High Temperature Electrochemical Corrosion Testing in a Hot Cell Environment – Problems and Pitfalls

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Abstract

A hot cell corrosion test set-up is being installed to investigate the corrosion properties of radioactive materials under BWR and PWR conditions. Major purpose is to investigate stress corrosion cracking problems of radioactive materials like Irradiated Assisted Stress Corrosion Cracking (IASCC). In addition to mechanical tests like Slow Strain Rate Testing, constant load and low cycle fatigue, electrochemical tests can be performed as well. Therefore a remote-friendly external Ag/AgCl reference electrode and a high temperature pH electrode have been developed. These electrodes can in principle be used in a hot cell environment. To be able to do electrochemical tests as well as crack growth rate measurements by the potential drop technique, electrical feed through and inside connectors are necessary. An electrical feed through has been realized by a "Christmas tree" like construction in which four mineral insulated cable are sealed with a metallic sealing. For the inside connector, a pragmatic approach resulted in the following solution: a commercial connector from aluminium oxide shielded with zirconium oxide. This construction lasted for at least 4 months.

Introduction

With the increasing age of nuclear power plants, stainless steel core components suffer from increasing irradiation damage. These irradiated stainless steels are susceptible to stress corrosion cracking, in this case called Irradiation Assisted Stress Corrosion Cracking (IASCC). IASCC occurs due to a combination of high temperature, stress and irradiation. Cracking due to IASCC has been observed in both Boiling Water Reactors (BWR) and Pressurized Water Reactors (PWR) [1,2]. To be able to study this phenomenon, a hot cell corrosion test set-up is being installed to investigate the corrosion properties of radioactive materials under BWR and PWR conditions. The test set-up consists of three autoclaves connected to a water recirculation loop to allow testing under various controlled water chemistries. Figure 1 shows the autoclaves in the hot cell and the recirculation loop in the basement.

Figure 1 Hot cell autoclaves and recirculation loop

Only the autoclaves are placed in the hot cell. Figure 2 shows a schematic of the set-up.

