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Contents

Corrosion Experience with Steam Generators in Belgian Utilities <i>Charles Lairé</i>	2
Recent Insights into the Mechanism of Secondary Side Cracking of Alloy 600 PWR Steam Generator Tubes <i>Peter Scott</i>	3
Corrosion Considerations in Geological Disposal of Belgian Radioactive Waste <i>Bruno Kursten</i>	4
Water Chemistry and Corrosion Aspects in ITER, the International Thermonuclear Experimental Reactor <i>Patrick Lorenzetto</i>	6
Irradiation-Assisted Stress Corrosion Cracking - Aspects of Science and Technology <i>Armin Roth</i>	7
Microstructural and Microchemical Evolution of Irradiated Materials <i>Stephen Bruemmer</i>	8
Fracture Mechanics Aspects in Crack Growth Evaluation of IASCC <i>Tetsuo Shoji</i>	9
Study of Mitigation Strategies for IASCC <i>Pascal Boydens</i>	11
Application of Electrochemical Impedance Spectroscopy for Monitoring of SCC-Cracks <i>Rik-Wouter Bosch</i>	13

Corrosion Experience with Steam Generators in Belgian Utilities

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Steam generator (SG) tubes of several Belgian plants were pulled for destructive investigations, especially for secondary side corrosion, which has been detected for nearly all the Belgian (old) SG's equipped with Inconel 600 tubing.

The affected locations, the corrosion morphology and the extent of the degradations depend on several parameters such as :

- the stresses, residual and applied stresses
- local chemistry
- number of the cycles
- the SG-design, tube support plate (TSP) material
- temperature, etc.

Through the expertise of pulled tubes, we were able to make correlations with the different key parameters and between the different plants, in order to prevent corrosion problems with the new SG's.

This investigation has indicated that :

- very high applied stresses can be exerted on the tube bottom
- the stress corrosion cracking occurs during operation, but the lay-up conditions and the start-up and shutdown conditions influence the evolution of the corrosion. This conclusion is based on a statistical study comparing the results of the inspection over different cycles to an interrupted cycle.
- the chemical environment in crevices is characterised by an acidic to neutral concentrated solution. Based on the deposit chemistry no fundamental difference between the different plants could be found, while the corrosion morphology can be different.

Corrosion tests were performed in several chemical environments for different tubing materials. Not only the Inconel 600 was extensively tested but also the new materials : alloy 800 and Inconel 690.

The local chemistry in crevices derived from the investigation on the pulled tubes was simulated in capsule tests.

The influence of different parameters, like temperature, stresses and addition of elements (Pb, Cu, etc.) was studied. Inconel 600 seems to be very susceptible to stress corrosion cracking, while the corrosion resistance for Inconel 690 is confirmed. Nevertheless Inconel 690 is quite vulnerable to the presence of Cu in the solution. The cracking mechanism is influenced by the electrochemical potential of the solution which is increased by Cu species. The influence of a cold shutdown is probably related to the oxidation of metallic Cu or other species.

Recent Insights into the Mechanism of Secondary Side Cracking of Alloy 600 PWR Steam Generator Tubes

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Secondary side cracking of PWR steam generator tubes fabricated from nickel base Alloy 600 in the mill annealed condition is a generic problem that is increasing in importance throughout the world. The observed tube degradation is normally in the form of generalised intergranular attack (IGA) and/or intergranular stress corrosion cracking (IGSCC). It occurs in recirculating steam generators mainly in low flow, occluded zones (such as crevices and under sludge) where secondary water impurities can hide out by the well-known wick boiling mechanism. Many design changes have been introduced over the years aimed at eliminating or at least minimising such occluded zones and replacing mill annealed Alloy 600 with more resistant tube materials such as thermally treated Alloy 600 and Alloys 690 and 800. Nevertheless, many of the older steam generators remain in service and there is a strong incentive to halt or reduce the rate of increase of tube cracking as well as to ensure that similar events do not, in due course of time, come to affect the others.

