the system follows this perturbation at steady state and the electric response of the system to the external perturbation is monitored. The acquired EIS data are usually represented by means of “Bode Plots” or “Nyquist Plots”. Using Euler’s relationship it is possible to express the impedance as a complex function where the impedance is composed of a real and an imaginary part. If the real part is plotted on the X axis and the imaginary part on the Y axis, this gives a Nyquist Plot [16].

Furthermore, the effect of increased chloride levels on the properties of the oxide layers of the specimens was analyzed by post-test microscopic examinations. The microscopic examinations included Stereomicroscopy, Scanning Electron Microscopy (SEM) and determination of the oxide layer thickness. The oxide layer thickness was measured with the help of the Focused Ion Beam (FIB) technique. Using the FIB-technique, it was possible to cut the oxide layer using a Gallium beam and directly measure the oxide layer thickness by SEM.

An analysis of the chemical composition of the oxide layer after testing at different chloride contamination levels and chloride transients was performed using Auger Electron Microscopy and Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS).

A series of SSRT tests were performed to systematically study the potential effect of different continuously increased chloride contamination levels on the crack initiation susceptibility of this low-alloy steel. During testing the chloride concentration was increased to the target chloride concentration after the end of the pre-oxidation phase. 24 hours after the increase of the chloride concentration straining of the SSRT specimens was started using an initial strain rate of 10^{-6} \text{ sec}^{-1}. In addition to these tests, one SSRT test was designated to study the possible memory effect of a temporary chloride transient. In this test straining of the specimen was started directly after the end of a 24 hour chloride transient with 50 ppb chloride (see Figure 5 A).

![Figure 4](image-url): A) Simplified schematic of the testing facility used for the crack initiation tests and B) detailed view on the autoclave and the specimen setup for SSRT testing.
To study the effect of chloride on EAC initiation behavior of LAS and possible repassivation processes, tensile tests with a modified testing procedure were performed. In these tests SSRT specimens were cyclically loaded in the range of the oxide fracture elongation level of approximately 0.05 to 0.20 % [17-19]. This procedure was used to generate a continuous, repeated exposure of bare metal to the environment. The chosen strain rate was $10^{-6}$ sec$^{-1}$ with a maximum elongation of 0.20 % and R 0.9 (rise time approx. 30 min fall time approx. 3 min, see Figure 5 B). While this loading pattern was applied, the chloride concentration was stepwise increased up to a maximum chloride concentration of 50 ppb.

![Figure 5: A) Testing procedure for SSRT testing after a 24 hour 50 ppb chloride transient. B) Loading pattern during periodic straining of the tensile tests with modified test procedure.](image)

### 2.2 Results of the exposure tests at different chloride levels

The electrochemical noise and impedance measurements performed during the immersion tests clearly revealed a change of the corrosion behavior of both, the C-ring and the coupon specimens at increased chloride levels. As shown in Figure 6 for an experiment with a chloride concentration of 50 ppb both, the current noise and the potential noise signal changed significantly after increasing the chloride concentration. Furthermore, a further increase of the noise signal after longer testing periods with increased chloride contamination levels was observed. The increase of the noise signal was already revealed after an incubation period of approx. 24 hours.

Results of the EIS measurements performed on coupon specimens before and after increasing the chloride concentrations are shown in Figure 7 A. The results of these measurements clearly demonstrate a change in the properties of the oxide after an increase of the chloride concentration. The observed change in the electrochemical properties of the oxide occurred within a rather short incubation time after increasing the chloride concentration. A comparison of the impedance spectra obtained at different chloride concentrations showed that the changes in the electrochemical properties of the oxides are more pronounced at higher chloride levels. It is furthermore of importance to note that the recorded changes in the electrochemical properties of the specimens occurred on both, pre-stressed C-ring and unstressed coupon specimens.
The observed change in the Nyquist curves can be attributed to a change in the charge transfer resistance ($R_{ct}$) of the oxide layer that developed on the specimens under HTW-conditions. The $R_{ct}$ (represented by the diameter of the semicircle) is an important parameter for general corrosion of the specimens. Therefore, EIS measurements provide the possibility to detect changes of the corrosion behaviour of the specimens online during testing.

In addition to the results from the tests with continuously increased chloride concentration, Figure 7 B depicts the results of the impedance measurements for specimens tested with a 24 hour 20 ppb chloride transient. The impedance spectra of the coupon specimens clearly revealed a change of the oxide properties after increasing the chloride concentration. This result is in good agreement with the results from the noise analysis. A comparison of the three different chloride levels showed a temporary effect at all tested chloride concentrations which was more pronounced at higher chloride levels (20 and 50 ppb chloride).