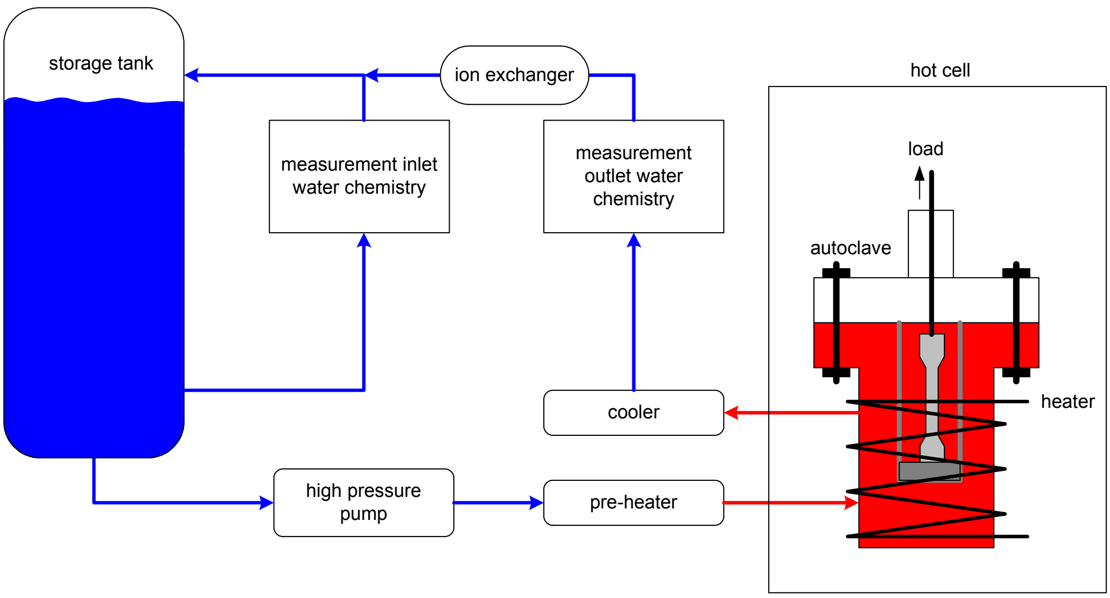

Figure 2 Schematic of the hot cell installation

The test water enters the hot cell when it is already at the test temperature and pressure. The water leaves the hot cell under the same conditions, but will go through two filters after cooling down to remove possible active species (corrosion products from the sample being tested). These filters are not placed in the hot cell, but separately shielded with lead. More details have been described in the paper of 2001 [3]. The maximum operating temperature is 360°C and the maximum operating pressure is 200 bar. All autoclaves are equipped with a computer controlled loading device enabling different mechanical loads: Slow Strain Rate, Constant Load, Rising Load and Slow Cycle Fatigue. All these tests are used to investigate if a certain material/environment combination is sensitive to stress corrosion cracking.

The Slow Strain Rate Technique is a qualitative experimental technique for evaluating the susceptibility to environmental cracking. Due to the accelerated nature of the test the results are not intended to necessarily represent service performance. This test is typically used for comparative evaluation of effects of metallurgical and environmental variables on the sensitivity to known environmental cracking problems. For instance in our laboratory we will use this technique to compare the SCC behaviour of irradiated (up to 3-4 dpa) and non irradiated materials.

The constant load test is closer to service conditions, but has the drawback that it can be time consuming to find a proper load for the tests. It is often used to obtain a time-to-failure or a crack growth rate, when used together with a crack growth rate monitoring device like a potential drop system.

Low cycle fatigue is supposed to represent service conditions were besides a corrosive environment the structure is also subjected to a low cycling load. The combination of both can result in the premature failure of the specimen.

Table 1 shows a summary of the specifications of the hot cell set-up.

Table 1 Specifications hot cell autoclaves and loops

Temperature	Max 360°C
Pressure	Max 200 Bar
Maximum load	20 kN
Displacement rates	4.10^{-1} to 2.10^{-7} mm/sec
Specimens to be tested	Tensile specimen, Compact Tension, Cracked Round Bar
Number of autoclaves and loading units	3
Autoclave volume	2 L
Autoclave materials	2 x 316L, 1x C276
Material recirculation loop	316L
Material stagnant loop	C276
Water chemistry BWR	Conductivity <0.1 μS/cm, DO ≤200ppb (NWC), DH 10-30 cc/kg (HWC)≤
Water chemistry PWR	2-3 ppm Li, 400 ppm B, conductivity 20-30 μS/cm, DH 20-40 cc/kg

In addition to these "mechanical" tests some electrochemical tests are being investigated to be used, like corrosion potential measurements, corrosion resistance measurements and electrochemical impedance measurements. In this paper we focus on some typical challenges that have to be tackled related to these electrochemical measurements. These challenges arise when the choice of materials is limited due to the high temperature and the presence of an intense radiation field. Three cases will be discussed:

1. An appropriate reference electrode – a home-made remote friendly external Ag/AgCl reference electrode and an Yttrium Stabilized Zirconium oxide high temperature pH electrode have been developed.
2. A pressure resistant electric signal cable feedthrough -consisting of a number of mineral insulated signal cables and a "Christmas-tree" like construction to have 4-6 cables entering the autoclave at the same location.
3. In the test solution an electric connector is required to isolate the signal cable from the test solution and the autoclave. Under PWR conditions a material like aluminium oxide can not be used, as this ceramic will be corroded by the boric acid that is present in the solution. Therefore an existing connector constructed from aluminium oxide has been modified in such way that it

survives up to 4 months (largest testing time realized and still no degradation of the connector) of continuous operation.

Electrochemical testing

Besides the "mechanical" tests some electrochemical tests are being investigated to be used as well. We will start with the measurement of the corrosion potential. The corrosion potential is a useful measure for monitoring of stress corrosion cracking as it can help to identify when it is likely to occur (high value of the corrosion potential) and when it is not likely to occur (low value of the corrosion potential). For example IASCC of stainless steels in BWR 's can be prevented if the corrosion potential is decreased below -230 mV (SHE) [5]. It has also been shown that there is a direct relationship between the crack growth rate and the corrosion potential of stainless steel components under BWR conditions. In addition when both the pH of the test solution and the corrosion potential are known, the thermodynamic state of the metal surface can be predicted by means of a Pourbaix-diagram [6]. It is possible to say whether, from a thermodynamic point of view, the metal is covered by an oxide layer, immune or sensitive to corrosion.

