LCC8 ANNUAL REPORT

Key Emerging Issues and Recent Progress Related to Structural Materials Degradation
Key Emerging Issues and Recent Progress Relating to Structural Materials Degradation

Authors

Pierre Combrade
Le Bessat, France

Peter Ford
Rexford, New York, USA

Peter Scott
Noisy Le Roi, France
Disclaimer

The information presented in this report has been compiled and analysed by Advanced Nuclear Technology International Europe AB (ANT International®) and its subcontractors. ANT International has exercised due diligence in this work, but does not warrant the accuracy or completeness of the information. ANT International does not assume any responsibility for any consequences as a result of the use of the information for any party, except a warranty for reasonable technical skill, which is limited to the amount paid for this assignment by each LCC programme member.
Contents

1 Introduction 1-1

2 Materials degradation in boiling water reactors (Peter Ford) 2-1

2.1 Carbon & low alloy steels 2-2
  2.1.1 SCC at dissimilar metal welds 2-3
  2.1.2 Effects of impurities on SCC susceptibility of low alloy steel 2-5

2.2 Stainless steels 2-7
  2.2.1 SCC initiation in non-irradiated stainless steels 2-8
  2.2.2 SCC propagation in non-irradiated stainless steels 2-17
  2.2.3 Irradiation Assisted Stress Corrosion Cracking (IASCC) 2-29

2.3 Nickel-base alloys 2-36
  2.3.1 Ductile nickel base alloys 2-37
  2.3.2 High-strength nickel-base alloys 2-38

2.4 Mitigation of environmentally assisted cracking 2-41
  2.4.1 Water chemistry control 2-42
  2.4.2 Coating technology 2-49

3 Materials degradation in pressurised water reactors (Peter Scott & Pierre Combrade) 3-1

3.1 Carbon & low alloy steels 3-1
  3.1.1 Flow-assisted corrosion (FAC) 3-1
  3.1.2 Irradiation effects 3-12

3.2 Stainless steels 3-12
  3.2.1 Field experience 3-12
  3.2.2 Stress corrosion of non-irradiated stainless steels in PWR primary water 3-15
  3.2.3 Stainless steels in chloride environments 3-23
  3.2.4 Irradiation effects and irradiation-assisted stress corrosion cracking 3-24

3.3 Nickel-base alloys 3-31
  3.3.1 Cation release 3-31
  3.3.2 IGSCC in primary PWR coolant 3-33
  3.3.3 Alloy 690 and associated weld metals 3-49
  3.3.4 Oxidation and PWSCC mechanisms 3-54
  3.3.5 Low temperature crack propagation 3-68
  3.3.6 Secondary side degradation of steam generator tubing 3-69

4 Corrosion fatigue crack initiation and propagation (Peter Ford) 4-1

5 References 5-1

Nomenclature

Unit conversion
1 Introduction

The aim of this report is to describe any new emerging issues and recent progress relating to environmental degradation of structural materials used for the pressure boundaries and internal static components of BWRs and PWRs. It builds on a similar previous exercise in 2010 [Combrade et al, 2010] as well as previous extensive reviews of environmental degradation of carbon and low-alloy steels, stainless steels, and nickel-base alloys by the present authors [Ford & Scott, 2008], [Ford et al, 2010], [Scott et al, 2011]. The present report is divided into two large sections devoted to BWRs and PWRs, with each section using, where possible, the same or similar sub-headings from those detailed reviews for the various technical topics in order to facilitate easy reference to the appropriate background information.

The main source of information reviewed for the present report is the 15th International Conference on Environmental Degradation Materials in Nuclear Power Systems - Water Reactors that was held August 7-11, 2011, in Colorado Springs. This is complemented by specific articles from appropriate technical journals published during the last two years or so.

Among the sessions at the 15th International Conference on Environmental Degradation Materials in Nuclear Power Systems - Water Reactors, one concentrated on the general theme of degradation management in light water reactors with more emphasis in fact on PWRs. One of the papers addressed the collection and analysis of data on operationally induced damage to mechanical components between 1970 and 2010 in the Swedish reactor fleet comprising seven BWRs and three PWRs [Gott, 2011]. Analysis of the reported degradation mechanisms revealed the breakdown shown in Figure 1-1 where it is compared with a similar analysis of the French fleet of 58 PWRs [Le Calvar, 2010].

Figure 1-1: Comparison of the breakdown of major failure degradation mechanisms in (a) Swedish nuclear power plants (7 BWRs and 3 PWRs) between 1970 and 2010 [Gott, 2011] and, (b) the French PWR fleet [Le Calvar, 2010].
It can be seen that flow-assisted corrosion (FAC) of carbon steels is a dominant mechanism of degradation in both of these studies. However, the Swedish paper emphasized the need for consistent reporting of this particular degradation phenomenon, which in their case now includes data for when FAC was first suspected as well as when the affected component was replaced, the former parameter possibly including some abnormal as-fabricated variations in pipe wall thicknesses. Cracking by SCC and fatigue were second in importance in the frequency of degradation, the Swedish figures probably including a sizeable proportion of incidents with stainless steels in BWRs. SCC seems to be relatively minor in the French PWR statistics but it was highlighted as highly generic and having a large impact on safety because it appears in the second containment barrier. The Swedish statistics also show that mitigation measures for SCC have been relatively successful in that their frequency appears to be declining somewhat in recent years. The development of larger international databases for component degradation in LWRs, their importance for trend analyses, development of defence in depth against pressure boundary failures, potential applications in probabilistic fracture mechanics codes and risk informed aging management applications were all emphasized in the Swedish paper.

In addition to this general theme categorizing the various degradation modes in terms of their frequency, attention was given at the 15th International Conference on Environmental Degradation Materials in Nuclear Power Systems to recent activities associated with regulatory actions. For example, Carpenter and colleagues at the USNRC [Carpenter et al, 2011], described advances from an earlier USNRC Proactive Materials Degradation Assessment (PMDA) of various degradation modes in more than 2000 components of the primary, secondary and tertiary systems in BWRs and a similar number in PWRs [Muscara, 2007]. These advances concentrated on: (a) an expansion of the components needing management to include concrete containments, irradiation embrittlement, and cable insulation; and (b) an expansion of the time frame of interest to 80 years or more. The approach taken for this expanded Proactive Management of Materials Degradation (PMMD) development involved two steps; first to identify the components of interest that might undergo future degradation over and above those identified in the initial PMDA and; second to identify the technical gaps. Inevitably such management may involve new regulatory approaches, such as the development of probabilistic risk assessments and the regulatory approval of detection and monitoring, and mitigation and repair procedures. The breadth of the scope of this approach suggests the value of collaborative research activities with the nuclear power industry (e.g. the Electric Power Research Institute), Department of Energy and the National Laboratories in the USA, and internationally (e.g. International Atomic Energy Agency, IAEA; Organization of Economic Co-operation, OECD; the Materials Aging Institute, MAI; etc.

In an associated paper [Ekstrom et al, 2011]; the regulatory conditions imposed in Sweden for long-term operations of nuclear power plants were discussed. At the present time there is no time limit to the operating licensees for the ten LWRs in Sweden and such operation can continue as long as the Swedish Radiation Safety Authority (SSM) considers them sound and safe. This judgment is based on adherence to an approved aging management programme and a comprehensive plant safety review (PSR) at least every ten years. This PSR takes into account the evolving knowledge and incidences of materials degradation that accrue internationally. Examples of such current materials degradation concern meriting regulatory attention include:

- Radiation embrittlement of low alloy steel pressure vessels, especially at welds at the high flux beltline region.

- Low cycle environmental fatigue and especially austenitic alloys in operating primary water chemistries in PWRs and hydrogen water chemistries in BWRs.

