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Research

Shadow Corrosion Mechanism of Zircaloy

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SKI perspective

Background and goals

Shadow corrosion has been recognised for the last 25 years as a phenomenon which occurs on fuel cladding in the vicinity of some other metals. It has not been possible to explain the increased corrosion rate satisfactorily using the hypotheses and experimental evidence which has been available.

Two alternative mechanisms have been suggested based on galvanic corrosion or local effects of beta-radiation from the metal on the water chemistry close to the zirconium alloy.

Normally shadow corrosion is of no practical importance. A potentially serious form of shadow corrosion was reported from Switzerland in 1997. Shadow corrosion has therefore been seen by SKI as relevant to study to improve understanding, not least since there have been a few minor cases in Sweden.

The goal of this project was to investigate to what extent the hypothesis based on galvanic corrosion is compatible with experimental results and the open literature. One problem has been to reproduce shadow corrosion in an autoclave environment. If possible the work should lead to a more detailed hypothesis as well as a recommendation for experimental support of the hypothesis.

Results

The investigation has comprised an assessment of available experimental results and literature. The experimental basis is with few exceptions in remarkably good agreement with the mechanism galvanic corrosion. The most important exception is that shadow corrosion can also occur when the two metals are nominally electrically insulated from each other. The exception can possibly be explained by photoconductivity. It is also possible to explain why shadow corrosion has only been observed in the strong gamma radiation fields in the reactor core.

The authors point out that it is possible to determine if galvanic corrosion is the root cause of shadow corrosion with a relatively simple experiment in a materials testing reactor. SKI has not yet made a decision about such an experiment.

Project information

The project has been carried out by Studsvik Nuclear AB.
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SKI:s project manager is Karen Gott.

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Contents

Summary

Local corrosion enhancement appears on zirconium-base alloys in-core in boiling water reactors when the zirconium alloy is in close proximity to another metal. The visual appearance often resembles a shadow of the other component. The phenomenon is therefore referred to as “shadow corrosion”.

Shadow corrosion has been known for more than 25 years. Mechanisms based on either galvanic corrosion or local radiolysis effects have been proposed as explanations. Both types of mechanism have seemed to explain some facets of the phenomenon.

Normally, shadow corrosion is of no practical significance. However, an enhanced and potentially serious form of shadow corrosion was discovered in 1996. This discovery stimulated new experiments that fully supported neither of the longstanding theories. Thus, there is till now no generally accepted understanding of the shadow corrosion phenomenon.

The aim of the present investigation was to analyse the available data and to identify, if possible, a plausible mechanism of shadow corrosion. It was found that the experimental evidence is, with a few exceptions, remarkably consistent with a galvanic mechanism. The main exception is that shadow corrosion may occur also when the two metals are nominally electrically insulated.

One way to account for the main exception could be to invoke the effect of photoconductivity. Photoconductivity results when a semiconductor or an insulator is irradiated with photons of UV or higher energy. The photons elevate electrons from the valence band to the conduction band, thereby raising the electron conductivity of the solid. In particular, photoconductivity lowers the electrical resistance of the normally insulating oxide on zirconium base alloys. Photoconductivity therefore also has the potential to explain why shadow corrosion is only seen in, or in proximity to, a nuclear reactor core.

The suggested mechanism of shadow corrosion can be tested in a reasonably simple experiment in a research reactor.

Sammanfattning

I härden i kokarreaktorer uppträder en lokal förhöjning av korrosionen på zirkoniumlegeringar då dessa är placerade nära andra metaller. Den tjockare oxiden ger visuellt ett intryck av en skugga av den andra komponenten. Fenomenet benämns därför ”skuggkorrosion”.

Man har känt till skuggkorrosion i mer än 25 år. Som förklaring har föreslagits mekanismer baserade på antingen galvanisk korrosion eller på lokal inverkan på vattenkemin av β-strålning från den andra metallen. Båda typerna av mekanism har tyckts förklara vissa aspekter av fenomenet.