To measure the corrosion potential of a metal sample, a reference electrode is needed. To use such a reference electrode in a hot cell, it must be constructed form radiation resistant materials and survive under high temperature and pressure conditions (300°C, 150 bar). Also the potential of the reference electrode must be related to the Standard Hydrogen Electrode (SHE) scale.

Development of a reference electrode

The major problems with a high temperature reference electrode in a hot cell are:

1. Sufficient long lifetime
2. Reference electrode should survive under irradiation
3. The design should allow manipulation with the hot cell manipulators

Two concepts are presented here. The first is an external (pressure balanced) reference electrode based on the Ag/AgCl redox couple [7]. This reference electrode has a sufficient long lifetime as it operates at room temperature. The second concept is the Yttrium Stabilized Zirconia reference or pH electrode, taken from the LIRES project. [8].

External Ag/AgCl reference electrode

The silver/silver chloride reference electrode is probably one of the most used reference electrodes [7, 9-11]. Unfortunately the Ag/AgCl redox couple can not be used at high temperatures due to the instability of the AgCl layer. Also this AgCl layer is sensitive to degradation by hydrogen when this gas is present in large quantities such as in BWR's under HWC and in PWR's. Therefore an external reference electrode based on the Ag/AgCl reference electrode couple was developed, which was connected to the test solution by means of a salt bridge. This salt bridge is then responsible for the transportation of the electrode signal out of the autoclave. Also it wouldn't suffer by radiation as the reference electrode is positioned outside the autoclave and so the radioactive sample is shielded by the autoclave and the test solution in the autoclave. Figure 3 shows how the external reference electrode is connected to the test solution.

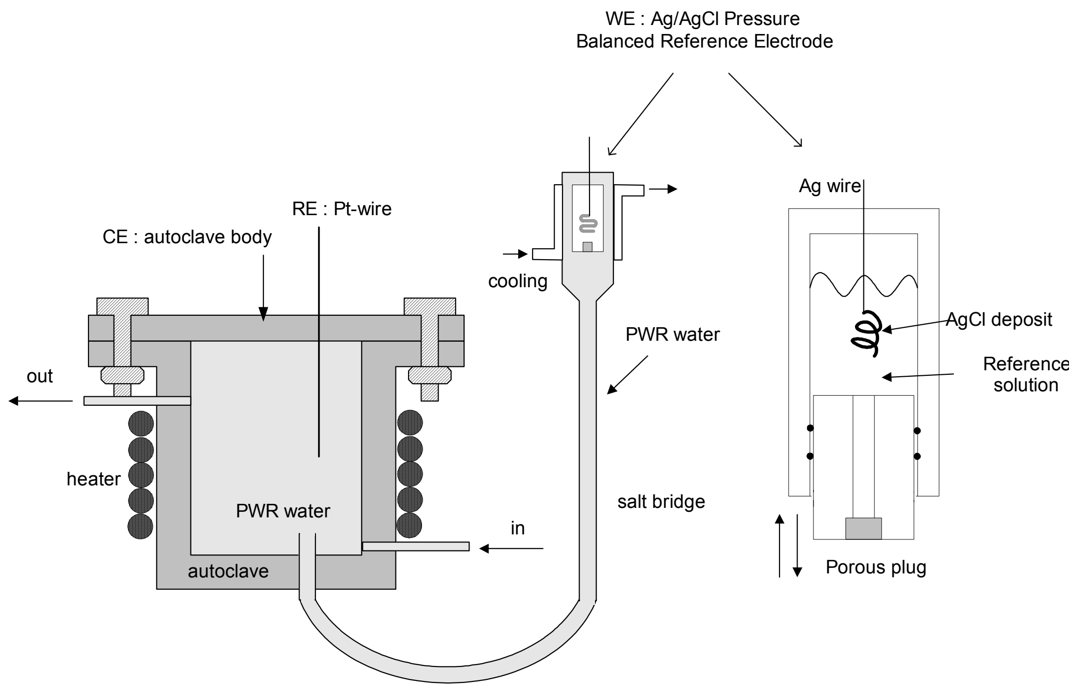

Figure 3 The external reference electrode is connected to the autoclave by means of a salt bridge

During start up and cooling down the pressure will change in the autoclave and so in the external reference electrode. Therefore the reference electrode is designed in such way that it can balance the pressure in the autoclave. This is also shown on the right hand side in Figure 3. A piston can move up and down, thereby maintaining pressure equilibrium between the reference electrode chamber filled with a reference solution and the outside test solution. Electrolytic contact between the reference electrode and test solution is maintained by a porous ceramic plug.

