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Steven Van Dyck

# Reactor Structure Materials: Corrosion of Reactor Core Internals

**Scientific Staff**
Rik-Wouter Bosch,
Pascal Boydens (PhD Candidate),
Ludo Eysermans,
Serguei Gavrilov (PhD Candidate),
Steven Van Dyck,
Marc Vankeerberghen,
Rudi Van Nieuwenhove,
Eric van Walle

## Background

The long-term irradiation of reactor core internals leads to changes in the microstructure and properties of the materials. Due to these changes, the originally corrosion resistant alloys, typically stainless steels and nickel based alloys, may become sensitive to stress corrosion cracking. The assessment of the Irradiation Assisted Stress Corrosion Cracking (IASCC) phenomenon has become an integral art of plant life management. The IASCC phenomenon results from an interaction between irradiation damage in the material, water chemistry changes and component stress. The interaction between these parameters calls for a multidisciplinary scientific approach, while also providing answers to the needs of industrial partners. The SCK•CEN research program on IASCC is embedded in the SCK•CEN research on reactor materials and interacts with several international organisations.

## Objectives

- to gain mechanistic insight into the IASCC phenomenon by studying the influence of separate parameters in well controlled experiments;
- to develop and validate a predictive capability on IASCC by model description; this model should assist the extrapolation of laboratory results to industrial practice;
- to define and validate countermeasures and monitoring techniques for application in reactors; these sensors should have a long life time under the reactor conditions and work in a non-destructive way.

## Programme

### *The IASCC research programme is focussed on four fields:*

- Gaining mechanistic insight into the IASCC phenomenon by modelling the interaction between environment, stress, material and irradiation. Theoretical and experimental insights will be integrated in a model, which should lead to prediction of IASCC in PWR components.
- Generate a well-documented set of relevant experimental data. Experimental data will be produced for validation of the modelling results and for comparison with literature data. Although many data are available today, comparison between data sets is difficult due to incomplete characterisation or lack of independent variation of key variables.
- Develop a set of instruments to monitor the corrosion process on-line in a reactor. These instruments are required to capture data during the irradiation experiments and should help to evaluate the countermeasures resulting from the mitigation strategy developed within this project.
- Define and test effective countermeasures for IASCC: mitigation of IASCC is envisaged for existing components by coating or water chemistry changes, while for new components, more resistant materials should be developed.

## Achievements

### *Modelling*

During 1999 the numerical simulation of corrosion has advanced with the further development and application of a computational electrochemistry code, ELEMD, in collaboration with the TW-ETEC department of VUB, Elsyca N.V. and Von Karmann Institute

The ELEMD code was extended for the calculation of corrosion systems containing homogeneous reactions. Implementation and verification have been completed and preliminary calculations for the polarisation behaviour of a metal in an aqueous solution including homogeneous reactions have been performed.

The calculation of the polarisation behaviour of a metal in an aqueous solution using the dilute solution model. The corrosion system consisted of three parallel reactions (oxygen reduction, hydrogen evolution and metal dissolution), taking place in the centre at the surface of a rotating disc electrode (RDE). The analytical and numerical calculations were in excellent agreement. The influence of the speed of the RDE and of the bulk dissolved oxygen and hydrogen ion concentrations on the polarisation behaviour have been calculated. In the computational approach migration was taken into account and no prior assumption on the diffusion layer thickness was made. This diffusion layer thickness was calculated, with good agreement between numerical and analytical calculation. The computational approach is more general and flexible. This application is but a first step towards the numerical simulation of stress corrosion cracking.

The calculation of the current density distribution and the potential around the tip of a flow-through reference electrode, to support the development of this new type of reference electrode (see below).

Calculations to support the experimentally identified influence of conducting walls on electrochemical measurements.

## Experiments

The irradiation of the CORIOLIS (Corrosion Irradiation Off-Line for assessment of IASCC Susceptibility) experiment was finished and the experiment was retrieved from the BR2 reactor at the end of 1999. The design of the CORONA experiment (Corrosion Research Online Assembly) was finalised; it will enter the reactor in 2000. The CORONA experiment is instrumented, so on-line monitoring of the corrosion process by electrochemical noise will be possible. This technique was demonstrated in the cold laboratory (see instruments).

