LCF Corrosion experiments on sensitized AISI 304 in a refreshed autoclave system

W.M.M. Huijbregts, P.H. Venderbosch, H.G. van Zuilen

On behalf of the 4th Workshop on Fracture MechanIcs. Prague, 13-14 May 1993
(paper 43)

Summary

Sensitised AISI 304 is susceptible to stress corrosion cracking and corrosion fatigue at high temperatures in neutral, high oxygen-containing water. The investigation on corrosion fatigue started on AISI 304 in BWR quality water at 200 °C and 70 bar. Crack growth in three-point bent beam specimens was measured using the compliance method. The water chemistry and the corrosion potential of AISI 304 was measured during the test runs in the refreshed autoclave system.

1. Introduction

This paper describes the autoclave system and the results of some experiments on AISI 304 as a start for a larger project in the near future. Due to cracking of sensitised AISI 304 and weld materials in BWR environments, much research has been done already. An extended report on intergranular cracking was published by Cowan and Gordon in 1973 [1].

The aim of this paper is to show that it is possible to measure cracking rates under low-cycle fatigue corrosion conditions in high-pressure high-temperature water applying the three-point bent beam specimens. Various materials and welds present in BWR systems will be tested for resistance to corrosion fatigue and stress corrosion cracking in the future.

2. Experiments

Autoclaves

For the investigation an appropriate water conditioning system with five autoclaves has been installed [2]. The water conditioning system regulates the desired flow of the water through the autoclaves at the set temperature, pressure, oxygen and ammonia content and specific conductivity. Three autoclaves have been assembled for the corrosion fatigue tests (Low-Cycle Fatigue, LCF). Two autoclaves have been assembled for the Slow Strain Rate tests. An external high pressure reference electrode (Ag/AgCl) was used for measuring the corrosion potential of an unstressed stainless steel sample in the autoclave.

Figure 1. The water conditioning system and autoclaves for SSR and LCF testing

Test specimen

Charpy-V notched specimens of AISI 304 have been chosen for the LCF tests (10 x 10 x 50 mm with a 2 mm notch) .Beforehand the specimens are mechanically cracked in a fatigue machine (Cracktronic type). In some tests the precracks were made in the specimens by sawing, using thin sawing blades (0.1 mm).

Measurement of crack growth

Crack growth is deduced from the compliance measurement. The compliance (C) is the ratio between the deflection of the test piece and the load on the test piece. Measuring the deflection is performed with an induction displacement cell which is placed between a fixed point of the autoclave lid and the pulling rod. In this way the compliances of the autoclave and the test specimen is measured. Subtracting the total compliance at the start of the experiment (autoclave plus precracked specimen) from the measured compliance during the test gives the extra compliance of the growing crack. The compliance was calibrated on specimens with different crack lengths. Before starting the test, the crack length on both sides of the specimen was carefully measured.

Calculation of the stress intensity factor K

The stress intensity factor K at the crack tip is calculated [4, 5]:

$$K = \frac{3PS}{2bW^2} f(a/W) \sqrt{\pi a}$$

where:
P = load in middle of specimen in MN
S = distance between the support points (0.04 m)
b = width of the specimen (0.01 m)
W = thickness of the specimen (0.01 m)
a = crack length in m
Z = a/w

$$f\left(\frac{a}{W}\right) = \frac{1}{\sqrt{\pi}} \frac{1.99 - Z(1 - Z)(2.15 - 3.93Z + 2.7Z^2)}{(1 + 2Z)(1 - Z)^{1.5}}$$

The loads Pmax and Pmin that are to be applied can be calculated for every K value desired, using the above relationships. The selected fatigue frequency is 0.02 Hz.

The crack growth da/dN is dependent on the AK values

Important values to determine are:

- the threshold value of Kmax above which crack growth occurs
- the crack growth rate in dependence of the AK value (Kmax-Kmin) = AK

The method of measurement was as follows: The crack growth rate was determined during the test by measuring the compliance at different times. The polynomial calculated through the measurement points. The crack growth rate (da/dt and da/dN) and crack length for the determination of Kmax and Kmin are calculated using this polynomial equation.