- Thermal aging embrittlement of cast austenitic components and stainless steel weldments that contain significant amounts of δ phase. In the normal situation, the presence of this δ phase is beneficial in that it improves weldability and/or castability, and increases resistance to stress corrosion cracking. However there is an unresolved concern about embrittlement at long operational times due to spinodal decomposition of the ferrite phase to form a chromium-rich α' phase.
Key Emerging Issues and Recent Progress Relating to Structural Materials Degradation

- Stress corrosion cracking of stainless steels and nickel-base alloys. Although this degradation mode has been widely investigated and mitigation actions based on control of the water chemistry, material and stress conditions have been developed and deployed internationally in both BWRs and PWRs, isolated incidents of continued cracking have been observed, even in so-called “mitigated systems”.

- Flow accelerated corrosion

Two additional overview papers of aging related degradation in LWR structural materials published since the 15th International Conference on Environmental Degradation Materials in Nuclear Power Systems merit review.

A general review of stress corrosion cracking in commercial LWRs has been recently published summarizing the history of materials degradation and highlighting where in the opinion of the author future degradation mechanisms might occur, particularly in the context of plant life extension beyond 40 years [Andresen, 2012]. Emerging generic concerns were listed as follows:

- Chloride effects on low alloy steels where extremely low ppb level concentrations of chloride can greatly accelerate stress corrosion crack growth.

- Electrolytic ‘crack flanking’ where noble metals injected into BWRs to catalyze hydrogen/oxygen recombination must penetrate a crack as far as any dissolved oxygen can reach for the noble metal to be effective and how this condition may no longer be satisfied when cracks grow rapidly or flow rate is increased.

- Oxygen ingress into PWR (and CANDU) primary coolant systems where an increasing fraction of PWRs no longer use de-aerated make-up water.

- Weld residual stress and cold work orientation effects such that if the plane of deformation and cracking coincide, significantly higher SCC growth rates result.

- dK/da effects where K increases rapidly when the crack is small (because K is proportional to $\sqrt{a}$, where ‘a’ is the crack depth) and can accelerate crack growth (at dK/da levels relevant to plant components) by as much as two or three orders of magnitude.

- Aqueous environmental effects on fracture resistance, i.e. apparent fracture toughness and tearing resistance.

- Synergies between different aging mechanisms.

It was concluded that despite the many improvements that have been implemented in materials and designs, achieving plant lives of 60 to 80+ years will require continued innovation and multiple forms of mitigation together with avoidance of over-optimism that single improvements will provide adequate protection against SCC. Declining levels of corrosion expertise and funding and historical conservatism were cited as aggravating factors.

The second of these two recently published general papers focused on degradation mechanisms unrelated to environmentally-assisted cracking, namely general corrosion of LWR carbon steel containments, flow accelerated corrosion of carbon steel piping systems, and corrosion of buried piping [Gordon, 2012]. LWR containments are airtight steel structures that may be free-standing or attached to the concrete containment building. Cases of severe localized corrosion were described, sometimes leading to bulging of the liner. The more serious tend to occur in gaps between steel liners and concrete buildings due to adventitious presence of trapped water and impurities from materials and foreign objects (often organic) left due to poor housekeeping at the time of construction. Flow accelerated corrosion is reviewed in detail in Section 3.1.1 and is not developed further here. Degradation of the kilometres of buried steel piping found at every LWR, often with difficult access for inspection and maintenance, is presently a significant issue for plant operators. Corrosion can occur from both sides of the pipe wall in this case. Examples of pitting, microbiological corrosion, fouling obstructing flow, cavitation (typically downstream of butterfly valves), and pipe collapse due to metal loss and mechanical loading were all cited.
2 Materials degradation in boiling water reactors (Peter Ford)

Environmentally assisted degradation of materials of construction in Boiling Water Reactors has been observed for decades. The dominant degradation modes, such as pitting, flow-accelerated corrosion, environmentally-assisted cracking, (EAC), may vary in frequency depending on: alloy composition fabrication conditions; microstructure; mechanical properties; reactor type and coolant chemistry and; power mode. The effect of the material and system conditions on structural integrity has been discussed in general, [Ford, 2006] and in detail in several ANT International Annual Reports and separate Special Topical Reports for carbon- and low-alloy steels [Ford & Scott. 2008], stainless steels [Ford et al, 2010] and nickel-base alloys [Scott et al, 2011], with occasional updates [Combrade et al, 2010].

Mitigation actions and aging management programmes for BWRs have been developed to deal with these materials degradation issues. However, isolated incidents continue to occur, even in “mitigated” systems, and this may be attributed to the complex interactions between the relevant stress, environment and material conditions. This situation has been exacerbated by the reactive management approach that limits the time available to define fully the mitigation actions, (Figure 2-1).

![Figure 2-1: Comparison between reactive and proactive management methodologies for addressing materials degradation issues. Note that, in the reactive management approach, action is not taken until the problem has been detected and this leads to a limited time (denoted in yellow) for developing mitigation actions before a structural integrity limit is reached. However, there would be a relaxation (denoted in green) in that time limitation if there were a prediction algorithm for the relevant degradation mode that foresees potential problems in the future.]

Consequently, in the last few years attention [Muscara, 2007], [Pathania, 2008] has focussed on the development of proactive management capabilities for the major degradation modes, whereby degradation events, which are not detectable currently, may be predicted to occur sometime in the future. Such capabilities would allow for timely decisions associated with, for instance, pre-emptive material replacement, the definition of more effective inspection techniques and schedules, and alterations to, for example, the water chemistry specifications.

The life prediction capabilities that are central to a proactive management approach, may be developed via an amalgamation of knowledge of, (a) the details of past plant incidents, (b) knowledge of the sensitivity of such degradation events to changes in the system conditions (material, environment, etc.), and (c), an adequate understanding of the fundamental mechanism of the specific materials degradation mode. These developments have also been discussed in the ANT International reports referenced above.
In the last few years such proactive developments have focussed primarily on continuing incidents of stress corrosion cracking in BWRs, especially those occurring under conditions of irradiation or of local strain localization. Such aggravating factors have been recognized for some time, but, uncertainty remains regarding the early stages of crack initiation and the subsequent short crack propagation. This is especially the case at regions of complex microstructural and residual stress detail associated with dissimilar metal weld interfaces.

Other degradation modes continue to give rise for concern, including flow accelerated corrosion of carbon-steels in both BWRs and PWRs. This subject has been discussed in other reports [Ford & Scott, 2008], [Combrade et al, 2010], and is updated in Section 3.1.1 of this report.

Although mitigation actions have been developed and have led to satisfactory decreases in cracking frequency, uncertainty regarding some aspects of crack initiation and propagation has led to on-going re-evaluations of the mitigation actions.

This section concentrates on recent advances in understanding and managing environmentally-assisted cracking in BWRs that have been reported upon at the 15th Biannual Conference on "Environmental Degradation of Materials in Materials in Nuclear Power Systems-Water Reactors' held at Colorado Springs, August, 2011, plus some additional papers from learned journals. The number of papers is significant and sufficient to give a balanced view of advances that have been made since the last assessment in 2010 [Combrade et al, 2010].

2.1 Carbon & low alloy steels

There is sufficient theoretical and experimental knowledge to (a), understand why SCC of carbon-and low-alloy steels is a relatively rare occurrence in BWRs, and to (b), define the material, environment and stressing conditions under which a limited amount of SCC has occurred in operating plant. If these conjoint conditions cannot be maintained then crack propagation will arrest.

There are two SCC phenomena of current concern for carbon and low alloy steels in BWRs. The first is the possibility that a stress corrosion crack, actively propagating in an Alloy 182 weldment, may continue to propagate into the underlying low alloy pressure vessel. Such a scenario might occur in subassemblies such as core spray brackets (Figure 2-2), control rod drive penetrations through the reactor bottom head, and weldments (such as H-9) attaching the core shroud subassembly to the reactor pressure vessel. The other concern is the anionic impurity concentration that could facilitate such a SCC advance at unacceptable rates.