A number of SSRT (slow strain rate tensile) tests has been performed on steam generator alloys in representative secondary water chemistry conditions. These tests support the replacement of alloy 600 by alloy 650 in several aggressive environments.

### *Instruments*

To monitor the corrosion processes at Pressurised Water Reactor (PWR) relevant conditions, several instruments have been developed within SCK•CEN:

- Development of a high temperature reference electrode: the corrosion process of a metal in an aqueous environment is reflected by its corrosion potential i.e. the corrosion potential can distinguish between active, passive or localised corrosion (like for example stress corrosion cracking). Such corrosion potential measurements require a reference electrode with a stable and reproducible potential. At high temperatures and high pressures problems occur with the lifetime and stability of the reference electrode. Under PWR-conditions additional complications arise with material stability due to irradiation. This research is focused on the development of a reference electrode that could be used under PWR conditions. Three types were investigated: the cathodically charged palladium reference electrode, the external pressure balanced silver/silver chloride reference electrode (EPBRE), and a new type of flow-through reference electrode (FTRE). Results to date show that the EPBRE and the FTRE can be used successfully under laboratory conditions.
- A flow through reference electrode has been developed which can work under PWR conditions with an accuracy of ± 15 mV. The FTRE has a number of clear advantages: 1) simple robust design 2) no maintenance 3) good accuracy 4) no leakage of harmful substances (e.g. KCl) into the loop water. Due to its small and flexible design, the tip of the FTRE can be positioned very close to the sample under investigation. One could even perform very local measurements near the crack region of a compact tension specimen. The FTRE could also be used for measurements on radioactive specimen in a hot cell, provided the tube with the heat-shrinkable PTFE (which is radiation sensitive) is replaced every few months.
- Stress Corrosion Cracking (SCC) detection with Electrochemical Impedance Spectroscopy (EIS): this in-situ electrochemical test method is, in principle, able to detect stress corrosion cracks. A specific advantage of this technique is that a reference electrode is not required to perform the measurements. Results with an experimental test set-up, where stress corrosion cracks were generated in sensitised stainless steel 304 in a Slow Strain Rate Test, showed that with EIS stress corrosion cracks can be monitored. Further research is dedicated to the detection of stress corrosion cracks in aqueous systems at high temperatures and pressures.
- Electrochemical noise measurements under PWR conditions: the feasibility of Electro Chemical noise (ECN) to detect cracking in PWR environment has been demonstrated in the cold lab with sensitised stainless steel samples, loaded above their yield strength to accelerate cracking. Sharp ECN spikes are clearly discernible, but up till now, no direct link between a specific crack and a specific ECN signal can be made (it may be possible to obtain spatial resolution with ECN, but the more complex sensors and data analysis would be necessary). It should be noted, however, that the design of the ECN sensor is very important, in order to achieve a sufficiently short response time in order to detect the short spikes (order of 1 second).
- Crack growth measurements by the DC reversing potential drop method on CT specimen: the method has been optimised for use in autoclave conditions.
- Acoustic emission (AE) detection of stress corrosion cracking in high-temperature water: This technique is applied for example during SSRT tests, where the pull rod of the installation is used as a waveguide, so no instrumentation is needed inside the SSRT autoclave. In principle, AE

measurements are also possible directly on the sample, but this requires the use of special heat-resistant sensors (e.g. strontium niobate) and signal cable transmission through the autoclave. The main difficulty, as in the case of ECN, is to relate the signals to physical events such as plastic deformation, crack initiation and propagation and general corrosion. The use of complementary techniques may be required to obtain a relationship between a certain signal pattern and the physical phenomena involved. Indeed, by combining AE and EIS it was possible to identify acoustic emission events as crack initiation events. Several measures (enhanced filtering techniques, better grounding, etc..) have been taken to enhance the sensitivity and reliability of the AE measurements and routine laboratory measurements with AE can now be performed on samples with various geometries (cylindrical, compact tension, etc..).

## Mitigation

The study of the application of dielectric zirconia coatings as a countermeasure for IASCC was continued in 1999. The feasibility study of the in-situ application of thin zirconia layers on reactor components was completed with promising results. In order to elucidate the mechanism of mitigation, the electrochemical response of zirconia coatings on stainless steel in high temperature water was further examined. Slow strain rate testing and constant load testing of coated specimens was prepared and will be the subject of continuing work.