Special attention has been given to the design, regarding control by manipulators. In close corporation with the hot cell engineers a reference electrode as shown in Figure 4 has been designed.

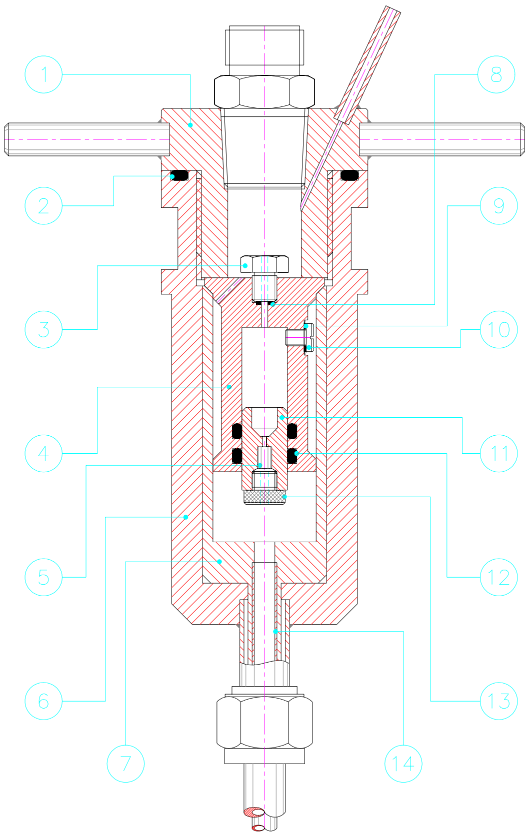

Figure 4 Schematic of the high temperature hot cell reference electrode

The cover (1) can be easily manipulated by means of the large handles. An O-ring (2) seals the cover with the stainless steel body (6). A bleed valve can be connected to the small stainless steel tube at the top of the cover. The reference electrode itself is completely constructed from Teflon and based on the principle of the external pressure balance reference electrode (EPBRE) [7]. In the movable piston (11) fits a porous ceramic plug (5). In case of malfunctioning the reference electrode can be replaced by the hot cell operator. The Teflon reference electrode is assembled outside the hot cell, after which it is fit into the stainless steel body. The Teflon parts are constructed in such way that they fit automatically in the right position. All inner parts of the stainless steel body and stainless steel flexible tube (the salt bridge) are covered with Teflon to avoid influence of conducting walls. At the end of the Teflon salt bridge an oxidised zirconium tube is fitted of approximately 20 cm long. This tube can survive the high operating temperature and the radiation coming from the radioactive samples to be tested.

High temperature pH-electrode

This high temperature pH-electrode (or quasi reference electrode) has been adapted from the LIRES –project (a European RTD project, Development of Light Water Reactor Reference Electrodes) [8]. The principle of this mixed metal oxide reference electrode is based on the zirconia pH sensor developed by Niedrach [11,12]. This zirconia pH sensor can be considered as the high temperature analogue of the low temperature glass pH electrode. The mixed metal oxide reference electrode consists of an Yttrium Stabilized Zirconia (YSZ) tube. The lower end of the tube is filled with a mixture of Ni/NiO powder. The rest of the tube is filled with aluminum oxide tube to close the tube and isolate the metal wire, which connects the Ni/NiO mixture with the mineral insulated cable. The YSZ tube becomes an oxygen ion conductor at sufficient high temperature (T> 180°C), which makes it possible to use this tube as part of a reference electrode. The potential of the electrode is determined by the nickel-nickel oxide reference couple at the inside of the tube and the pH of the water at the outside of the tube [13]. A schematic and photograph of the reference electrode is shown in Figure 5.