Normalt saknar skuggkorrosionen praktisk betydelse. En potentiellt allvarlig typ av accelererad skuggkorrosion upptäcktes emellertid 1996. Denna upptäckt ledde till att flera nya experimentella studier av skuggkorrosion genomfördes. Resultaten av dessa försök var inte i uppenbar överensstämmelse med varken den ena eller den andra av de traditionella teorierna för skuggkorrosion. Hittills finns därför ingen allmänt accepterad förståelse för fenomenet skuggkorrosion.

Målsättningen med den här rapporterade studien har varit att analysera tillgängligt material och, om möjligt, identifiera en trolig mekanism för skuggkorrosionen. Det resultat som uppnåtts är att det experimentella underlaget med några få undantag är i anmärkningsvärt god överensstämmelse med mekanismen galvanisk korrosion. Det viktigaste undantaget är att skuggkorrosion även uppträder när de två metallerna nominellt är elektriskt isolerade från varandra.

Det nämnda undantaget förefaller möjligt att förklara med hänvisning till fotokonduktivitet. Fotokonduktivitet innebär att fotonbestrålning av en halvledare eller isolator exciterar elektroner från valensbandet till ledningsbandet. Detta leder till en ökning av elektronledningsförmågan hos materialet. Speciellt ökar ledningsförmågan hos det normalt isolerande oxidskiktet på zirkoniumlegeringar. Fotokonduktivitet kan därför potentiellt även förklara varför skuggkorrosion endast har observerats i det kraftiga gammastrålfältet i och intill reaktorhärdar.

Ovan föreslagna mekanism för skuggkorrosion kan prövas genom ett relativt enkelt försök i en forskningsreaktor.

Introduction

Local corrosion enhancement of zirconium-base alloys in proximity to other components is sometimes observed in-core in Boiling Water Reactors (BWRs). The corrosion effect on the zirconium alloy commonly resembles a shadow of the other metallic component. The phenomenon is therefore referred to as “shadow corrosion”. As an example, the imprint of a stainless steel control blade on a Zircaloy fuel channel is shown in Figure 1. More background on shadow corrosion is given in e.g. Andersson et al. (2001).

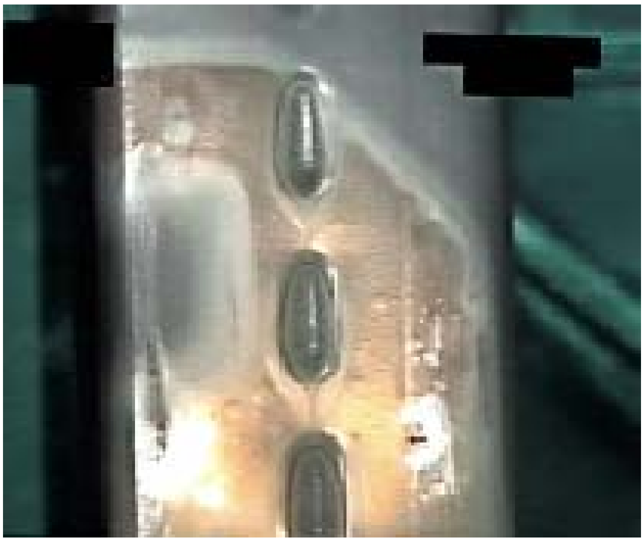

Figure 1: Control blade imprint on fuel channel (from Châtelain et al. (2000)).

Shadow corrosion has been known for more than 25 years (Trowse, Sumerling, and Garlick, 1977). Several attempts have been made to find an explanation. Still, recent investigations differ considerably in their conclusions.

In a general review of zirconium alloy corrosion in nuclear power plants (IAEA, 1998) two alternative mechanisms for shadow corrosion are presented under the headings ‘Galvanic analysis’ and ‘Local radiolysis’, respectively. It is stated that local radiolysis has been accepted as the major contribution for the formation of the shadows.

Experiments were performed at the Halden Reactor to study the effects of heat flux and irradiation conditions, such as neutron flux, β and γ rays, on the corrosion behaviour of Zircaloy-2 cladding tubes under simulated BWR-conditions (Etoh et al., 1997, Shimada et al., 2000). Rings of Pt and Hf were used as local sources of β and γ radiation, respectively. It was found that the Pt rings caused distinct shadows. A weak effect of the Hf rings was noted in some cases. There was little dependence on neutron flux or on heat flux.