3. Results

Crack growth

Conductivity, pH and oxygen content of the water and the corrosion potential of a stainless steel sample were measured continuously. During the test some ammonia was dosed in the circulating water system to avoid a high Fe content in the water. The data of the water composition together with the compliance was plotted during the test. See Figures 2, 3 and 4.

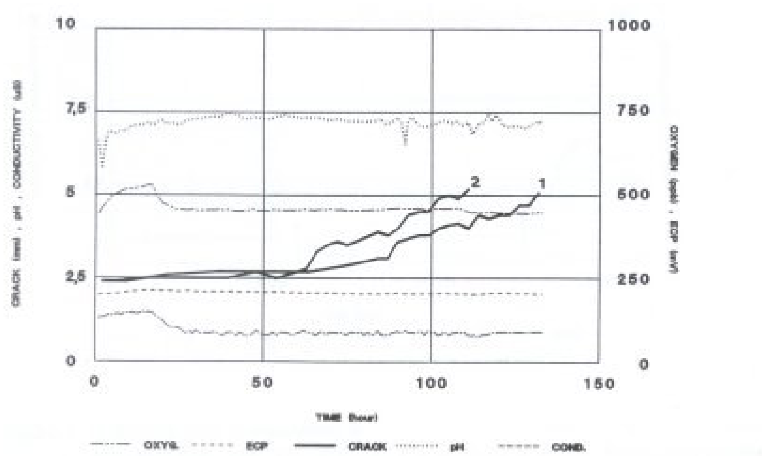

Figure 2 Measuring data of experiments 1 and 2. Sensitised AISI 304, T = 200 °C, f = 0.02 Hz Kmax = 13.4 MPa Vm, deltaK = 12.1 MPaVm, R = 0.1

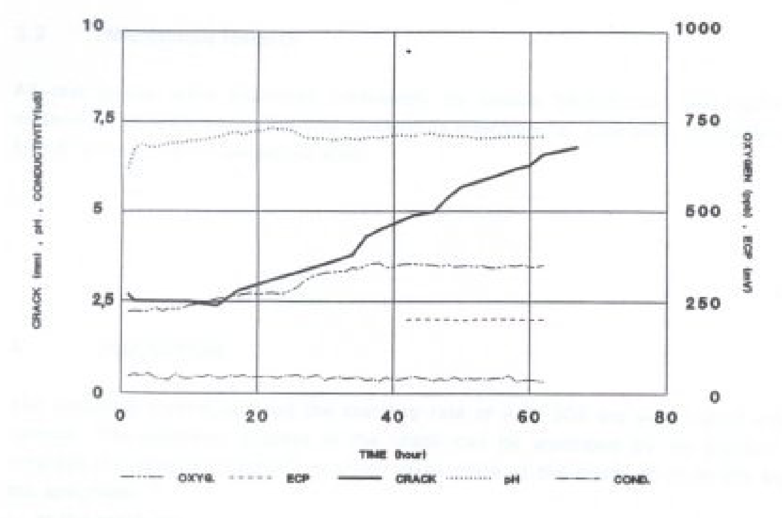

Figure 3. Measuring data of experiment 3. Sensitised AISI 304, T = 200 °C, f = 0.02 Hz, Kmax = 16.8 MPa Vm, deltaK = 15.1 MPa Vm, R = 0.1