The underlying cause of IGA/IGSCC of Alloy 600 tubes of recirculating steam generator generators has hitherto been thought to be the formation of concentrated alkaline or acidic solutions from the hide out of secondary water impurities. The pH then depends on the molar ratio of the strongly alkali or acid forming ions such as sodium, chloride and sulphate. A few special cases are also known where accidental pollution with lead has occurred, leading to transgranular stress corrosion cracking as well as IGA/IGSCC that is not particularly dependent on pH.

With modern, ever stricter secondary water specifications, it is apparent that not enough soluble impurities can enter the steam generators to fill the available crevice volume with a sufficiently concentrated solution whose boiling point is close to the primary water temperature at the secondary circuit pressure. Thus, occluded zones with restricted mass flow must either be completely steam-blanketed or largely so with just a few droplets of concentrated liquid. It is argued here that IGA/IGSCC in a superheated, albeit polluted, steam environment is much more plausible than concentrated acids or alkalis. This view is reinforced by recent observations of rather widespread IGA/IGSCC in the superheated steam, free span areas of Alloy 600 tubes of once-through (OTSG) steam generators.

Recent progress in applying advanced surface analysis techniques, specifically Secondary Ion Mass Spectrometry (SIMS) and Analytical Transmission Electron Microscopy (ATEM), to examine cracked tubes removed from service has given considerable insight into the underlying mechanism of material failure. Internal oxidation at grain boundaries beyond crack tips has been observed in specimens of OTSG tubes. Work is also in progress on tubes extracted from recirculating steam generators. The morphology of the internal oxidation is similar to that observed in Alloy 600 specimens with primary water cracks. The preliminary conclusion of this work based on the arguments above and these observations is that secondary side IGA/IGSCC probably occurs in an environment similar to "doped" steam used extensively in laboratory investigations to test the resistance of Alloy 600 to IGSCC.

Corrosion Considerations in Geological Disposal of Belgian Radioactive Waste

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Waste and Disposal

SCK•CEN

The safe disposal of radioactive waste requires that the waste be isolated from the environment until radioactive decay has reduced its toxicity to innocuous levels. The current worldwide trend for the final disposal of conditioned high-level radioactive waste (HLW) focuses on deep geological disposal. The present Belgian repository concept consists of a horizontal network of concrete galleries in the Boom Clay formation. Long tubular metallic overpacks will be placed in the center of these galleries. The galleries are then backfilled with either a bentonite-type material or Boom Clay. Afterwards, the canisters, containing the conditioned radioactive waste, will be pushed one after the other inside the overpacks. During the geological disposal, the isolation between the radioactive waste and the environment is realized by the *multibarrier principle*, in which the buried waste is separated from the biosphere through the complementary nature of several natural and artificial barriers.

The corrosion behaviour of the metallic containers is an important issue in any geological disposal concept since these containers constitute a physical barrier to the release of radionuclides in the environment and, for the Belgian concept in particular, to their migration in the geosphere through contact with the interstitial clay water. To study the long-term corrosion behaviour of various candidate container materials under repository conditions, SCK•CEN developed, with the support of NIRAS/ONDRAF, an extensive research programme in the early 1980's. This programme consists of *in situ* immersion experiments on the one hand and *laboratory* corrosion experiments (electrochemical and immersion experiments) on the other hand.

The *in situ* corrosion experiments were performed in the underground laboratory, the High Activity Disposal Experimental Site, or HADES facility, situated in the Boom Clay formation at a depth of 225 metres below ground level. Three test concepts were elaborated which represent three different environments that might evolve in the course of the geological disposal period. The corrosion experiments place the samples either in 'direct contact with clay' (type I), in contact with a 'humid clay atmosphere' (type II), or in contact with a 'concrete saturated clay atmosphere' (type III). The first type simulates normal long-term repository conditions. The latter two simulate either 'exploitation' or 'accidental' conditions. Corrosion experiments were performed at 16°C (natural clay temperature at 225 metres depth), 90°C, and 170°C (due to the heat emission of the radioactive waste).

Each *in situ* corrosion experiment consists of a sufficiently long stainless steel carrier tube on which the container samples are mounted. Between 12 and 40 samples are mounted on the outside of the tube or on a Teflon[®] holder which is suspended in the inside of the tube, depending on the type of experiment. The samples placed on the type I corrosion experiments are welded rings of about 100 mm in diameter, 30 mm wide, and 2 to 4 mm thick. The samples placed on the type II and III corrosion experiments are square plated of 30 by 30 mm and 2 to 4 mm thick. The materials that are evaluated as candidate container materials are on

the one hand corrosion-allowance materials (carbon steel) and on the other hand corrosion-resistant materials (stainless steels, nickel-, and titanium alloys).

