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Letter to the Editors

Shadow corrosion or crevice corrosion?

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Abstract

Local corrosion phenomena in proximity to other components may have different reasons. In narrow gaps, crevice corrosion can be formed under BWR and to a lesser degree under PWR conditions independent of the counter material. At positions, where dissimilar metals are close to Zry under oxidizing conditions, shadow corrosion, driven by large potential differences, can occur. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In-reactor local corrosion enhancement of zirconium base alloys in proximity to other components has been reported since the late seventies [1]. Today, this phenomenon is believed to occur almost exclusively under oxygenated coolant conditions and is mostly called shadow corrosion. In the following it will be shown that local corrosion enhancement can also occur under hydrogenated coolant conditions and crevice corrosion may be responsible besides shadow corrosion.

2. Observations and experimental results

During inspections and examinations of BWR fuel assemblies by Framatome ANP locally enhanced corrosion was observed on water channels opposite to stainless steel (SS) control blades and SS instrumentation tubes, on fuel rods opposite to Inconel spacers or Inconel springs, and on Zry spacers below and beside Inconel springs [2]. In all these cases different materials were in contact or neighboring each other. However, sometimes locally enhanced corrosion was also observed

on contact points between Zry fuel rods and Zry spacers in BWR. Fig. 1 shows the oxide layer thickness profile of such Zry/Zry contact points measured by an eddy current distance probe as well as an oxide layer due to the proximity of an Inconel spring. A thick oxide layer ($>100\ \mu\text{m}$) was also found on the fuel rod end plug pins, which extend in the upper and lower SS end pieces of the BWR elements (small gaps), although the neutron flux is rather low in these positions. A late β -quenching of the end plug material was found to be effective to reduce this effect. Other low flux areas, which showed enhanced corrosion in BWRs, are the contact areas between channels (Zry) and upper core grid (SS). The oxide layer thickness was found to grow rapidly at such positions but saturates at a certain thickness. Saturation has been seen at an oxide layer thickness of 100–170 μm on Zry-2/Zry-4 components [2].

Local corrosion enhancement was also reported from in-reactor loop tests under oxygenated environmental conditions [4–6]. Metallurgical bonded Inconel/Zry and Pt/Zry samples showed localized corrosion in such tests [4]. However, also electrically isolated Zry-2 samples under irradiation exhibited locally enhanced corrosion when opposite to Inconel, Pt and Hf counter metals and to a much lesser degree when opposite to Zr and Nitronic 32 in such an environment [6]. In the latter tests the oxide thickness decreased with increasing distance between the two metals. Maximum corrosion occurred at distances of 0.5 mm.

There are strong hints that also the material composition and condition affect the locally enhanced

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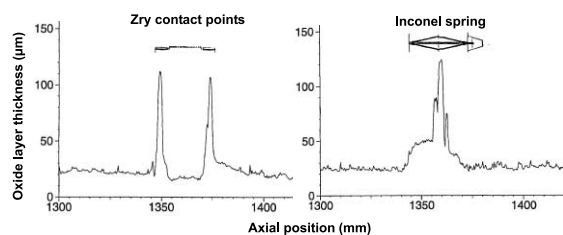


Fig. 1. Oxide layer thickness profile of a BWR Zry-2 fuel rod opposite to Zry contact points (a) and Inconel contact points (b) after a burnup of 46 MWd/kgU.

corrosion in proximity to other components. Fuel rods with Zr1Nb claddings exposed to three years in a Russian pressure tube reactor (RBMK reactor) under oxygenated conditions showed oxide layer thicknesses up to 180–380 μm opposite to SS spacers, whereas experimental fuel rods with Zr1.3Sn1Nb0.4Fe cladding exhibited only 100 μm after a comparable exposure [7].

All these local corrosion observations stem from reactors operated under oxygenated coolant conditions. However, also under a hydrogenated PWR environment locally enhanced corrosion was occasionally observed. Zry-4 spacers exhibited local corrosion in narrow gaps where the coolant was stagnant. Fig. 2 shows a metallographic cross-section of two slots of such a spacer connection after an exposure of four cycles to a fuel assembly burnup of 52 MWd/kgU. The maximum oxide layer thickness is <40 μm in one gap and about 200 μm in the other gap with definitely stagnant conditions.

In order to get more information about the mechanisms, Framatome ANP performed electrochemical measurements out-of-pile at 290°C. In a simulated BWR environment quite large potential differences were measured between Inconel and fresh Zry whereas the potential difference in simulated PWR environment was low (Table 1). A thick oxide layer was found to be very effective to reduce the potential difference between Zry-4 and Inconel in a BWR-type environment (from –420 mV after 5d/290°C to –120 mV after 1000d/360°C). This correlates with our observation that spacers autoclaved at 400°C for few hours show usually less shadow corrosion in-pile compared to those with no final surface treatment.



Fig. 2. Crevice corrosion in a PWR component after a burnup of 52 MWd/kgU.

Table 1
Corrosion potential difference between Zry and Inconel in BWR and PWR environment

Environment	Material coupling	
	Inconel-Zry-4 ground	Inconel-Zry-4 pickled
PWR type	–60	–75
BWR type	–420	–640

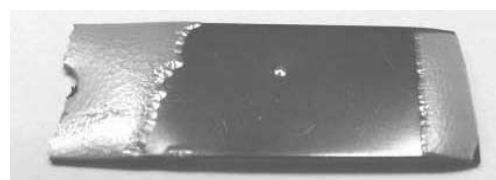
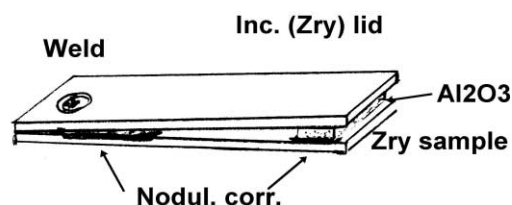


Fig. 3. Crevice corrosion formed out of pile in 450°C/105 bar steam after 288 h.