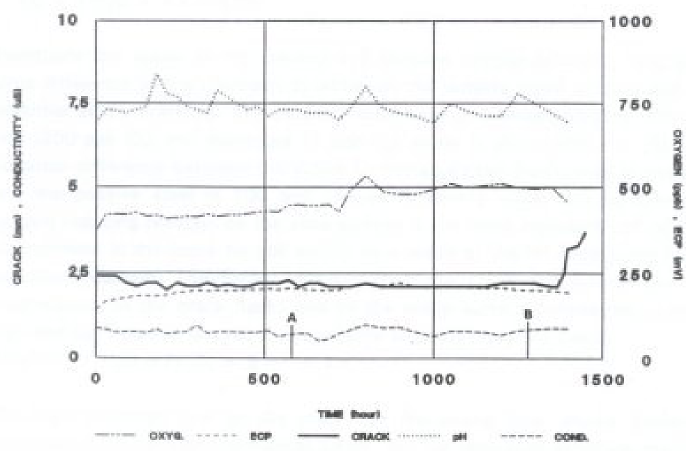

Figure 4. Measuring data of experiment 4. Annealed AISI 304, T = 200 ℃, f = 0.02 Hz, R = 0.1. Kmax was increased stepwise from 8.9 to 13.2 (at A) and to 15.1 (at B). Cracking started at Kmax = 15.1 MPa Vm and deltaK = 13.6 MPa Vm

In some experiments cracking started at once, while sometimes longer incubation times were found. In test no.4 the Kmax and deltaK values were increased stepwise. The crack growth rates (calculated from the polynomial) versus the deltaK values are given in figure 5.

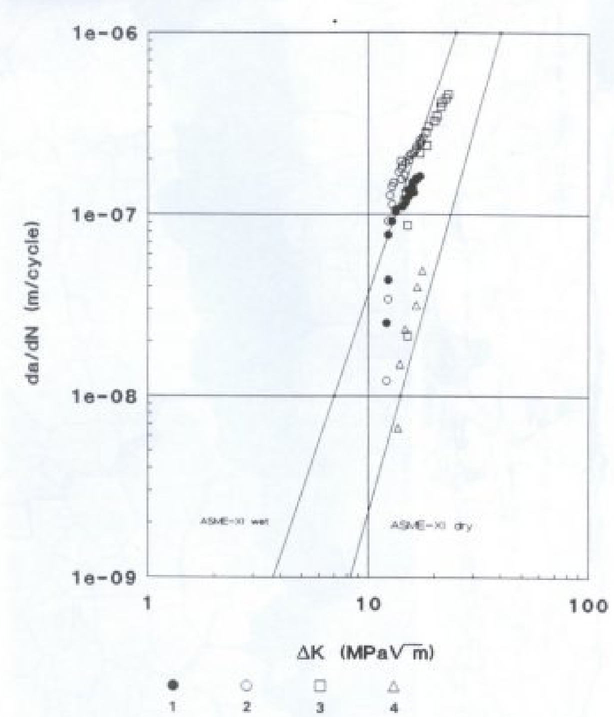

Figure 5. Crack growth rates of AISI 304, T = 200 ℃; R = 0.1; f = 0.02Hz.
annealed: exp 4 ; sensitised: exp 1, 2 and 3.

4. Microscopic research

All test pieces were examined extensively by Optical Microscopy. See figure 6. The material is severely sensitised and cracking is intergranular. Corrosion products were not found in the cracks of sensitised steel.