A total of twelve *in situ* corrosion experiments were installed in the underground laboratory during the period 1985-1994. All samples are recuperated, cleaned, and individual weight loss measurements were performed. Extensive analyses by stereomicroscopy, optical microscopy, scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), electron probe for microanalysis (EPMA), and X-ray diffraction analysis (XRD) showed that carbon steel is not a suitable candidate container material for the geological disposal of radioactive waste in clay. Carbon steel exhibits severe signs of localised corrosion, viz. pitting, after interaction with Boom Clay. Stainless steel, nickel- and titanium alloys remain unaffected. Stainless steel showed very good corrosion resistance to the underground repository environment. As a result, a shift in the reasoning of the national authorities has occurred with regard to the choice of container material from carbon steel to stainless steel.

An important shortcoming of the *in situ* corrosion experiments was that they did not allow to study and quantify the aerobic and anaerobic corrosion separately. However, the corrosion mechanism is liable to change as the oxygen content and the chemical characteristics of the clay environment, surrounding the HLW containers, change as a function of time. Therefore, a laboratory corrosion programme was elaborated to assess the corrosion behaviour of candidate container materials in environmental conditions relevant for the disposal of HLW in Boom Clay. This programme consists of electrochemical experiments and immersion experiments.

The main aim of the electrochemical experiments is to quantitatively assess the influence of several environmental factors (temperature, aerobic/anaerobic conditions, anion content, and alloy composition) on the localised corrosion of candidate container materials. This influence is studied by recording polarisation curves with a backward scan and determining the characteristic pitting parameters: the free corrosion potential (E_{corr}), the critical potential for pit nucleation (E_{np}), and the protection potential (E_{pp}). These experiments are still ongoing. But preliminary results seem to indicate that the nickel alloy Hastelloy C4 resists pitting in synthetic oxidised Boom Clay water at chloride concentrations up to 10000 ppm. Stainless steel Cronifer 1925 hMo resists pitting at 100 and 1000 ppm Cl^- . Stainless steels AISI 316L, AISI 316L hMo, AISI 316Ti, and UHB 904L only showed minor or no pitting attack at the reference solution containing 100 ppm Cl^- , but do suffer from pitting corrosion at elevated chloride concentrations. Carbon steel shows uniform corrosion at all chloride levels. A SEM study revealed rose shaped pits formed on AISI 316L hMo and UHB 904L: a large central pit surrounded by several smaller satellite pits. This morphology probably indicates subsurface pit growth, with the pit covered by a thin layer of metal.

The aim of the immersion experiments is to identify the various modes of attack that can occur under disposal conditions in an underground clay environment. The immersion experiments should also help to establish the time dependence of the corrosion processes under aerobic and anaerobic conditions. The immersion experiments are performed at 16, 90, and 140°C in specially designed stainless steel containers with a Teflon[®] lining. Pellets of the backfill material (Boom Clay or bentonite) and metallic samples (30 by 30mm) will be stacked alternately inside each container. The samples will be removed at different times over an extended duration and analysed. The first results are planned to be available at the beginning of 1999.

Water Chemistry and Corrosion Aspects in ITER, the International Thermonuclear Experimental Reactor

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The intense radiation fields present in ITER, the International Thermonuclear Experimental Reactor, and its peculiar operation conditions have raised the need to implement a R&D programme to assess the achievable water chemistry and to study the corrosion behaviour of In-Vessel component materials.