![Figure 2-2: Typical dissimilar metal weld configuration of a BWR core spray bracket attachment.](image-url)
2.1.1 SCC at dissimilar metal welds

Five papers have been published recently [Seifert & Ritter, 2008], [Kubo et al, 2009], [Kumagai et al, 2009], [Peng et al, 2010] and [Ritter et al, 2010] that address the continuing crack propagation from an Alloy 182 attachment weld into the underlying low alloy steel pressure vessel steel. Such welds are associated with the core shroud support in various BWR designs which are hard to inspect and expensive to replace or repair.

All four investigations used similar experimental approaches to the investigation and came to similar conclusions, namely:

- High hardness values were observed in the dilution zone adjacent to the fusion boundary, indicative of high residual stress [Peng et al, 2010] and [Ritter et al, 2010].

- All stress corrosion cracks in Alloy 182 in high purity 288°C water arrested at or near to the weld fusion line when the stress intensity factor was below 60 MPa√m [Ritter et al, 2010]. At that point the crack tip blunted into a pit or an oxide-plugged crack (Figure 2-3a). However, these arrested cracks could be reactivated from the pit in 2 ppm oxygenated water with an increase in sulphate to 20 ppb or in 0.25 ppm oxygenated water with an increase in sulphate to 400 ppb (Figure 2-3b), [Peng et al, 2010].

More recently Abe and colleagues [Abe et al, 2011] have expanded on these earlier findings. In their case, tests were conducted on Creviced Bent Beam (CBB) specimens such that the propagating crack in the Alloy 182 impinged on the fusion boundary between the nickel-base alloy and the A533B low-alloy steel. It should be noted that in these experiments the bulk 288°C environment was unusually severe (8 ppm O₂, 1 ppm Na₂SO₄, or 680 ppb SO₄²⁻) quite apart from the concentrating effect of the crevice.

Figure 2-3: Arrested crack at, or near to the interface of Alloy 182 weld and low alloy steel [Kubo et al, 2009], (a) [Peng et al, 2010] and (b) [Ritter et al, 2010].

1 It should be noted that under normal operating conditions BWRs operate currently with <5 ppb sulphate impurity levels.
As noted in the earlier investigations, there was an increase in hardness adjacent to the fusion boundary, which was attributed to a mixture of strain localization due to weld contraction, and to the formation of a carbide or “martensite-like” microstructure in the dilution zone. Again, in agreement with the earlier investigations, the sharp crack in the Alloy 182 arrested as the crack passed through the fusion boundary into the low alloy steel (Figure 2-4a), taking on the morphology of a blunt pit (Figure 2-4b). Again, as noted earlier [Ritter et al, 2010], there was the tendency in this very aggressive environment for the reactivation of a sharp oxide filled crack, especially after extended exposure times.

It was hypothesized that the intergranular nature of this reactivated crack down the prior austenite grain boundary in the low alloy steel and/or the fusion boundary (Figure 2-5) indicated the requirement of a continuity between the trajectory of the interdendritic crack in the Alloy 182 weld metal and position of the prior austenitic grain boundaries in the low alloy steel. It is theorized that the reactivation (re-initiation) and continued propagation of SCC in such complex dissimilar metal subassemblies should be a function of the material (i.e. S, P compositions in prior austenite grain boundaries of the low alloy steel), fabrication details (weld procedures and temperature/time combinations) and, as discussed in the next section, the environmental conditions.

Figure 2-4: Cross sectional view of low alloy steel bulk specimens after 1500 hour CBB exposure [Abe et al, 2011], illustrating (a) the formation of a blunt pit in the low alloy steel, and (b) a reactivated crack initiated after 1500 hours (but not 750 hours) and propagating down a prior austenite grain boundary.

Figure 2-5: (a) Back scattered electron image of typical cracks forming in the low alloy steel along prior austenite grain boundaries and the fusion boundary, (b) illustration of interdendritic morphology of cracks in Alloy 182 weld metal, the formation of a spherical pit in the low alloy steel and the reactivation of the crack down microstructural features, possibly prior austenite grain boundaries [Abe et al, 2011].
2.1.2 Effects of impurities on SCC susceptibility of low alloy steel

As might be expected, there are combinations of stress intensity and sulphate concentration that lead to sustained crack growth as the crack advances from an Alloy 182 weldment into A533B low alloy steel. Proposed combinations of stress intensity factor and sulphate concentration that would sustain crack propagation in the low alloy steel at rates >1x 10^{-8} \text{ mm/s} are shown in Figure 2-6a. The corresponding threshold combinations for chloride concentrations are given in Figure 2-6b, [Kumagai et al, 2009]. Very similar threshold conditions for chloride were observed by Ritter and his colleagues [Ritter et al, 2010] (Figure 2-7). It is noted that these threshold combinations are similar to those observed in SCC tests where the starter crack is introduced by cyclic loading. In other words, the fact that the “starter crack” is provided by a crack in Alloy 182 does not introduce a complicating factor, such as a galvanic effect.

It is apparent from comparisons of Figure 2-6a, Figure 2-6b and Figure 2-7 that chloride impurities are more deleterious than sulphate anions, to the point that very low chloride concentrations in the bulk environment, of the order of 5 ppb Cl\textsuperscript{-} may, depending on the stress intensity factor, give sustained propagation into the low alloy steel\textsuperscript{2}. This is to be expected based on the separate SCC investigations by Seifert and Ritter [Seifert & Ritter, 2008] but it should be pointed out, however, that the reason for this anion specificity is not understood at this time.

\footnote{It should also be noted that BWRs currently operate with less than 5 ppb Cl\textsuperscript{-}.}

Figure 2-6: Tentative threshold conditions for crack propagation into low alloy steel from Alloy 182 as a function of (a) sulphate and (b) chloride concentration [Kumagai et al, 2009]. Also shown by the shaded regions are the combinations of stress intensity and anion concentration that lead to sustained propagation in the absence of a “starter crack” in Alloy 182 [Seifert & Ritter, 2008].
Herbst and colleagues [Herbst et al, 2011] investigated the effect of chloride impurities on general corrosion and crack initiation behaviour of a German low alloy steel, 22NiMoCr3 7, (similar to SA508 Cl 2) in simulated BWR water at 288°C, containing 400ppb oxygen. The particular focus was on the effect of permanent chloride contamination at levels relevant to the VGB water chemistry guidelines (5, 20 and 50 ppb) and on transients where these impurity levels were introduced for 24 hours before reverting to acceptable chloride concentrations (<2 ppb) for times of 100, 200 or 500 hours. The on-line corrosion rate was monitored via Electrochemical Noise (ECN) and Electrochemical Impedance Spectroscopy (EIS); the oxide thickness was measured using Focussed Ion Beam (FIB) foils and; the oxide composition was quantified via Auger Electron Microscopy (AEM) and Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS). Stress corrosion crack initiation susceptibility was determined via C-ring samples and by Slow Strain Rate Testing (SSRT).

It was observed in on-line measurements that the general corrosion rate increased with chloride concentration. The higher halide concentrations led to a decreased oxide thickness as well as an increased amount of pitting. (It should be noted that pitting of carbon and low alloy steels is somewhat unusual in good purity high temperature water, and when it does occur it is usually associated with MnS non-metallic particles; pitting in clean steels is usually associated with prior exposure to aerated water at lower temperatures circa 100°C). The 24 hour transient tests indicated that the detrimental effect of increased chloride concentrations on the protective nature of the oxide recovers within at the most 48 hours after the transient (i.e. there is no memory effect).