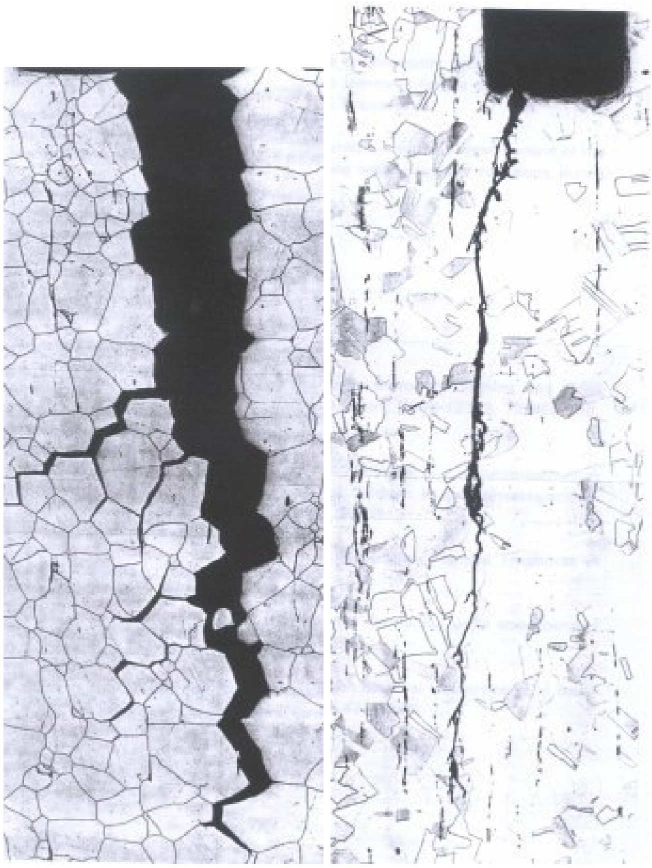

Figure 6

Cross section of crack in sensitised (left) and non-sensirtised (right) AISI 304

5. Discussion

The corrosion mechanism and the cracking rate of AISI 304 are well known and are as follows. The corrosion process in the crack can be described by an anodic reaction, whereas the matching cathodic reaction takes place at the crack tip or at the surface of the specimen.

at the crack tip:

- anodic reactions in water $Fe + H_2O \rightarrow FeOH^{++} H^{+} + 2\ e$
- cathodic reaction $2H^{+} + 2\ e \rightarrow H_2$

on the steel surface:

cathodic reaction: $O_2 + 2\ H_2O + 4\ e \rightarrow 4\ OH''$

Eventually the water at the cracktip will become oxygen-deficient. This will result in a large difference in the corrosion potential on the outside metal surface and the corrosion potential at the crack tip. The potential difference of stainless steel at 200 °C in oxygen rich (200 ppb O2) and deaerated (2 ppb O2) water is about 450 mV [6]. The corrosion potential difference between the active Cr depleted grain boundaries in oxygen-free water and the passive steel in 200 ppb oxygen-containing water will be even larger. If the oxygen reducing reaction on the steel surface is the most important cathodic reaction, the environment in the crack tip will acidify as a result of the H^+ production from the anodic corrosion reaction. The $FeOH^+$ diffuses from the crack and will oxidize to magnetite octahedrons on the crack flanks and on the metal surface (where the oxygen content is high and the water is neutral) in accordance with the reactions below:

$3\ FeOH^{++}\ H_2O \rightarrow Fe_3O_4 + 5\ H^+ + 2\ e$

The high corrosion rate on the crack tip (the strong local anodic dissolving reaction) combined with the high mechanical strain, and the sensitized structure results in intergranular corrosion and cracking. The crack rates determined with the three bent beam specimens agree fairly well with those of the ASME-XI code. The lines of dry and wet ASME XI lines are drawn in figure 5 as well.

6. Conclusions

The autoclave system and the compliance technique on three-point bent beam specimens can be used for testing materials for resistance to low-cycle fatigue corrosion in high temperature water.

The results agree with the ASME XI code lines.

The corrosion potential measurement of the steel correlate with the oxygen content of the water. The measuring technique made it possible to determine cracking rates under varying water chemistry conditions, during which corrosion potentials could be measured too

7. References

1. Cowan R.L., Gordan G.M. Intergranular Stress Corrosion Cracking and Grain Boundary Composition of Fe-Ni-Cr Alloys. General Electric NEDO-12399, 73 NED 106, Class 1, September 1973.
2. Huijbregts, W.M.M., Venderbosch P.H., Kokmeijer E. Laboruntersuchungen nach KorrosionsermOdung im Zusammenhang mit Schaden in Speissewasserentgassern. V GB Kraftwerkstechnik 72, (1992), Heft 10, 908..913
3. ASTM E 399-83-A3, Standard Test Method for Plane-Strain Fracture Toughness of Metallic Materials.
4. Lang E, H. Rissausbreitung in Stahl 316L bei erhohter T emperatur under statischer und zyklischer Belastung, Report KfK 4823, January 1991.
5. Osch, G.A.A. van, Huijbregts, W.M.M. Corrosion Potential Measurements in Boiler Water: The Influence of Oxygen Content. Corrosion 42, (1986), .2.