When the radiation effects of the Hf and Pt rings were calculated (Shimada et al., 2000), it was found that the contributions from these intentional sources were insignificant compared to the background radiation levels. The β radiation from the Pt ring was e.g. a factor 10^6 lower than the flux of electrons due to γ rays. The authors speculate that the shadow effect might be due to the flux fluctuations caused by β radiation, but conclude that further studies are necessary to clarify the mechanism. No alternative mechanism to a local radiation effect was considered by Shimada et al.

Local contributions from activation products to the electron flux in the core region were also computed, and found to be insignificant, in unpublished work by Lundgren (1997).

The local radiolysis hypothesis was further tested in an experiment in the MIT test reactor. The main results are presented in Châtelain et al. (2000) and some supplementary results are given in Andersson et al. (2001). It was found that Pt and Inconel cause shadow corrosion, but not Zircaloy or Nitronic 32. The latter is an austenitic stainless steel containing 12% Mn, which is a strong β emitter when activated. Another notable result is that shadow corrosion was actually more pronounced when the two metals were electrically insulated, compared to when they were in (physical) contact with each other.

Châtelain et al. conclude that β radiation is not the main mechanism of shadow corrosion. Instead, shadow corrosion is considered essentially dominated by an electrochemical effect that requires a certain threshold concentration of radiolysis products. In Andersson et al. (2001) the shadow effect is considered to be due to a galvanic phenomenon in conjunction with low radiation fields and/or formation of long-lived radiolytic products. No detailed arguments are given in support of these conclusions.

A number of hot cell observations of shadow corrosion are described in Adamson, Lutz, and Davies (2000). It is noted that oxides in shadows are dense and uniform and appear to be associated with a lowered hydrogen pickup fraction. The fact that one piece of Zircaloy can sometimes cause a shadow on another piece of Zircaloy is seen as an indication that galvanic effects do not dominate, but the authors take no firm position for or against any mechanism.

Some laboratory results related to shadow corrosion are presented in Garzarolli, Hoffmann, and Seibold (2001). A significant Inconel-Zircaloy potential difference was measured in a simulated BWR environment out-of-pile. It is concluded that the large potential difference between Inconel and Zry in an oxygenated environment is probably the main reason for the observed shadow corrosion in BWRs. However, appearance of shadow corrosion under electrically insulated conditions is seen as an indication that the mechanism is not a simple galvanic one.

In summary, the situation appears to be the following.

- The β-shine/local radiolysis explanation for shadow corrosion has severe difficulties and may be regarded as disproved.
- The galvanic corrosion hypothesis also has difficulties and is not generally accepted.

The aim of the present work is to give a more detailed discussion of the mechanism of shadow corrosion, especially the galvanic corrosion hypothesis. As a background for the analysis, we first review one of the recent shadow corrosion experiments in some detail.

Some experimental results

The experiments of Châtelain et al. (2000), performed at the MIT research reactor MITR-II, were directly aimed at illuminating the mechanism of shadow corrosion. The results of these experiments are therefore a good starting point for a detailed discussion.

The experiments investigated shadow corrosion using two types of modules, contact module and non-contact module. Each type of module was studied both in-core and ex-core (downstream of the core).

With each type of module, the shadow effects of four different metals were investigated. The metals studied were Alloy X-750, Pt, Nitronic 32 and Zircaloy-2. Nitronic 32 is a low-nickel austenitic stainless steel containing 12% manganese. It was chosen specifically to test the hypothesis that associates shadow corrosion with beta radiation. Manganese is a particularly strong beta emitter when activated.

The contact modules were made up of a piece of cladding with two counters made by cutting a tube in two halves. The counters were placed in contact with the cladding and held together by a stainless steel snap-ring, see Figure 2. The whole assembly was mounted between alumina insulators.

Figure 2: Contact module (from Châtelain et al. (2000)).

The non-contact module consisted of a piece of insulated cladding surrounded by four counters held together by alumina insulators on top and bottom, see Figure 3. The slanted portion of the counter gave distances to the cladding from 0.5-5 mm. The counter had a straight part at 0.5 mm where maximum oxide growth was expected.