**Figure 6:** Current noise A) and potential noise B) signal of coupon specimens in chloride free environment and at different testing times during exposure to a chloride contamination level of 50 ppb chloride.

**Figure 7:** A) Nyquist plots of EIS measurements on coupon specimens during pre-oxidation and after an increase of the chloride concentration to 50 ppb chloride for 100 hours (Note: The last EIS measurement has been performed after 75 hours with continuously increased chloride concentration).

B) Nyquist Plots of EIS-measurements on coupon specimens before, during and after the end of a 24 hour 20 ppb chloride transient.
Furthermore, the Nyquist plots indicate no memory effect caused by the temporarily increased chloride contaminations at the end of the 24-hour chloride transient. The measured impedance curves returned to the same values as before the transients within several tens of hours after the temporary chloride transient. In the tests performed at lower chloride concentrations (5 and 20 ppb), total recovery occurred within 24 hours after the end of the chloride transient. In the tests performed at the highest chloride concentration (50 ppb), total recovery occurred approximately 48 hours after the end of the transient.

The macroscopic examinations that were performed after completion of testing under HTW conditions showed slight pitting on the surface of all specimens which is not unlikely to be observed under the chosen testing conditions and might have occurred in particular at temperatures and testing conditions during heating up and shutdown of the tests [18, 20]. The comparison of the visual appearance of the specimens exposed to different chloride concentrations clearly showed that pitting was more pronounced at increased chloride concentrations. Despite the observed pitting, no crack initiation was observed on all investigated C-ring specimens (for tests with up to 1000 testing hours at a maximum chloride concentration of 50 ppb). For the tests with 24 hour chloride transients with different chloride concentrations no effect on the visual appearance of the specimen was observed after the end of the HTW tests.

To further investigate the effect of chloride on the properties of the LAS oxide layer after testing was completed, measurements of the oxide layer thickness were performed supported by the FIB-technique. The results showed that the thickness of protective oxide layer decreased at higher chloride levels, as shown in Figure 8 for a test run with 200 hours increased chloride concentration. Analysis of the oxide layer thickness was performed for the specimens from all test runs and the results of the oxide layer determination can be summarized as follows:

- Tests with permanently increased chloride concentration
  - The increased chloride concentrations caused a decrease of both, the inner and the outer oxide layer for the tests with 100, 200, and 500 hours increased chloride concentration. The observed thinning was more pronounced at higher chloride concentrations.
  - For the tests with 1000 hours increased chloride concentration a predominant decrease of the inner oxide layer and a localized thinning of the outer oxide layer was observed for all applied chloride concentrations.

- Tests with 24 hour chloride transients
  - No effect of the single chloride transient on the oxide layer thickness was observed in all tests.

![Figure 8](image.png)

**Figure 8:** SEM figures showing the oxide layer thickness on coupon specimens after exposure to pure HTW for 450 testing hours and additional 200 testing hours A) without chloride (normal operating conditions) and B) 200 hours with 50 ppb chloride.
In addition to the determination of the oxide layer thickness, further analysis of the chemical composition of the oxide layer was performed using TOF-SIMS. These investigations revealed that the chloride concentration in the oxide of the specimen tested at increased chloride concentrations is significantly higher than the concentration in the oxide layer of the reference specimen, where almost no chloride could be detected. It was observed, that chloride is inhomogeneously distributed at the specimen surface. The highest chloride concentration occurred in the outer part of the oxide. Penetration of chloride into the oxide layer occurred only localized at some spots in the specimen tested at a chloride concentration of 50 ppb. In this particular specimen, a rather large penetration of chloride into the depth of the oxide was observed. Similar TOF-SIMS investigations were also performed on the surface of specimens from the transient tests. The results of these tests showed that the chloride concentration in the oxide layer caused by a single, temporary chloride transient is only slightly increased as compared to the chloride content in the oxide of the reference specimen tested without a chloride transient.

From this observation, it can be concluded that no long-term memory effect of temporary chloride transients on the electrochemical properties and the structure of the oxide layer is to be expected.

![Figure 9](image)

**Figure 9:** Top view and depth profiles of the chloride concentration of the reference specimen (A) and a specimen tested with an increased chloride concentration of 50 ppb chloride for 200 hours (B). Areas with increased chloride concentrations are depicted in orange. Lighter colors represent higher chloride concentrations.