Addition of hydrogen into the primary water coolant is a simple and proven method used in fission reactors to prevent continuous radiolytic decomposition of the water and give low concentrations of oxidising species. However, irradiation conditions in the ITER First Wall are less favourable for the radiolytic recombination of the water than in Boiling or Pressurised Water Reactors. In particular, ITER presents larger irradiation intensity (1.4 MRad/s compared to 0.3-0.9 MRad/s), a larger Linear Energy Transfer (LET) because of a lower ratio gamma flux/neutron flux (0.01 compared to 0.2), and a lower water temperature (140-190 °C compared to 270-325 °C). All these parameters decrease the efficiency of hydrogen to inhibit water radiolysis. Therefore, a R&D programme has been implemented in Europe to develop and validate a computer modelling of the water radiolysis under ITER conditions and to predict the concentrations of molecular species produced by radiolysis (e.g. oxygen, hydrogen peroxide). The main results of this R&D programme are presented in this lecture. In particular, the simulation predicts that with addition of 1 wppm of hydrogen into the water, the oxygen concentration at the First Wall region is below 1 wppb but the hydrogen peroxide concentration is about 0.2 wppm.

In parallel to this R&D work on water chemistry, an experimental programme has been implemented to check the corrosion behaviour of material candidates for In-Vessel components. Stainless Steel type 316LN and Copper based alloys such as Dispersion Strengthened Cu alloys (e.g. Al25) and Precipitation Hardened Cu alloys (Cu-Cr-Zr) are the main candidates. Operation conditions are: 140/190 °C and 100/110 °C as the inlet/outlet water coolant temperature for the Blanket and the Vacuum Vessel respectively, baking phases at 250 °C for reactor conditioning, pulsed operation mode (13,000 cycles) with a neutron fluence goal during the Basic Performance Phase of maximum 3 dpa in the First Wall steel, water coolant velocities up to 10 m/s with incident heat flux of up to 15 MW/m² for Divertor components. Stress Corrosion Cracking, Irradiation-Assisted Stress Corrosion Cracking, Corrosion Fatigue, Galvanic Corrosion and Erosion Corrosion of base materials and joints are more particularly addressed in this R&D programme. Various water temperatures, in the range 90-325 °C, and water chemistries, from pure water to acidic environment with impurities at reducing and oxidising potentials, have been considered. The main results obtained so far are presented in this lecture. In particular, Stainless Steel 316LN (ITER Grade) has shown good corrosion resistance, except in acidic environment containing chloride and sulphate in which specimens failed from transgranular Stress Corrosion Cracking. Limited but promising results so far have been obtained with Copper based alloys, which have shown in particular low erosion corrosion rates under isothermal conditions even with water velocities of 10 m/s.

Irradiation-Assisted Stress Corrosion Cracking - Aspects of Science and Technology

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Irradiation-Assisted Stress Corrosion Cracking (IASCC) is used to explain phenomena of environmentally assisted corrosion cracking where either:

- a "classical" mechanism of stress corrosion cracking - e.g. intergranular stress corrosion cracking (IGSCC) of austenitic stainless steels in high temperature (HT-) water - is enhanced by the additional effects of fast neutron irradiation on the governing parameters of material, environment and stress

or

- a susceptibility to stress corrosion cracking is caused solely by the alteration of the corrosion system due to fast neutron irradiation.

IASCC therefore is a global term covering more than one mechanism and a further distinction seems necessary.

This presentation highlights practical examples of operation experience and aspects of both scientific as well as empirical evaluations. A conclusion will be drawn regarding the assessment of currently operating plants.

Microstructural and Microchemical Evolution of Irradiated Materials

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Radiation-induced segregation (RIS) at grain boundaries has received considerable interest over the last decade because of its potential influence on the irradiation-assisted stress corrosion cracking (IASCC) of Fe- and Ni-base stainless alloys.

Segregation mechanisms are driven by the production of defects in the grain matrix and their subsequent migration to grain boundary sinks. Local composition changes occur because specific chemical species interact differently with these defect flows. Inverse-Kirkendal (IK) segregation results from differences in vacancy diffusion rates for alloy elements. Faster diffusing elements, such as Cr and Fe, become depleted at grain boundaries, whereas slower diffusing elements, such as Ni, become enriched. Minor alloying and impurity elements also segregate due to differential binding of solute atoms to self-interstitials. Species that have strong binding, such as Si, become enriched at grain boundaries after irradiation.