No stress corrosion cracking initiated on the C-ring specimens at times up to 1000 hours and chloride concentrations up to 50 ppb. Transgranular stress corrosion cracks did, however, initiate at pits under the more aggressive SSRT conditions in 288°C water containing 50 ppb chloride.

![Figure 2-7: Combinations of stress intensity factor and chloride concentration for sustained crack growth into the low alloy steel under BWR *normal water* chemistry conditions [Ritter et al, 2010]. Reference (20) in this Figure refers to the data from Kumegai et al. in Figure 2-6b. (FL denotes “fusion line”).](image-url)
2.2 Stainless steels

Stress corrosion cracking (and corrosion fatigue) of unirradiated stainless steels in BWR environments has received an extensive amount of study since the early observations of cracking in BWR piping and fuel cladding during the 1960s and 1970s. The system parameters that control cracking susceptibility are well recognized. The details of these interdependencies are fully reviewed in [Ford et al, 2010].

Quantitative models of the crack propagation process have been developed and qualified against observations of crack propagation in the laboratory and plant. These qualified models emphasise the varying dependencies of the crack propagation rates on the combinations of the material conditions, environment chemistry and stress condition.

Various mitigation actions have been developed based both on this theoretical knowledge base and on extensive empirical observations of the effect that the system parameters have on EAC of stainless steels in unirradiated environments. Examples of such mitigation actions include: the use of L-grade or stabilized stainless steels; the application of higher purity water and “Hydrogen Water Chemistry (HWC)” specifications and; the reduction in stress due to modified welding practices. In many cases, combinations of these individual mitigation actions are employed.

These mitigation actions have, in the main, been effective but, as mentioned briefly earlier, there have been unexpected failures in recent years [Ford et al, 2010] even in “mitigated” systems (i.e. stabilized or L-grade stainless steels operating in good purity water). These unexpected failures may be associated with, for instance, significant effects of surface abuse and strain localization. Further, although there is an adequate understanding of the crack propagation mechanism for relatively deep cracks (i.e. >50µm), there is a lack of quantitative, fundamental understanding of the processes that lead to micro-crack initiation and crack coalescence (Figure 2-8).

As discussed in detail in earlier ANT International reports, the progress of a stress corrosion crack may involve a sequence of different phenomena such as: (i) pitting (for carbon steels) or intergranular attack (for austenitic alloys) in high temperature LWR environments; (ii) microscopic crack initiation and; (iii) coalescence, followed by; (iv) crack propagation (or arrest) (Figure 2-8). This sequence may be preceded by a “precursor” period which may be very short in duration when associated with high stresses and yield strengths caused by surface cold work or with excessive water impurity transients during initial reactor operations. On the other hand, precursor events may take place over many years if they are associated with a change in metallurgical microstructure involving thermal aging, irradiation embrittlement, or the creation of the necessary stress due to corrosion product formation and volume expansion.
2.2.1 SCC initiation in non-irradiated stainless steels

The criteria for crack initiation and subsequent crack growth have been extensively reviewed elsewhere [Hickling, 2005]. Only a very brief review of the subject is given here in order to lay the basis for a discussion of recent developments.

There have been several investigations to quantify the schematic relationship depicted in Figure 2-8, for Type 304 stainless steel and for nickel-base (Alloy 600) alloys in BWR environments [Andresen et al, 1990]. In these cases, it was observed that cracks initiated at chromium depleted grain boundaries and coalesced, with this coalescence period being completed when the crack depths were of the order of 50-100 µm. An example of this is shown in Figure 2-9 for a sensitized, Type 304 stainless steel, blunt notch specimen that was dynamically loaded in relatively impure (10 µS/cm) water at 288°C. It is seen that under these aggressive environmental and stressing conditions, “microscopic” crack initiation and coalescence is completed within 50 hours. There are few data to cover such microscopic crack initiation phenomena in more representative BWR water chemistries. However, Seifert and colleagues [Seifert et al, 2009] have conducted similar experiments with similar results for low carbon or stabilized stainless steels operating in representative environments associated with BWR “Hydrogen Water Chemistry” or PWR primary environments. More recently, Andresen [Andresen, 2011a] has confirmed this sequence of events for Alloy 182 in PWR primary environments. In this case, crack coalescence occurs at crack depths of 10-50 µm within 400 hours. Thus, this “short crack” part of crack development seems to be a common phenomenon for austenitic alloys in LWR primary circuits, with the uncertainty being the time required for the coalesced crack of 10-100 µm to be formed.

However, as discussed briefly in Section 3.3.2.1 for crack initiation in Alloy 600 in PWR primary environments, there continue to be uncertainties in predicting life in reactor components on the basis of laboratory observations of coalescence obtained under atypical loading conditions.
KEY EMERGING ISSUES AND RECENT PROGRESS RELATING TO STRUCTURAL MATERIALS DEGRADATION


Figure 2-9: Crack depth-time relationship for intergranular cracks initiating, coalescing and propagating in a notched 1T CT specimen of sensitized stainless steel in 288°C water, after [Andresen et al, 1990].

It is apparent, therefore, that a distinction needs to be made in the definition of “initiation” when discussing evolving stress corrosion data. Historically “initiation” has been associated with, for example, the detection of macroscopic cracks with dimensions >1 mm. This is referred to in Figure 2-8 as “engineering crack initiation”. In fact a dominant crack has formed due to coalescence of micro-cracks in adjacent grain boundaries with a crack depth of the order of only 50-100 μm. For the purpose of further discussion, therefore “crack initiation” relates to the microscopic events occurring in and adjacent to the surface oxide on the specimen surface. The phenomena that are relevant to microscopic crack initiation include: oxide composition and internal stresses; grain boundary compositions; grain boundary orientations relative to each other; dislocation morphologies; etc. Evolving analytical techniques make it possible to quantify such effects on “microscopic crack initiation”.

As an example of innovative analytical approaches Yonezawa and colleagues [Yonezawa et al, 2011b] have designed an autoclave (Figure 2-10a) that accommodates a modified CT specimen, which has a mirror finish flat surface at the root of the notch. This surface may be exposed to 17 keV X-rays from a synchrotron, thereby allowing analysis of the composition of the surface oxide as it grows in high temperature water as well as measuring the residual stress in the oxide and the underlying metal substrate. By judicious control of the angles of X-ray incidence and detection and other beam parameters (Figure 2-10b) these measurements may be made at constant penetration depth at submicron increments.

Figure 2-10: (a) Refreshed autoclave with diamond windows for in-situ synchrotron X-ray measurements. The angles of X-ray incidence and other beam parameters, (b) may be controlled to give constant X-ray penetration.


2-9(2-54)
Preliminary experiments have been conducted on non-sensitized type 316 stainless steel in 288°C, 2 ppm oxygenated water with inlet/outlet conductivities of 0.05/0.18 µS/cm respectively. The primary conclusions are:

- The surface oxides are as expected from high temperature thermodynamic calculations, hematite $\alpha$-Fe$_2$O$_3$, FeCr$_2$O$_4$, NiFe$_2$O$_4$, Fe$_3$O$_4$, with the proportions depending on the environment chemistry and temperature. (The more recent unpublished work by these authors has extended these findings to different water chemistries, confirming the range of oxide compositions). This observation is of significance to the validity of analyses of oxides on laboratory and component surfaces conducted at room temperature. It is also noted that the composition of the oxide film depended very much on the cation concentrations in solution and therefore on the nature of the materials of the loop and their relative surface areas, again predictable from Pourbaix diagram type calculations.

- The residual tensile stress on the metal substrate is controlled by the balancing compression in the oxide, and to differences in thermal expansion of the oxide and substrate. The upshot is that tensile stress in the substrate metal increases by modest amounts with exposure time and with position just below the oxide/metal interface (Figure 2-11). This observation is of potential significance in defining SCC precursor events associated with growing oxides with time.