### 2.3 Results of the crack initiation tests at different chloride levels

The comparison of the reference stress-strain curve (obtained from a specimen tested without chloride) with the stress-strain curves of the specimen tested at chloride concentrations of 5 and 50 ppb reveals a systematic decrease of the measured total strain and the yield strength with increasing chloride concentrations (see Figure 10 A).

However, two tests that were conducted at a chloride concentration of 20 ppb chloride showed a rather large and unexpected scatter of the obtained stress strain curves (see Figure 10 B curve “20 ppb chloride (1)” and curve “20 ppb chloride (2)”). The scatter of these two tests performed under identical environmental conditions illustrates that the evaluation of the effect of different chloride concentrations has to be performed carefully.

Despite this scatter at 20 ppb chloride, there seems to be a systematic trend to lower maximum strain and stress levels at increasing chloride concentrations. However, the observed changes are small, the change of the measured strain is within approx. 5 to 10% and the change of the maximum strain is in the range of approx. 70 MPa.
Figure 10: Stress-Strain Curves comparing the results of SSRT tests performed at different chloride concentrations.

The post-test SEM investigation showed that pitting was more pronounced at the surface of the specimen tested under increased chloride concentrations. Significantly more crack initiation locations were observed at the specimen tested at a chloride concentration of 50 ppb in comparison to e.g. the reference specimen tested without chloride. The observed cracks typically initiated from corrosion pits on all SSRT specimens. Due to these observations, the microscopic examinations were extended which resulted in a counting of crack initiation locations (designated as “cracks”) and crack starting points (designated as “initiation”). This evaluation is depicted in Figure 11 A. In this diagram the scatter between the two SSRT tests that were performed at 20 ppb chloride is again obvious. In spite of this scatter there is an obvious trend to a higher number of cracks and crack initiation locations with increasing chloride concentrations. In addition to this evaluation the assessment of the reduction of the fracture area also shows a trend to lower reduction of area with increasing chloride concentrations (see Figure 11 B).

Figure 11: A) Number of crack locations (Crack) and pre-crack locations (Initiation) on the surface of the tested SSRT specimens. B) Reduction of Area of the SSRT specimens strained at different chloride concentrations. Note: (1) is representing the results from the SSRT test “20 ppb chloride (1)” and (2) represents the results for the SSRT test “20 ppb chloride (2)”.

Figure 10: Stress-Strain Curves comparing the results of SSRT tests performed at different chloride concentrations.

The post-test SEM investigation showed that pitting was more pronounced at the surface of the specimen tested under increased chloride concentrations. Significantly more crack initiation locations were observed at the specimen tested at a chloride concentration of 50 ppb in comparison to e.g. the reference specimen tested without chloride. The observed cracks typically initiated from corrosion pits on all SSRT specimens. Due to these observations, the microscopic examinations were extended which resulted in a counting of crack initiation locations (designated as “cracks”) and crack starting points (designated as “initiation”). This evaluation is depicted in Figure 11 A. In this diagram the scatter between the two SSRT tests that were performed at 20 ppb chloride is again obvious. In spite of this scatter there is an obvious trend to a higher number of cracks and crack initiation locations with increasing chloride concentrations. In addition to this evaluation the assessment of the reduction of the fracture area also shows a trend to lower reduction of area with increasing chloride concentrations (see Figure 11 B).

Figure 11: A) Number of crack locations (Crack) and pre-crack locations (Initiation) on the surface of the tested SSRT specimens. B) Reduction of Area of the SSRT specimens strained at different chloride concentrations. Note: (1) is representing the results from the SSRT test “20 ppb chloride (1)” and (2) represents the results for the SSRT test “20 ppb chloride (2)”.

Figure 10: Stress-Strain Curves comparing the results of SSRT tests performed at different chloride concentrations.

The post-test SEM investigation showed that pitting was more pronounced at the surface of the specimen tested under increased chloride concentrations. Significantly more crack initiation locations were observed at the specimen tested at a chloride concentration of 50 ppb in comparison to e.g. the reference specimen tested without chloride. The observed cracks typically initiated from corrosion pits on all SSRT specimens. Due to these observations, the microscopic examinations were extended which resulted in a counting of crack initiation locations (designated as “cracks”) and crack starting points (designated as “initiation”). This evaluation is depicted in Figure 11 A. In this diagram the scatter between the two SSRT tests that were performed at 20 ppb chloride is again obvious. In spite of this scatter there is an obvious trend to a higher number of cracks and crack initiation locations with increasing chloride concentrations. In addition to this evaluation the assessment of the reduction of the fracture area also shows a trend to lower reduction of area with increasing chloride concentrations (see Figure 11 B).