This presentation evaluates the current ability to measure and model RIS in Fe-Ni-Cr stainless alloys. The nanometer-scale composition profiles of interest have been most effectively characterized using analytical transmission electron microscopy (ATEM) and scanning Auger microscopy (SAM). Extensive grain boundary composition measurements on materials irradiated by charged particles or neutrons have demonstrated boundary-to-boundary RIS anisotropy, variability along individual boundaries, and the strong effect of irradiation temperature and dose on the interfacial composition. Temperature and dose effects on RIS have been systematically studied using charged-particle irradiations of controlled purity alloys.

Grain boundary composition of Ni and Si increased, while Cr and Fe decreased, with increasing irradiation temperature (constant dose) or dose (constant temperature). No significant enrichment of phosphorus or sulfur is detected even in doped alloys consistent with results on neutron-irradiated steels. The extensive ion-irradiation data base is employed to quantify predictions of both temperature and dose effects. Model predictions are then assessed versus ATEM and SAM measurements on neutron-irradiated stainless steels. Good agreement is documented between measured Fe, Ni and Cr segregation and IK predictions. This is not the case for RIS of minor elements like Si and P, where the interstitial binding model sharply overpredicts measured grain boundary enrichment.

Mechanisms limiting RIS are discussed, and model modifications made, to help quantify predictions. Results of this study are used to determine RIS development in light-water-reactor core components and if grain boundary composition changes play a primary role in IASCC susceptibility.

Fracture Mechanics Aspects in Crack Growth Evaluation of IASCC

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It is generally recognized that an enhanced crack growth in corrosion fatigue, stress corrosion cracking and even SSRT (slow strain rate test) can be uniquely explained by a complex synergistic interaction among materials, environments and mechanics for a given materials/environment system.

The difference in loading modes such as a cyclic load, a monotonic rising load, a constant load and a constant displacement has significant effects on crack tip strain rate which controls both a film rupture frequency at growing crack tip and, subsequently a resultant metal dissolution and/or hydrogen evolution at crack tip. These processes can enhance crack growth either slip dissolution type cracking or hydrogen cracking or mixture both of them.

As has been well recognized, environmentally assisted cracking (EAC) behavior is controlled by so many parameters that it is extremely difficult to examine the effects of all possible relevant parameters by experiments. Hence, extensive efforts have been focused to develop both EAC models for the various material/environment systems and also quantitative prediction methodology based upon the models. Among the models, the slip dissolution model can provide the most feasible and quantitative prediction for some particular cases providing that the necessary data are available and crack tip strain rate can be adequately evaluated for a given condition. Also, an attempt has been made to develop a computer simulation code for environmentally assisted cracking to avoid the ambiguity of crack tip strain rate calculation. This numerical simulator has been successfully applied to evaluate the crack growth rate as a function of K for pressure vessel steels, stainless steels, and also a Ni-base alloy in LWR environments. In spite of the fact of its extreme usefulness, computer simulation codes are used only for a limited cases because, in general, corrosion engineers are not familiar to FEM and mechanics, unfortunately.

In this paper, a purely theoretical formulation was developed for a quantitative prediction of crack growth rate particularly in terms both of a threshold behavior and of a plateau growth rate in the da/dt - K diagram. The formulation was developed based upon the Faraday's equation for metal dissolution and crack tip strain rate for a growing crack in an elastic/plastic work hardening material under either rising load or constant load. The crack tip strain redistribution due to crack advance was taken into consideration in the formulation.

The obtained formulation was solved numerically and the results showed that a threshold K and a plateau growth rate at higher K range were the result of crack tip strain rate dependence upon. Namely, threshold behavior can be explained simply from a view point of crack tip strain rate effects, namely from a mechanics view point. Validation of this formulation for prediction of EAC growth behavior was examined by use of experimental crack growth data for pressure vessel steels, stainless steels and a Ni-base alloy in high temperature water. This formulation was also used to correlate the data obtained by different testing modes such as SSRT and a constant load SCC tests. Finally, the theoretical prediction of crack growth rate as

a function of film rupture frequency was compared with those obtained by a FEM simulation code, FEACS (Finite Element Environmentally Assisted Cracking System) and more extensive research on crack tip solution chemistry is emphasized.