![Residual stress data adjusted for corroded depth](image)

Figure 2-11: Residual stress data adjusted for corroded depth [Yonezawa et al, 2011b].

Takeda and co-workers [Takeda et al, 2011] have addressed the long term objective of developing a real-time, non-destructive monitoring system for crack initiation. The shorter term objective is to confirm that there is a relationship between microscopic crack initiation and localized oxide penetration regardless of the fundamental drivers, such as: strain localisation; grain size and misorientation; dislocation morphology; degree of cold work; etc. that give rise to that penetration. The approach has been to analyse the profile of the oxide/metal interface in terms of: the depth of local oxide penetration; the flatness of the interface and; the sharpness of the localized oxide penetrations. An example of such a profile for the Alloy 600 in simulated PWR primary water is shown in Figure 2-12.
The total oxide thickness is expected to increase approximately parabolically with time for both nickel-base alloys and stainless steels, and this was observed in this investigation [Takeda et al., 2011] with the time constants depending on the surface finish, stress and alloy type. Much the same type of time dependence might be expected for the localized oxide penetrations; there are, however not enough data to confirm this currently (Figure 2-13).
A comparison is also shown in Figure 2-13 between the depth of localized oxidation in laboratory experiments and those in plant components, where microscopic cracks have been observed (red circled points) in a PWR Alloy 600 safe end and a sensitized Type 304 stainless steel in a BWR recirculation line. A preliminary conclusion from this investigation is that SCC cracks may initiate when the oxide penetration is of the order of 150-225 nm. This work is on-going [Takeda, 2012].

In contrast to the approach taken by Takeda and his colleagues, where oxide penetration was hypothesized to be the "root cause" for microscopic crack initiation, three other studies by [Sakakibara & Nakayama, 2011], [Miura et al, 2011] and [Devrient et al, 2011] have focussed on the role of cold work on crack initiation in stainless steels.

The objective of the investigation by Sakakibara and Nakayama was to quantify the role of cold work on micro-crack initiation in non-sensitized Type 316NG and 304NG stainless steels in BWR water. In this case the steel was deformed up to 20% by rolling, and the 50x10x2 mm specimens were exposed in a creviced bent beam (CBB) test to 8 ppm oxygenated water at 288°C. Although the inlet water had a reasonable conductivity level (<0.1 µS/cm), the local environment was made more aggressive via the placement of a graphite fibre wool (GFW) over the strained area that created a crevice in which the local anionic impurity level could be increased, (Figure 2-14a).

Although the SCC micro-crack initiation resistance differed among the three heats of stainless steel, there was little change in that resistance with cold work (Figure 2-14b). The samples were analysed via Electron Back Scatter Diffraction (EBSD) for changes in the internal strain energy within the grains. This may be quantified via the Kernel Average Misorientation (KAM) which measures the average strain between atoms in the grain matrix. As expected there was a direct relationship between the KAM value and the cold work applied to the specimen, but there was little difference between the KAM values for the three stainless steels (Figure 2-14a). Thus it was concluded that the lack of a SCC crack initiation relationship with cold work for the test alloys (Figure 2-14b) could not be attributed to the differences in internal strain energy within the grains.

Further EBSD analysis focussed on the misorientation between the adjacent grain lattices since the higher energy grain boundaries that had significant misorientations would be expected to exhibit different susceptibilities to creep, segregation, grain re-crystallization, cracking, etc. from those of the lower energy grain boundaries [Crawford & Was, 1991], [Thaveepringsriporn & Was, 1997], [Watanabe, 1984].

Sakakibara and Nakayama used EBSD to determine the frequency of coincident site lattice boundaries (CSLBs) that had misorientation angles (θ) < 15°, in comparison with the higher angle (θ > 15°) "random" grain boundaries.

The misorientation between adjacent grains was quantified by the parameter, Σ3, defined as the reciprocal density of coincident points in the CSLB formed by the two adjacent crystal lattices. The misorientation angles and grain boundary energies may be altered via cold rolling and annealing to rotate and tilt the grains such that the lattices of the adjacent grains may move in and out of coincidence. It is noted in Figure 2-15b that there is, in fact, such an interrelationship between the increasing plastic strain imposed on the sample and the decreasing proportion of low angle, low energy, Σ3 (twin orientation) grain boundaries compared with the higher angle, higher energy, random grain boundaries. This leads, in turn, to the observation (Figure 2-16) that the depth of intergranular cracks decreases with an increasing Σ3 ratio.

The conclusion from this work is that, although the different IGSCC susceptibilities of the non-sensitized stainless steels in BWR water may be affected by compositional differences (such as Mo, Ni and their possible effect on stacking fault energy and dislocation morphology), cold work does not influence micro-crack initiation at grain boundaries but it does have an effect on subsequent intergranular crack coalescence and short crack growth.
Figure 2-14: (a) Schematic of the CBB test assembly, (b) Number of cracks on the CBB sample as a function of the % reduction in thickness due to cold rolling.

Figure 2-15: (a) Strain dependence of the KAM values as a function of the rolling reduction or tensile strain % and, (b) the change in Σ3 fraction (defined as the total length of Σ3 boundaries to the total length of high angle boundaries) by cold work.

Figure 2-16: Relationship between total intergranular crack depth for Type 316NG stainless steel in 8 ppm O2 water as function of the Σ3 ratio.
Miura and colleagues [Miura et al, 2011], like Sakakibara and Nakayama, concentrated on the effect of cold work on microscopic crack initiation in non-sensitized Type 316L stainless steel in BWR water. They also used a CBB test procedure in 8 ppm O₂ water at 288°C with inlet conductivity < 0.1 µS/cm. In this case, however, Miura and his colleagues deformed their samples first by introducing bulk cold work by cold rolling and then surface deformation by milling at different feed rates and spindle rotation speeds.

Typical micrographic features of the milled surfaces were periodic regions of high cold work, illustrated by the dark banded regions in Figure 2-17a, with the accompanying hardness values varying periodically in the range 210-350 VHN (Vickers Hardness Number) (Figure 2-17b) This heterogeneity was associated specifically with the milling operation.

Subsequent examination of the specimens after exposure in the CBB test revealed microscopic crack initiation at grain boundaries (Figure 2-18a) followed by crack coalescence (Figure 2-18b) to form dominant cracks.

It was further noted that these coalesced cracks underwent short crack growth not so much in the high hardness regions, but at the boundary between the "hard" and "soft" regions where the strain gradients were most marked, (Figure 2-19). This observation has a marked similarity to the data of Andresen and Morra [Andresen & Morra, 2005] that the crack propagation rate is markedly increased when the stress intensity gradient is positive.
Materials degradation in pressurised water reactors (Peter Scott & Pierre Combrade)

3.1 Carbon & low alloy steels

3.1.1 Flow-assisted corrosion (FAC)

The technical literature on FAC has evolved quite significantly in the last few years with significant contributions noted both at the 15th Environmental Degradation of Materials Conference and in technical journals.

3.1.1.1 Field experience

A paper in the J. of Nuclear Materials [Singh et al, 2012] reports the examinations of carbon steel feeder pipes from a heavy water Indian reactor of CANDU based design after 15.67 EFPY. As expected, FAC was found to increase with water velocity (Figure 3-1) and with local turbulence due to surface irregularities. Weld metal exhibited smaller losses of thickness due to their different composition with higher Cr, Mo and Cu.