Figure 5 Schematic of the YSZ reference electrode and photograph of the final design

The most innovative part of the electrode design is the metal ceramic connection made by means of the fast magnetic forming (compression) technique. A nickel tube was connected to the ceramic tube by means of this magnetic compression technique. A strong magnetic field pulse compresses the nickel tube to the zirconia tube. This makes it possible to construct the whole high temperature pH electrode from radiation and high temperature resistant materials resulting in a design that can survive in-side a hot cell environment under high temperature, high pressure and radiation. Test results under typical PWR conditions, a pressure of 150 bar and a temperature between 300-350°C, showed that the reference electrode is mechanically stable and gave reasonable reliable potential measurements.

The potential of the YSZ reference electrode is only dependent on the pH. That means that when the pH is known the YSZ electrode can be used as a reference electrode. On the other side when the pH is not known and a proper working reference electrode is available this electrode can be used to determine the pH of an aqueous solution at high temperature.

Electrical feed through

To be able to do electrochemical tests in an autoclave, it is necessary to have a signal cable that enters the autoclave, without having electrical contact with the autoclave. This also holds for crack growth rate measurements with the potential drop technique. This requirement is illustrated in Figure 6.

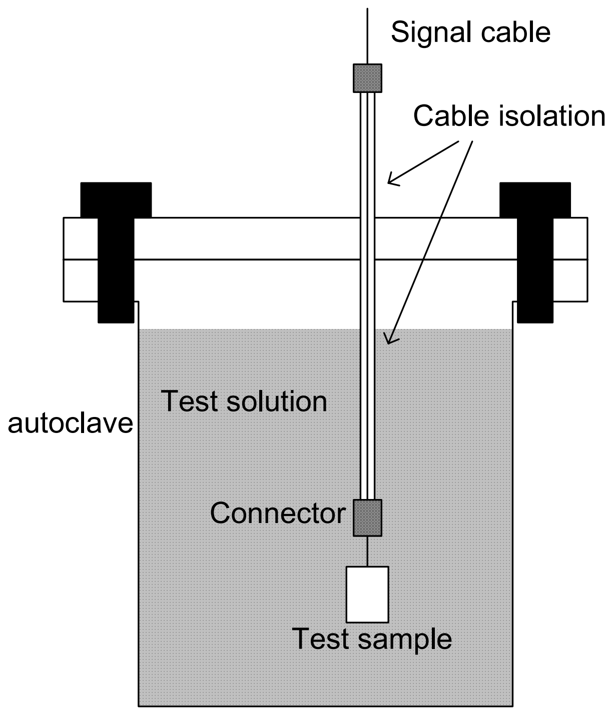

Figure 6 Signal cable entering the autoclave, two connectors required.

Essentially there are two feed through or connectors required: one that enters the autoclave and secondly a connector in the autoclave. The first problem, how to enter the autoclave with a signal cable that is not in contact with the autoclave and can resist 150 bar and 300°C, is shown in Figure 7.

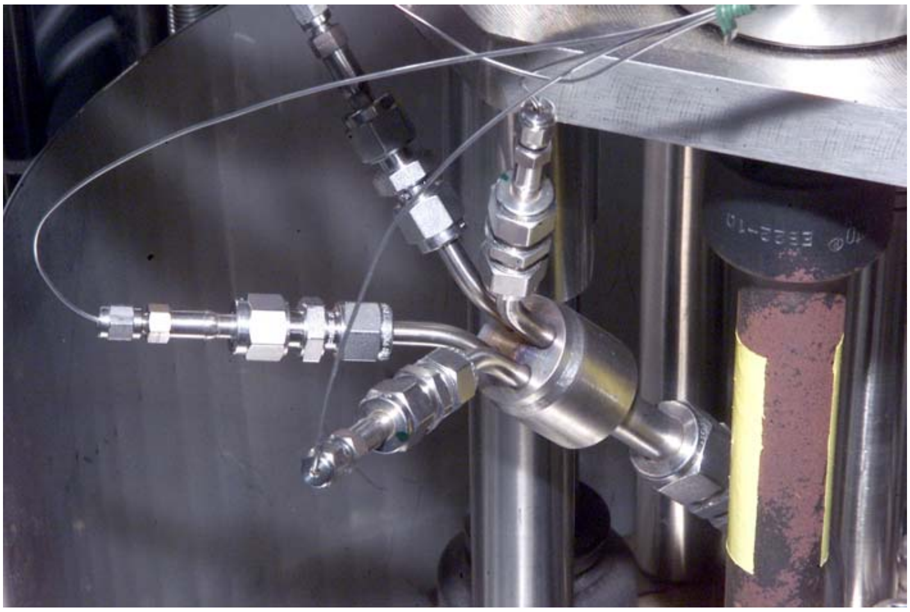

Figure 7 A "Christmas tree" like construction for entering the autoclave

Mineral insulated signal cables are sealed with metallic pressure parts. Four to six signal cables can enter the autoclave using this construction.