Environmentally assisted cracking behavior in LWR systems was experimentally investigated under different loading modes by use of trapezoidal wave form with a different holding time and at a very slow rising load. Emphasis was focused on the effects of dynamic loading effects on SCC crack growth under constant load in comparison with a theoretical prediction.

Study of Mitigation Strategies for IASCC

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This presentation gives an overview of different approaches to reduce the susceptibility of a system to IASCC. Some of the mitigation strategies addressed have already found application in operating nuclear power plants, while the use of other methods is prospective.

Since IASCC results from a synergistic interaction between mechanical stress, material, and hot water (each under influence of irradiation), either of these three levels offer possibilities for mitigation. Acting on the level of mechanical stresses, however, is a little attractive mitigation strategy. The reduction of stresses and stress intensities in plant components should decrease susceptibility, but is hard to achieve in existing plants.

The development of more resistant materials has received more attention. The improvement of manufacturing and pre-treatment procedures, as well as innovative alloying could lead to mitigation. One example of this is a new high nickel, high chromium and high purity alloy, subjected to a special treatment to obtain a higher resistance to IASCC. New alloying can also focus on reducing the amount of radiation-induced segregation. An example of this approach is the addition to the metal of oversized elements such as Hf, Zr or Ti which pin down point defects. This reduces the driving force for segregation. Finally, a prospective approach for mitigation through material changes is to improve the performance of passive films by alloying. Little attention has been paid to possible improvements of the repassivation behaviour or mechanical stability of oxides by adding specific chemical elements to the metal.

The third level for mitigation is through the environment, i.e. via changes in the reactor water. This obviously is the most effective route for mitigation in operating nuclear power plants. Therefore, there is a continuous effort into optimising water chemistry guidelines in order to obtain a maximum mitigation of corrosion. Of course these guidelines need to respect considerations for fuel integrity and activity build-up.

In this frame, the application of Hydrogen Water Chemistry and Noble Metal Chemistry in Boiling Water Reactors probably are the best known mitigation strategies. Both techniques aim at reducing oxygen and other oxidising components in the reactor core water to lower corrosion potentials.

Alternatively, mitigation can result from modifications of the passive films on structural components achieved by injection of chemicals into the water. The incorporation of these chemicals into the existing oxides should improve their performance in protecting the material. An interesting example of this approach is the injection of zinc compounds. The uptake of zinc into the oxides does not only seem to lead to a lower build-up of activity in these oxides, but could also have a positive effect on the strength of these surface films. Apart from zinc, little is known about the possible effects of other chemical elements on passive films.

Finally, another prospective mitigation strategy is the in-situ application of dielectric coatings on component surfaces. The presence of a surface layer with high electric resistance would eliminate the electrical path between material bulk and water. This would seriously impede the chain of electrochemical reactions that occur when a crack grows. Furthermore, these coatings would restrict mass transport of oxidants to the underlying metal and thus induce lower corrosion potentials. Zirconium oxide appears to be a good candidate to form such dielectric coating, since it associates a good stability in hot water with a low electrical conductivity. Thermal spray coating or (electro-)deposition from solution are possible techniques to apply this zirconia coating. There remains a lot of work to prove the feasibility of this mitigation strategy, though initial results from different researchers seem to show good perspectives.

Application of Electrochemical Impedance Spectroscopy for Monitoring of SCC-Cracks

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With Electrochemical Impedance Spectroscopy (EIS) a small sinusoidal (potential) perturbation of a certain frequency is used to distort an electrochemical system. The (current) response is measured and the modulus ($|E/i|$) and phase shift of the impedance are determined¹⁻³. A particular characteristic of EIS is that a reference electrode is not needed to perform the measurements. This makes application under severe conditions (aqueous solutions at high temperatures and pressure, like in Nuclear Power Plants) possible, where a reference electrode is difficult to use. EIS has hardly been used for the investigation of Stress Corrosion Cracking (SCC), but has potential of detecting surface inhomogeneities related to stress corrosion cracks.^{4,5} Also there are not many techniques available that are suited for stress corrosion detection. Therefore it seems worthwhile to investigate if EIS can be used for SCC monitoring.

First a model was developed that described the impedance response of a cracked surface, i.e. the model could distinguish between a flat electrode surface and a surface with cracks. Figure 1 shows the equivalent circuit of this crack model for a single crack.