![Figure 3-1: Effect of flow velocity in a straight segment of feeder pipe on corrosion rate after 15.67 EFPY, after [Singh et al, 2012].](image)

3.1.1.2 Effect of material composition

Two papers published in the 15th International Conference on Environmental Degradation Materials in Nuclear Power Systems - Water Reactors and one in NPC 2012 include experimental results on the effect of material composition on FAC.
In all these papers, the beneficial effect of Cr (due to the low solubility of its oxides in de-aerated environments) is confirmed, but all data do not appear to be fully consistent:

- Data published by Trevin et al. [Trevin et al, 2010] and, more recently, by Moutrille et al. [Moutrille et al, 2012] show (Figure 3-2) that the effect of Cr depends on mass transfer in the fluid and that there is no effect of Cr at contents lower than 0.04%. However, Phromwong et al. observed a reduction of FAC (by 42 to 70%) when increasing Cr concentration from 0.001 to 0.019%.

- An apparent inconsistency also appears regarding the effect of “high” Cr concentrations: according to Mansour et al. [Mansour et al, 2011], no FAC rate could be measured for Cr concentration of 0.15% and higher. This represents an effect of Cr stronger than that seen in the data of Moutrille (Figure 3-2). On the other hand, Phromwong et al. mention that increasing the Cr content from 0.019 to 0.33% in CANDU feeder pipes decreased the FAC rate by 50%, which is obviously a much lower effect than reported in the EDF data in Figure 3-2.

The reasons for these discrepancies are not known but it is likely that effect of Cr depends on mass transfer in the liquid (as in Figure 3-2) and also on the environment chemistry. This is suggested by the fact that FAC in CANDU primary circuits and PWR secondary circuits occurs in environments where the solubility of Cr can be significantly different due to the higher pH and temperature in CANDU.

Another effect of material has been investigated by Mansour et al. who found that weld and base metals exhibit similar FAC behaviour if they have similar Cr concentration, i.e. that the FAC rate is independent of the microstructure of the materials, at least for temperatures higher than 150°C. At lower temperatures, the weld metal seems to behave differently to the base metal, with no maximum observed in the FAC rate near 150°C. This observation is not explained but Mansour et al. suspect an effect of microstructure on the dissolution rate of iron at low temperatures. This point is still being investigated.
3.1.1.3 Mitigation

An Oxygen Water Chemistry (OWC) aimed at mitigating FAC in PWR secondary circuit was described by Sugino et al. at the 2012 NPC [Sugino et al., 2012]. The effect of oxygen injection into condensate has been studied by laboratory experiments and then by a series of tests performed at the Tsuruga-2 PWR plant in 2007. The changed water chemistry was finally implemented in Tsuruga-2 from January 2011.

The basis of the water treatment (Figure 3-3) is the injection of oxygen after the condenser in order to raise the corrosion potential of the carbon steel in the range of magnetite stability between the condenser and the high pressure heat (HPH) exchangers. At the HPH, the reaction with hydrazine causes a drop in oxygen concentration to the low values required by the secondary water chemistry specification at the SG inlet.

Tests in Tsuraga-2 were performed on the feedwater system (Figure 3-4), i.e. the oxygen injection was installed after the deaerator and corrosion potential (ECP) measurements were made at the inlet and outlet of the HPH. The results show that the injection of 2 to 5 µg/kg (ppb) of oxygen raised the ECP by more than 100 mV at the inlet of the HPH but did not affect the ECP at the outlet of the HPH, which means that no oxygen entered the steam generators.

![Figure 3-3](image-url) Concept of OWC for FAC suppression in PWR secondary system [Sugino et al, 2012].

![Figure 3-4](image-url) Schematic diagram of the facility to test OWC in Tsuruga-2 in 2007 [Sugino et al, 2012].
An OWC system was installed in Tsuruga-2 in January 2011 on the condensate system (Figure 3-5). Oxygen is injected just after condensate demineralisers and ECP electrodes were installed after the oxygen injection point after the low pressure heat exchangers as well as at the inlet and outlet of the HPH. In addition, monitoring of the FAC rate by UT was installed in two critical locations at the inlet of the condenser. A series of tests performed from January to March 2011 allowed the range of oxygen injection required to mitigate FAC to be defined (Figure 3-6): the main result is that the minimum oxygen concentration required for mitigating FAC is 2 µg/kg in high AVT (pH 9.8) water chemistry conditions and 5 µg/kg in low AVT (pH 9.3) conditions. Since a maximum oxygen concentration of 5 µg/kg is allowed in the feedwater system, this implies the use of high AVT conditions for FAC mitigation.

![Schematic diagram of the OWC facility in operation at Tsuruga-2 since 2011](Sugino et al, 2012)

![Results of OWC tests performed on the Tsuruga-2 condensate system](Sugino et al, 2012)
3.1.1.4 Modelling

Moutrille et al. [Moutrille et al, 2012] presented the latest developments (version 3.2) of the EDF BRT-CICERO code (see schematic flow sheet in Figure 3-7) that is presently applied in all French PWR plants. The poster presentation is quite similar to the paper presented by Trevin et al. at the Fontevraud VII conference [Trevin et al, 2010]. Comparison of results with field and laboratory experience (Figure 3-8) show a good prediction capability, in particular, with very few predicted points that are slightly non-conservative relative to the observations.

Figure 3-7: Flow-sheet of the BRT-CICERO code version 3.2 for calculating FAC rates [Moutrille et al, 2012].

Figure 3-8: Measured versus calculated component thicknesses using BRT-CICERO™ version 3.2 [Moutrille et al, 2012].
Phromwong et al. [Phromwong et al, 2011] have extended the model developed by Lister et al. for FAC in CANDU feeder pipes to take into account the effect of the Cr content in carbon steel. It is recalled that this model is based on the principle that FAC occurs by dissolution of magnetite into the high temperature aqueous environment that is assumed not to depend on the mass transfer coefficient but on erosion of the oxide layer due to the shear forces created by the flow velocity. In order to take into account the effect of the Cr content of carbon steel, a “passivating” layer of mixed Cr-Fe oxide is assumed to be formed almost instantaneously at the metal/oxide interface that limits the corrosion rate (Figure 3-9). Accordingly, a “Passivation Parameter” (PP) that is proportional to the Cr content of the steel is introduced into the model. The authors checked their model by comparing FAC rates on two steels with Cr contents of, respectively, 0.001 and 0.019% under different mass transfer rate conditions and observed very good accuracy of their predictions (Figure 3-10).

![Schematic showing the Cr effect on FAC](image1)

![Experimental and Predicted FAC Rates](image2)
Comparison of the FAC prediction models developed for CANDU and EDF BRT CICERO models shows that they have somewhat different theoretical bases:

- It is seen that in the Canadian code the effect of mass transfer on FAC rate comes only from erosion of oxide particles from the oxide film, while the BRT-CICERO code does not include (to our knowledge) any erosion effect.

- Secondly, the effect of the mass transfer rate on the FAC rate does not obey the same physical laws: in BRT-CICERO, the FAC rate is proportional to the mass transfer coefficient, $k$, while in the Canadian code, the FAC rate increases linearly with the mass transfer coefficient in neutral environments but much faster in higher pH ammoniated water where the FAC rate increases as $k^n$ with $n \geq 3$ [Lister et al, 2010]. This last figure is more consistent with results of Bignold et al. [Bignold et al, 1980] in ammoniated feed water.

Following the accident at Mihama-3, Uchida et al. undertook the development of a sophisticated code for predicting hazards due to FAC. This code has been presented in several papers in the past few years (see for example the presentation in NPC 2010 [Uchida et al, 2010]), and a simplified version requiring reduced computation time presented in NPC 2012 [Uchida et al, 2012]. The prediction of FAC hazards is based on a six-step analysis (Figure 3-11), including coupled or individual analysis of six sets of major parameters summarized in Figure 3-12. The three first steps of the analysis (indicated by (1) in Figure 3-12) are devoted to the identification of the zones at risk. The three last steps (indicated by (2) in Figure 3-12) involve a 3-D analysis of mass transfer in zones at risk (step 4) and a coupled electrochemistry model and oxide growth pertinent to the local conditions thus allowing calculation of local FAC rates (step 5). The calculations lead to an evaluation of the residual lifetime of the component and to a preventive maintenance and countermeasures programme (step 6). A “verification and validation” method has shown that this code is able to predict local wall thinning to within a factor of 2 and residual wall thickness to within 20% (Figure 3-13).