Figure 11: A) Number of crack locations (Crack) and pre-crack locations (Initiation) on the surface of the tested SSRT specimens. B) Reduction of Area of the SSRT specimens strained at different chloride concentrations. Note: (1) is representing the results from the SSRT test “20 ppb chloride (1)” and (2) represents the results for the SSRT test “20 ppb chloride (2)”.
The evaluation of the SSRT test that was performed after the end of a 24 hour chloride transient is plotted in Figure 12. The stress-strain curve obtained from this test is positioned between the curve of the reference specimen and the 50 ppb chloride specimen in the range of the curve obtained from the test performed at 5 ppb chloride. From this result it seems that there is no drastic memory effect of a single chloride transient on the crack initiation susceptibility.

Figure 12: Comparison of the stress-strain curves obtained from the SSRT test after a chloride transient and SSRT tests at different chloride concentrations.

During the tensile tests with modified test procedure, the external strain (measured at the electromechanical tensile test machine) and the actual strain of the SSRT specimen (measured directly at the specimen in the HTW) were monitored to study possible crack initiation processes due to the applied loading pattern and the stepwise increased chloride concentration (see Figure 13). In addition, electrochemical noise measurement, which is a very sensitive technique to study crack initiation in laboratory tests, was applied. During the whole testing period with different chloride concentrations and continuous application of the above described loading pattern, no potential or current transients that might be correlated with crack initiation and crack growth processes were detected. This result was confirmed by post-test macroscopic and microscopic examinations that did also not reveal any cracking on the specimen surface.
3 Discussion

Due to the observed change in the thickness of the oxide layer and the more pronounced pitting at increased chloride concentrations, the following mechanistic model of the effect of chloride on crack initiation is proposed.

According to the slip-step dissolution model, which is a broadly accepted model for SCC of LAS under HTW conditions, crack initiation and growth occurs due to a local rupture of the oxide developed on the surface or at crack tips of LAS under HTW conditions. Continued straining during rising load tests, such as during SSRT (CERT), leads to a local rupture of the otherwise protective oxide. Bare metal, which is thereby temporarily exposed to high-temperature water, will dissolve until this area is repassivated again. The time to crack initiation and the crack growth rate therefore depend on the:

- the strain level and local strain rate,
- the oxidation rate occurring at the strained crack surfaces or tips, and
- the repassivation rate under given electrochemical conditions determined by local ECP and anionic activity.

Accordingly, based on the test results obtained so far, the proposed hypothesis regarding the effect of chloride on the SCC-behavior of LAS under HTW conditions is as follows:

Increased chloride concentrations cause adsorption of chloride at the outer surface of the oxide layer, thereby causing a decrease in oxide layer thickness and more pronounced pitting. As local breakdown of the oxide layer occurs due to local sliding along slip planes (according to the slip-step dissolution mechanism), smaller slip steps are then already sufficient to cause local breakdown of the thinner oxide layers which develop at increased chloride concentrations. Chloride additions thereby cause both, accelerated crack initiation and further enhanced crack growth. In addition, local flaws caused by locally increased chloride concentrations can act as crack initiation sites. Moreover, the repassivation kinetics, especially at pre-existing cracks at surfaces of LAS or in crevices, may be retarded due to the locally variable anionic activity due to the accumulation of chloride.
Consequently, based on the assumption of the acting slip-step dissolution mechanism, the experimentally observed effects caused by chloride clearly explain the enhancement of crack initiation and crack growth of LAS in BWR-relevant HTW.

4 Summary and conclusion

The general corrosion behavior was analyzed by exposure tests with either permanently increased chloride concentration levels or temporary chloride transients. During these exposure tests a change in electrochemical properties of the oxide layers was observed online during testing through electrochemical measurements using EIS and EN. In particular, a decrease of the charge transfer resistance ($R_{ct}$), a controlling parameter for the kinetics of electrochemical corrosion processes, was observed during testing due to the deliberate increase in the chloride contamination. The effect of chloride on the electrochemical properties of oxide layers depends on the chloride concentration to which a material is exposed. The presence of increased chloride levels results in a more pronounced change in oxide layer properties. Furthermore, longer testing periods at increased chloride concentrations seem to have an increasingly detrimental effect on protective oxide layer properties, since the $R_{ct}$ further decreases during longer time periods at increased chloride concentrations.