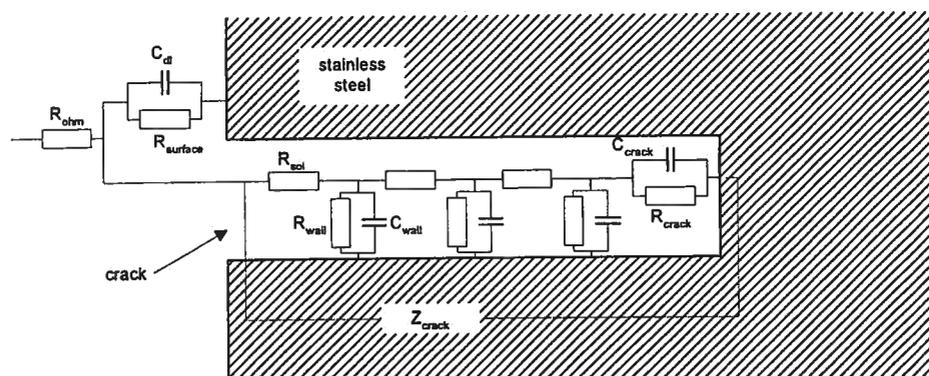


Figure 1: Equivalent circuit of a crack model

Experiments with stainless steel electrodes with artificial "cracks" (electrically drilled small holes) in 0.1 M Na_2SO_4 showed that the influence of the artificial "cracks" on the impedance response was mainly reflected in the phase shift at frequencies between 100 and 1 Hz. To generate real stress corrosion cracks, Slow Strain Rate Tests (SSRT) were performed with sensitised SS 304 specimen in a 5 N H_2SO_4 + 0.1 M NaCl solution at room temperature. Analysis of the fracture surface clearly shows intergranular fracture, suggesting that stress corrosion cracks were formed (see Figure 2).

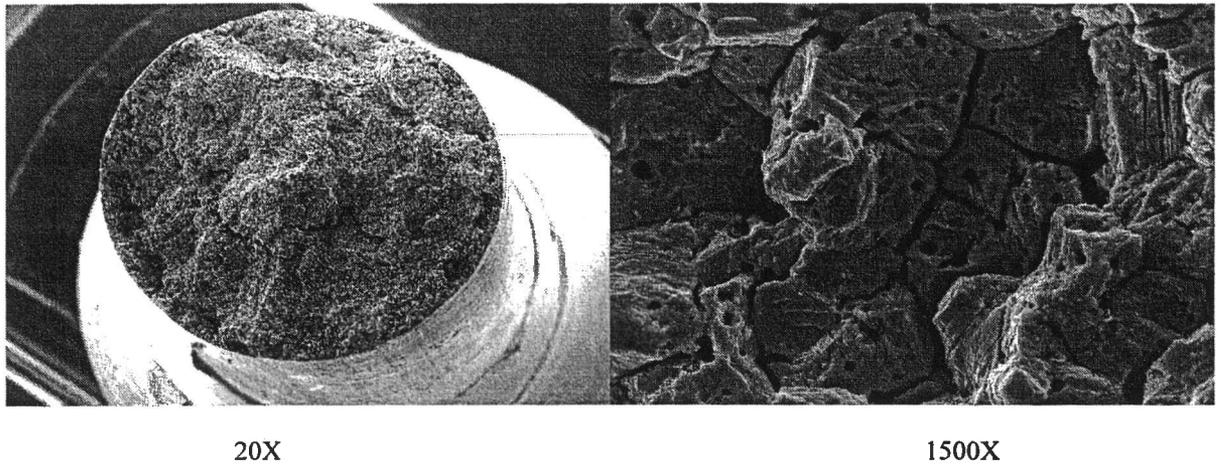


Figure 2: SEM photographs after SSRT tests of sensitised SS 304 in a 5 N H₂SO₄ + 0.1 M NaCl solution

Impedance measurements were performed twice an hour during experiments with stress (SSRT) and without stress. Phase shifts at frequencies 100 and 10 Hz showed a clear difference between the results with stress and without stress suggesting that stress corrosion cracks were detected by the impedance measurements.

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