---

**Figure 3-11:** Six-step procedure for the evaluation of FAC hazards [Uchida et al, 2012].

KEY EMERGING ISSUES AND RECENT PROGRESS RELATING TO STRUCTURAL MATERIALS DEGRADATION

Figure 3-12: Analysis of parameters involved in FAC [Uchida et al, 2012].

Figure 3-13: Comparison between calculated and measured residual wall thicknesses with the Japanese code using 3-D CFD analysis [Uchida et al, 2012].
In their NPC 2012 paper, Ushida et al. present a simplified code designed to reduce computation time. The model is still based on the 6-step analysis (as described above): the three steps for selection of zones at risk are unchanged but in step 4 for the analysis of mass transfer in the zones at risk, the simplified code uses instead of a 3-D CFD a simplified 1-D CFD analysis for a straight pipe together with geometrical factors for bends, orifices and other complex geometries. This model was shown to lead to an estimation of residual wall thicknesses within a factor of 2 (+100% / -50%) compared to the 3-D code (Figure 3-15).

Figure 3-14: Calculation procedures and major inputs for the simplified 1-D FAC code (DREAM-FAC) [Uchida et al, 2012].
Figure 3-15: Comparison between residual wall thicknesses calculated using 2-D and 3-D CFD analyses [Uchida et al, 2012].

The FAC rates obtained in step 4 of the code are used to predict wall thickness taking into account uncertainties related to the knowledge of the actual pipe thicknesses and to the accuracy of the code (Figure 3-16). Assuming a Gaussian distribution of probability to take into account these uncertainties, an estimation of the probability of rupture time is calculated (Figure 3-17). By including a “hazard scale” (whose determination does not appear clearly in the paper), the priority for inspections and maintenance is ranked (Figure 3-18).
Finally, the code also allows mitigation actions to be evaluated, e.g. the use of steel with a higher Cr content (> 0.2% according to Figure 3-12), higher pH (except on plants using copper alloys for condenser tubing) and injection of oxygen which requires a trade-off between the requirements for FAC mitigation without damaging the SG tubes.
3.1.2 Irradiation effects

The Environmental Degradation series of conferences has not in recent years been a major forum for discussing irradiation effects on the fracture toughness of reactor pressure vessel steels but one recent paper from the 15th International Conference on Environmental Degradation Materials in Nuclear Power Systems - Water Reactors highlighted concerns with the accumulation of neutron dose associated with anticipated life extension of plants between 60 and 80 years [Hosler et al, 2011]. Only limited amounts of fracture toughness data exist for reactor pressure vessel steels with fluences above approximately 3x10¹⁹ n/cm² for nine US PWRs that had reached the end of their initial 40 years license period in 2008 although this number is anticipated to rise to around 34 plants. Test reactor data for higher fluences tend to show greater degrees of embrittlement than predicted for 60 years operation from data correlations established from power reactor surveillance specimens. This could have significant consequences for plant life extension applications where reactor pressure vessel fluences up to 10²⁰ n/cm² are anticipated. A new programme has been devised to fill gaps in the database with high fluence surveillance data from the US PWR fleet by 2025 so that future projections for life extension between 60 and 80 years will not be based on potentially overly conservative test reactor data.

3.2 Stainless steels

In PWRs, field experience shows that most cases of cracking of stainless steels are due to the presence, at least transitory, of dissolved oxygen and contaminants in the water, mainly chlorides and sulphates [Combrade et al, 2010] and that, in the nominal PWR primary environment, cold work and/or irradiation to a certain minimum level is a pre-requisite for cracking of stainless steels.

3.2.1 Field experience

In the open literature, only two papers have reported stainless steel cracking in PWR service in the last two years.

Xu et al. [Xu et al, 2011] reported cracking of a Type 316 socket weld in a boron injection tank sampling line (Figure 3-19). The temperature was between 60 and 82°C. A crack was observed in a crevice zone between the socket and the pipe where there was also slight IGA that was considered evidence for the presence of dissolved oxygen. The crack initiated at the root of the weld at the metal/weld interface and propagated for a short distance into the base metal where it was intergranular in the first few grains and then became transgranular. It then propagated through the weld where it was fully transgranular with some branching and several crack arrest marks. Even though no traces or contaminants were detected by EDS on the crack surfaces, this failure was attributed to TGSCC (i.e. probably chloride cracking). Fatigue was discarded as an explanation.
Thébault et al. [Thébault et al, 2011] presented a solution for mitigating SCC of stainless steels heaters in PWR pressurisers. The cause of the failures has been attributed to cold work during fabrication [Couvant et al, 2006]. They claimed [Couvant et al, 2005] that cold work can promote crack initiation when the hardness is higher than 250 HV₀.₁ and propagation when the hardness is higher than 310 HV₀.₁.

In addition, high pHₚ may have aggravated the occurrence of SCC. High pH conditions can occur, at least temporarily, due to the concentration of lithium ions on heated surfaces inside support plates, particularly at the end of fuel cycles when primary water contains almost no boron. Laboratory tests have shown that increasing pH decreases the susceptibility to cracking of cold worked stainless steel up to a pHₚ of about 8, but that higher pHₚ values of the order of 9 are quite deleterious (Figure 3-20).
In the reviewer’s opinion, the very low hardness (250 HV) claimed to be able to lead to crack initiation in nominal PWR primary coolant is quite surprising since crack initiation on smooth surfaces is generally more difficult than crack propagation and, therefore should require more cold work. In fact most of the data used to derive this threshold were obtained by constant extension rate tests producing very shallow cracking of a few micrometre depth, which, in the majority of cases, should not have been considered as SCC because they would not have been initiated and/or propagated under constant load conditions. At most, these cracks could have been considered as the sign of a susceptibility to Strain Induced Cracking, i.e. a form of cracking which requires a significant plastic strain rate. Indeed, in all PWR plants, many stainless steels with bulk or surface hardness in the 250-300 HV hardness range have a long field experience without any sign of detectable cracking.

The second point to note is that in Figure 3-20, the abrupt change in the effect of pH for pH between 8 and 9 is likely to correspond to a change from “near neutral” to “caustic” cracking and therefore to a change in the processes controlling the formation of protective oxide films.

Finally, in the reviewer’s opinion, cracking of pressuriser heaters could be due either to dynamic loading from heater temperature changes and/or to the increase of pH during the periods (Hot Functional Tests and core “Stretch out” periods) where the primary circuit water contains significant lithium concentration and no or very low boron concentrations. During these periods, the heat flux can produce a significant increase in lithium concentration and, thus, in pH on the heater surfaces. The role of lap defects from swaging of the outer can during manufacture may also play a significant role in local concentration of lithium by boiling.

![Figure 3-20: Effect of pH on the susceptibility to SCC of cold worked stainless steel in PWR primary water (evaluated by CERT at 360°C) [Thébault et al, 2011]. The susceptibility index used in this figure represents the ratio between elongation in the environment and in air.](image)

In order to mitigate SCC in French PWRs, a heat treatment has been designed and validated to mitigate the surface cold worked structure in order to decrease hardness to less than 240 HV and to decrease residual stresses below 120 MPa without damaging the heating element and the magnesia insulator. This is performed by using an induction heat treatment designed to apply a temperature between 900 and 1000°C on a thickness of ~1 mm.

An industrial device has been set up and validated. Hardness is decreased to less than 240 HV on a depth greater than 1.5 mm. No grain size growth has been observed near the surface, and residual stresses are low enough not to cause cracking in standard MgCl₂ tests at 154°C.