In accordance with the results of the electrochemical measurements performed during testing, the post-test examinations by stereo microscope and SEM showed that pitting was more pronounced at higher chloride concentrations. In addition, the measurement of the oxide layer thickness clearly revealed a decrease in thickness due to exposure to increased chloride concentrations. The comparison of test results from specimens tested at different chloride concentrations showed that the oxide layer thickness decreased with exposure to increased chloride concentrations. For very long test durations (1000 hours) a predominant decrease of the inner oxide layer and a localized thinning of the outer oxide layer have been observed for all applied chloride concentrations.

From the results of the 24-hour chloride transient tests, it appears that the detrimental effect of increased chloride concentrations on the protective oxide layer properties recovers within at the latest 48 hours after the end of the chloride transient, i.e. after the complete disappearance of dissolved chloride in the aqueous environment. Hence, it can be concluded that there is no memory effect of increased chloride concentrations on smooth surfaces.

Total recovery of the chloride-induced effects was observed 24 hours after the small chloride transient ceased (chloride concentration 5 ppb) and approximately 48 hours after the highest chloride transient (chloride concentration 50 ppb). These results were confirmed by the post-test microscopy. The measurement of oxide layer thickness did not indicate that the 24-hour chloride transient had a significant effect on the oxide layer thickness after the HTW-tests. Also SEM on Coupon and pre-stressed C-Ring specimens did not indicate that the chloride transients had a significant effect on the oxide layer. Hence, the effect of the chloride transients on the corrosion behavior of the tested specimens appears to recover completely in specimens with smooth surfaces with additional testing time under the specified pure water chemistry conditions.

None of the pre-strained C-ring specimens indicated crack initiation, due to either permanently increased chloride contaminations or temporary chloride transients. It can, therefore, be concluded that there seems to be no immediate and drastic increase in crack initiation susceptibility for pre-strained specimens, at least for smooth surfaces and small chloride concentrations up to 50 ppb. Regarding the assessment of BWR LAS-components during plant operation, it can be concluded that neither temporary 24-hour chloride transients nor permanently increased chloride concentrations up to 50 ppb cause immediate crack
initiation on smooth uncracked surfaces within up to 1000 hours under constant strain conditions without additional mechanical load transients.

The surface analysis by TOF-SIMS revealed the adsorption of chloride on the outer surface of the oxide layer and some penetration of chloride into the oxide layer for specimens exposed to HTW with a chloride concentration of 50 ppb for 200 hours. The chloride is inhomogeneously distributed at the surface of the oxide layer. At some local spots, rather high local chloride concentrations were observed. In contrast to these results, little or no increase in the chloride concentration was detected in the oxide layer of the specimens exposed to a 24-hour 50 ppb chloride transient. For these specimens, only a slight accumulation of chloride at the surface of the oxide was observed, and no penetration of chloride into the oxide layer took place.

From these results, it seems that chloride is adsorbed at the outer surface of the oxide layer, thereby causing a thinning of the oxide layer which develops under oxygenated HTW-conditions. In addition to this adsorption, a localized thinning of the oxide layer also occurs in areas with locally increased chloride concentrations. Where the chloride concentration is locally high, penetration of chloride into the oxide leads to the formation of local flaws and pits which may act as crack initiation locations.

The results of the tests with temporary chloride transients showed that adsorbed chloride dissolves or desorbs given additional testing time in pure water conditions following the chloride transient.

The SSRT tests with actively strained specimens showed that the total strain and yield strength of the specimen tested at increased chloride concentrations decreased compared to the values obtained from a reference specimen tested without chloride. These results were also confirmed by evaluation of the fracture elongations and counting of crack locations. However, these results have to be evaluated very carefully, since the observed change of both, the yield strength (approx. 5 to 10%) and the total strain (approx. 70 MPa) are very low and some of the tests showed a rather large scatter in the results (SSRT tests at 20 ppb chloride).

No crack initiation was observed on the SSRT specimens that were cyclically loaded at the oxide fracture elongation level. The reported results show that this loading pattern was not sufficient to cause crack initiation at all applied chloride concentrations (up to 50 ppb) it therefore seems that a continuously rising strain is needed to cause crack initiation even at increased chloride concentrations.

From these results, it may be concluded that at least up to 50 ppb there is no immediate, significant effect of increased chloride concentration on the EAC susceptibility of low-alloy steel components with smooth, uncracked surfaces.

Acknowledgement

This program was partially funded by the VGB PowerTech e.V. The fruitful discussions with the German materials experts of the VGB working group on materials and corrosion and their substantial contributions are gratefully acknowledged.
References