## Partners, sponsors and customers

### Scientific partners

KUL — Katholieke Universiteit Leuven, dept. Metaalkunde & Toegepaste Materiaalkunde (Leuven, Belgium): STWW project (IWT) & joint PhD studies

VUB — Vrije Universiteit Brussel, dept. Metallurgie, Elektrochemie en Materialenkennis (Brussels, Belgium): STWW project (IWT) & joint PhD studies

Laborelec — (Linkebeek, Belgium): Consortium agreement for participation in EPRI-CIR & Westinghouse programmes

EPRI — Electric Power Research Institute (Palo Alto, Ca, USA): CIR (Co-operative IASCC Research programme).

HRP — Halden Reactor Project (Halden, Norway)

JAERI — Japan Atomic Energy Research Institute (Tokai-mura, Japan); informal exchanges of staff (4 week visit to corrosion research group in 1999).

VKI — Von Karmann Institute

### Sponsor

TEE — Tractebel Energy Engineering (Brussels, Belgium): Consortium agreement for participation in EPRi-CIR & Westinghouse programmes; Convention for joint research programme.

## Scientific output

### Publications

R. VAN NIEUWENHOVE, "Development of new instruments and detection methods for the study of Irradiation Assisted Stress Corrosion Cracking of structural components of ITER", Annual Report for the Steering Committee of the Association Euratom-Belgian State for Fusion 1999, BLG-833.

S. VAN DYCK, "Irradiation assisted stress corrosion cracking in LWR Core Internals" BLG 814

R-W. BOSCH, P. BOYDENS, M. VANKEERBERGHEN, R. VAN NIEUWENHOVE, S. VAN DYCK "State of the art report on the materials testing capabilities for IASCC susceptibility testing at SCK•CEN",BLG 824, August 1999.

R. VAN NIEUWENHOVE, "Electrochemical Noise Measurements under PWR conditions", journal CORROSION, (2000), in press

R. VAN NIEUWENHOVE, R-W. BOSCH, S. GAVRILOV, M. VANKEERBERGHEN, S. VAN DYCK, L. EYSERMANS, "Development of a flow-through reference electrode for PWR conditions", EUROCORR 2000, September 10-14, 1999, London.

R. VAN NIEUWENHOVE, R-W. BOSCH, "Acoustic Emission Detection during Stress Corrosion Cracking at elevated pressure and temperature", EWGAE 2000, 24 th European Conference on Acoustic Emission Testing, May 24–26, 2000, Senile, France

### Presentations

R-W. Bosch, F. Moons, J.H. Zheng, W.F. Bogaerts, "Application of Electrochemical Impedance Spectroscopy for Monitoring of SCC-Cracks", CORROSION 99, 54th Annual Corrosion Conference of the NACE, San Antonio, April 1999.

R-W. BOSCH, "Investigation of stress corrosion cracking at elevated temperatures with electrochemical impedance spectroscopy, EUROCORR 99, Aachen, Germany 1999.

R-W. BOSCH, "Investigation of the influence of an external applied AC-signal on the corrosion rate of a corrosion system under various controll modes like: activation, diffusion and mixed control", presentatie voor de Studiekern Corrosie, De Sectie Corrosie van de Bond voor Materialenkennis, Arnhem (KEMA), January 27, 1999.

R-W. Bosch, "Development of a new electrochemical technique for on-line corrosion monitoring: Electrochemical Frequency Modulation (EFM)", Studiekern Corrosie, section Corrosion, Bond voor Materialenkennis, Utrecht (NL), September 29.

R. VAN NIEUWENHOVE, "Electrochemical Noise Measurements under PWR conditions, WACOL (High Temperature On-Line Monitoring of Water Chemistry and Corrosion)", Helsinki, June 7-10, 1999.

S. VAN DYCK, "Irradiation assisted stress corrosion cracking in LWR Core Internals", Cursus Nucleaire Corrosie, prof. W. Bogaerts, KU Leuven, specialisatieopleiding nucleaire techniek.

S. VAN DYCK, "Corrosion Research at SCK•CEN", Presented at JAERI, Tokai laboratories, December 9, 1999.