Out-of-pile corrosion tests with metallurgical bonded Inconel/Zry samples did not show any localized corrosion indicating that shadow corrosion needs irradiation. However, it was possible to simulate crevice corrosion out-of-pile in oxygen-free refreshed 450°C steam at 105 bar in wedge-shaped Zry samples with Inconel and Zry lids welded on one side and 0.5–1.5 mm thick Al_2O_3 distance pieces on the other side. Crevice corrosion was seen after 12 days on Zry-4 with an A-parameter (as defined in [10]) of 2E-17 h in areas where the gap to the Inconel and Zry counter lid was less than 0.15–0.45 mm and below the Al_2O_3 distance pieces (in contact with Zry), as shown in Fig. 3. In the same test Zry-4 with a much lower A-parameter (1.5E-18 h) was resistant to crevice corrosion. A lower A-parameter means that the material has much more but finer intermetallic particles. The tendency to crevice corrosion depends obviously on the size of intermetallic particles, which correlate to the A-parameter.

3. Basic mechanisms

The above-mentioned observations point out two different mechanisms for local corrosion enhancement of Zr alloys. One mechanism is triggered by the proximity of two dissimilar metals. The other type is observed at narrow gaps between two components even when both

consist of the same material. In the following, the first type will be called shadow corrosion, the other crevice corrosion.

Shadow corrosion is explained by two different hypotheses in the literature. One is a galvanic contribution to corrosion [1], the other is a contribution from β irradiation [3,8]. The β radiation may increase radiolysis locally which leads to increased corrosion. Theoretical analysis [5] and tests with Nitronic 32, which is more than 10 times a higher β emitter than Inconel, has only shown a relatively small effect [6] and therefore did not confirm the β radiation hypothesis.

The large potential difference between Inconel and Zry in oxygenated environment is probably the main reason for the observed shadow corrosion in BWR, however, appearance of shadow corrosion under electrically isolated conditions indicates that the mechanism is not a simple galvanic one.

In BWR radiolysis leading to significant concentrations of H_2O_2 further increases the potential difference between dissimilar metals by increasing the corrosion of Zry as well as the redox potential of the coolant. On the other hand, at local positions where the coolant is almost stagnant and corrosion is very high, hydrogen from the corrosion reaction may even suppress oxidative species and reduce the surface potential drastically.

TEM examinations of Zry samples exhibiting significantly accelerated corrosion revealed a globular microstructure, which is indicative of the formation of new oxide grains at the oxide/metal interface. Grain boundary pores extend to the interface. In contrast, normally corroding samples exhibit a columnar oxide structure which is indicative of growing crystals from the oxide/metal interface [9].

A high corrosion rate itself may stabilize a globular structure. In addition higher concentrations of protons reducing the surface energy will facilitate the formation of new grains at the metal/oxide interface. In regions with large potential differences between dissimilar metals, protons may concentrate at the more negative component (Zry) and a process described below for the formation of nodular corrosion can be triggered.

In an oxidative environment large potential differences can arise between local positions with large variations of the oxide barrier layer thickness. In an area where the barrier layer is deteriorated the corrosion rate is strongly increased and a lot of hydrogen is formed from the corrosion reaction. At these positions the potential is shifted to negative values by increasing the cathodic current and changing the cathodic part reaction from the oxygen to the hydrogen reaction. The latter is several 100 mV more negative than the oxygen reaction. Under this condition a very large potential difference can be formed between the large areas with normal corrosion and the smaller ones with disturbed barrier layer. Protons from the corrosion reaction will

concentrate in the more negative spots and stabilize the less protective globular oxide.

Out-of-pile, nodular corrosion was only observed at high temperatures ($\geq 450^\circ\text{C}$) and high pressures (≥ 70 bar). Under these conditions high proton and hydrogen concentrations can also arise at imperfections of the barrier layer due to the very fast local corrosion rate. In PWR, where the normal cathodic reaction is always the hydrogen reaction, local potential differences are small. This may explain why nodular corrosion and shadow corrosion only occur in BWR but not in PWR. Other positions where hydrogen can concentrate are those with almost stagnant conditions in narrow gaps. Out-of-pile tests described above indicate that the oxide structure may become less protective under such conditions.

This type of increased corrosion is obviously a special kind of crevice corrosion. It is responsible for the locally increased corrosion observed in PWR spacers and is probably also responsible for the locally increased corrosion between the end plug pins and the endpieces of BWR fuel assemblies and at the contact points between Zry fuel rods and Zry spacer contact points. In any case, a fine size of intermetallic particles was found to reduce the tendency to shadow corrosion in out-of-pile tests and to minimize the oxide formation on the end plug pins. The intermetallic particles also influence shadow corrosion but the correlation is different. Materials with very fine intermetallic particles have been observed to be resistant to nodular corrosion but sensitive to shadow corrosion. On the other hand, materials with larger intermetallic particles tend to exhibit some nodular corrosion but less shadow corrosion. We often observed, that corrosion opposite to Inconel components is even reduced, when nodular corrosion appears in the neighborhood. Probably nodular corrosion in the vicinity changes the electrochemical conditions of the Zircaloy component at the contact point to the Inconel component.

4. Conclusions

Local corrosion phenomena in proximity to other components have different reasons. In narrow gaps, crevice corrosion can be formed under BWR and to a lesser degree under PWR conditions independent of the counter material. At positions, where dissimilar metals are close to Zry under oxidizing conditions, shadow corrosion, driven by large potential differences, can occur. The detailed electrochemical process responsible for shadow corrosion needs to be better understood.

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