---

8 SCC is the form of Environmentally Assisted Cracking which is defined as occurring under static loading.
Corrosion fatigue crack initiation and propagation (Peter Ford)

Corrosion fatigue under cyclic strain or stress loading conditions may be regarded as the superposition of two independent degradation modes; (a), fatigue in a “dry” environment, and; (b), environmentally assisted crack initiation and propagation under various loading modes, such as monotonically increasing strain (Strain Induced Corrosion Cracking, SICC), and constant strain or stress (Stress Corrosion Cracking, SCC). The relative contributions of these modes will depend on the load/time pattern (sinusoidal, trapezoidal, saw-tooth, etc.), environment, etc. These interactions are complex and have been reviewed elsewhere for carbon steels [Ford & Scott, 2008] and stainless steels [Ford et al, 2010].

Degradation due to corrosion fatigue is highly regulated, being an important input to license renewal and Plant Safety Review (PSR) decisions, with attention being paid to crack “initiation” via, for example, the ASME III code, and propagation via the ASME XI code. In the former case, the initiation times (or numbers of load cycles) are based on strain-controlled tests, where “initiation” is defined when the maximum load drops by a given amount. In this case, the crack has, in fact, initiated and propagated to a significant depth (from a metallurgical viewpoint) of the order of millimetres, depending on the test specimen design and crack monitoring. Thus, there has been a considerable amount of debate concerning the interactions between microscopic (or “true”) crack initiation and “engineering” crack initiation (see Figure 2-8 and Figure 2-9), and this has clouded the whole discussion of crack initiation.

The original ASME III design curves for fatigue crack initiation were based primarily on fatigue data curves obtained in air at 25°C which, for design purposes, was offset from the data curves by a specific amount to account for various factors such as the then unknown (in 1969) effects of temperature, surface roughness, environment, etc. (Figure 4-1). These corrections were regarded not as safety factors but as “adjustment factors” [Cooper, 1992] that were applied to small laboratory specimen data in order to make reasonable estimates of the fatigue lives of large industrial components.

Based on engineering judgment, the “design curve” was displaced from the room temperature air curve by a factor of 2 on stress/strain amplitude or 20 on fatigue life, whichever was the more conservative [ASME, 1969]. The origin of the factor of “20” arose out of presumed effects of data scatter, specimen size, surface finish etc., as shown in Table 4-1.

<table>
<thead>
<tr>
<th>Physical phenomenon</th>
<th>Factor of reduction in N_{init} values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scatter in data</td>
<td>2.0</td>
</tr>
<tr>
<td>Component size</td>
<td>2.5</td>
</tr>
<tr>
<td>Surface finish, atmosphere, temperature, etc.</td>
<td>4.0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>20</td>
</tr>
</tbody>
</table>

Table 4-1: Design Correction Factors for ASME III Fatigue Cycles to Crack Initiation, N_{init} (measured in room temperature air) at a given strain amplitude.
The environmental or “atmospheric adjustment factor” was less than a factor of four and was originally meant to cover only the effect of an “industrial environment” compared to a “laboratory air environment”. It was left up to the reactor designer or licensee to determine the specific adjustment factor for any particular reactor environment [Cooper, 1992], and to then demonstrate for safety significant components that the cumulative cycles defined by the ASME III design curve at a given strain amplitude\(^{10}\) where not exceeded.

There has been increased urgency in resolving the uncertainties in these analyses because of the movement towards reactor power uprates and life extension, both of which inevitably lead to increases in the cumulative fatigue usage factor. In particular, it has become apparent that the ASME III design curves are not always conservative both for carbon and low alloy steels in oxygenated, high temperature water environments [Ford & Scott, 2008] and for austenitic stainless steels (Figure 4-1) and nickel base alloys under certain low corrosion potential and low frequency loading conditions [Ford et al, 2010].

The following discussion derived from reviews of recent publications focuses on the material, environmental and loading conditions that lead to such non-conservatism in fatigue life estimations for stainless steels and the actions that have been undertaken to manage such situations.

![Figure 4-1: Effect of surface roughness and environment on the fatigue life of (a) Type 316 and (b) Type 304 stainless steel in air and high purity water at 289°C [Chopra & Shack, 2007].](image)

A significant amount of corrosion fatigue data have been compiled by the Argonne National Laboratory culminating [Chopra & Shack, 2007] in the formulation of an environmental correction factor, $F_{env}$, defined as:

$$F_{env} = \frac{N_{air, RT}}{N_{water}}$$

where $N_{air, RT}$ is the number of cycles to “engineering crack initiation” in air at room temperature, and $N_{water}$ is the number of cycles to “engineering crack initiation” in a reactor water environment. This latter factor may be formulated in terms of temperature, dissolved oxygen concentration and loading strain rate. Different $F_{env}$ formulations have been suggested by Japanese investigators and these were included in the analyses by Chopra and Shack. More recently, modifications to the $F_{env}$ formulations have been proposed by analysts from China [Xiao et al, 2012].

\(^{10}\) That is, the Cumulative Usage Factor (CUF), defined as the ratio of the actual cycles to the allowed design cycles at a given strain amplitude, must be $< 1.0$ for Class 1 components.
The upshot is that BWR licensees can submit, with the approval of the NRC [USNRC, 2007], a fatigue analysis that is specific to their operating conditions rather than relying on the “2 and 20” ASME III rule, which only concentrates on the loading conditions and gives scant attention to the reactor environmental conditions. Some of the recent regulatory activities in this area were reviewed at the 15th Environmental Degradation conference by Stevens and Tregoning [Stevens & Tregoning, 2011].

Several other papers were also presented at the 15th Environmental Degradation Conference that address these corrosion fatigue crack initiation and propagation phenomena. Some of the papers [Solomon et al, 2011], [Platts et al, 2011] focussed on low corrosion potential conditions associated specifically with PWR primary environments; these are included briefly in the following discussion since they may also impact on the corrosion potential conditions relevant to BWR-HWC.

Three papers specifically address BWR environmental conditions and report on an extensive program (KORA-I and -II) addressing stabilized and L-grade stainless steels. They concentrate on the various aspects of microscopic corrosion fatigue crack initiation and short crack growth [Seifert et al, 2012a], including the effect of hold times during short crack growth [Seifert et al, 2011], as well as the factors that control deep crack propagation [Seifert et al, 2012b]. As shown schematically in Figure 2-8, and factually in Figure 2-9 for a sensitized stainless steel under low frequency loading [Seifert et al, 2012a], the evolution of cracking involves microscopic crack formation occurring early on, followed by crack coalescence, short crack growth and deep crack propagation.

For the case of non-sensitised stainless steels in BWR-HWC environments, the evolution of corrosion fatigue cracks is similar (Figure 4-2a) with microscopic transgranular cracks of 10 µm depth forming relatively quickly, followed by a transition period over a crack depth range 50-500 µm where it is assumed that the individual microscopic cracks on the smooth notch surface coalesce. A dominant crack exists with the crack tip chemistry established at the end of this transition stage. The crack propagation rate for this short crack is very similar to that measured on deep cracks monitored on, for instance, 25 mm thick CT specimens. This similarity in propagation rates for short (e.g. 500 µm) and deep cracks is illustrated in Figure 4-3.

![Figure 4-2: (a) Crack initiation and growth from a notched Type 304L stainless steel surface strained in hydrogenated high temperature water; (b) comparison of crack initiation and growth in BWR HWC water chemistry and air [Seifert et al, 2009].](image)

---

11 Seifert categorizes this evolution stage as "physical crack initiation".
References


Arioka K., Yamada T., Terachi T. and Miyamoto T., Dependence of Stress Corrosion Cracking for Cold-Worked Stainless Steel on Temperature and Potential, and Role of Diffusion of vacancies at Crack Tips, Corrosion, 64, 9, p. 691, 2008.