In the autoclave itself the problem is more complicated. The signal cable should be connected to a sample (tensile specimen or CT specimen) without touching the outer metal shielding. Commercial connectors are available made from aluminium oxide. Aluminium oxide is a good isolator and can easily be brazed to metals. Unfortunately this ceramic is not chemically stable in PWR primary water (400 ppm boric acid and 2 ppm lithium hydroxide) at 300 °C. This is demonstrated in Figure 8.

Figure 8 Corrosion of aluminium oxide connectors in PWR primary water after one months of exposure

The three connectors on the left hand side show severe corrosion of the ceramic parts after one months of exposure to PWR primary water at 300°C. Alternative solutions are to use Teflon shrink tube for isolation. This works well for non active samples and a maximum temperature of 320°C. Teflon is however not suitable for use in a hot cell environment. A pragmatic solution is to shield a commercial aluminium oxide connector with a zirconium oxide tube. This has been done with the connector on the right hand side of Figure 8. This connector doesn't show any material degradation. We have done tests up to 4 months with these shielded connectors with still good results.

In addition development work is going on to produce connectors based on zirconium oxide. Unfortunately zirconium oxide is difficult to braze. Therefore the fast magnetic forming technique has been utilized to make a connector. A typical connector is shown in Figure 9. This work is still in progress.

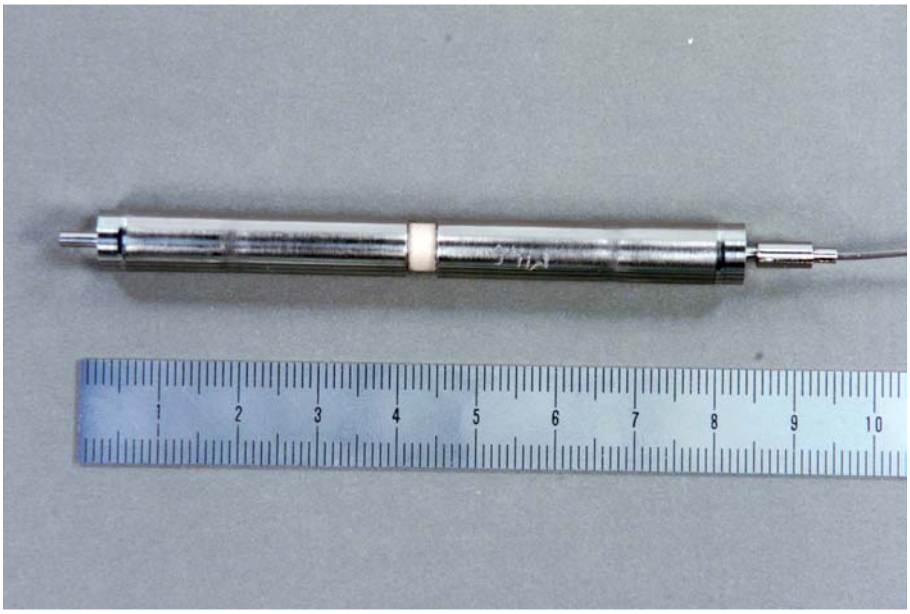

Figure 9 Connector from zirconium oxide made with fast magnetic forming.

Conclusions

An external high temperature reference electrode Ag/AgCl has been developed that can be used in a hot cell. In addition a high temperature pH-electrode can be used completely constructed from radiation resistant materials.

To be able to do electrochemical tests as well as crack growth rate measurements by the potential drop technique, electrical feed through and inside connectors are necessary. An electrical feed through has been realized by a "Christmas tree" like construction in which four mineral insulated cable are sealed with a metal sealing. The best result for the connector in the autoclave was to modify a commercial connector from aluminium oxide by shielding it with a zirconium oxide tube. This construction lasted for at least 4 months.

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