The modules were placed in three in-core positions and in one ex-core position. The ex-core position was approx. 60 cm above (downstream of) the core. The gamma dose rate was about two orders of magnitude lower at the ex-core position and the neutron dose rate approx. five orders of magnitude lower.

Briefly, the main results of Châtelain et al. were as follows.

Figure 3: Non-contact module (from Châtelain et al. (2000)).

Non-contact modules

- Shadow corrosion was obtained for Alloy X-750 and Pt, but not for Nitronic 32 or Zircaloy-2.
- Shadow corrosion in the ex-core position was about half that in the in-core positions.
- Shadow corrosion varied inversely with the cladding-counter distance.

Contact modules

- Oxide thickness measurements made on claddings from contact modules did not show an enhanced corrosion build-up under the counters, but instead the shadow effect was found in the seam between the two counter “half-moons”.
- Despite minimal cladding-counter distance, the peak oxide thickness was lower for the contact modules than for the non-contact modules.
- With regard to influence of material and position, experience with the contact modules was identical to that with the non-contact modules, i.e. shadow corrosion was obtained in in-core positions as well as in the ex-core position, but only for the counter materials Alloy X-750 and Pt.

Visual inspection of the claddings from the modules with Pt and Alloy X-750 counters revealed the imprints from the counters while the Nitronic and Zircaloy counters gave no or only a weak imprint. Typical photos of contact cladding samples are shown in Figure 4.

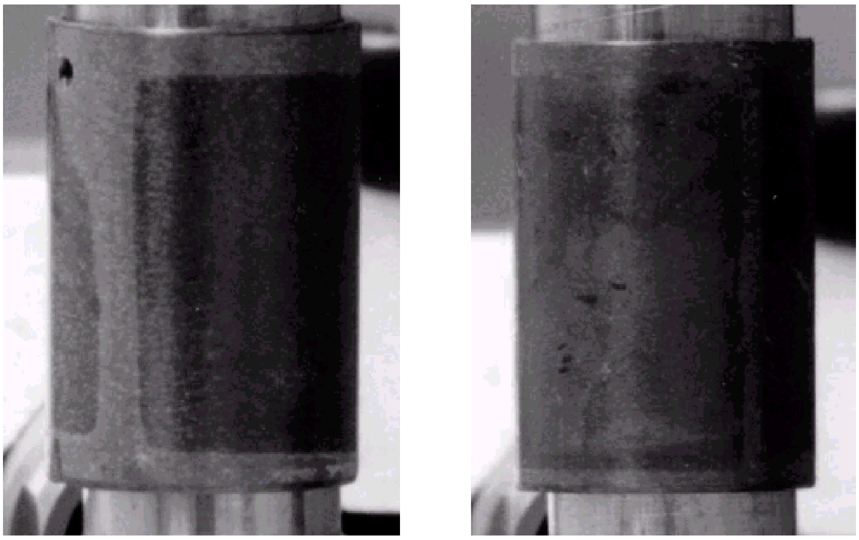

Figure 4: Claddings from contact modules with Alloy X-750 and Nitronic 32 counters, respectively (from Châtelain et al. (2000)).

Problem analysis

Our analysis of the experimental results described in the previous section will be subdivided into two parts, an electrochemical part and a radiation related part.

Electrochemical part of mechanism

There seems to be an ‘action at a distance’ between the Zircaloy cladding and some of the counters of the non-contact modules. What could mediate this action at a distance? The possibilities are limited if we strive for a simple and conventional explanation. The counter is most likely to modify the chemical or the electrical environment of the Zircaloy surface (corrosion in an aqueous environment is normally an electrochemical phenomenon). Radiation effects are not expected to vary inversely with the cladding-counter distance (exponential fall-off is more common) and are therefore not likely to be controlling.

A modification of the chemical environment due to the counter seems unlikely since this would imply that mass transfer was an important factor. There are no indications of a strong flow rate effect on shadow corrosion, as there ought to be if mass transfer was involved.

The remaining possibility is an electrical influence, which could in principle be either an electrostatic field or a current. Since water is a conducting electrolyte, there can be no electric field in the water gap without a current. We should therefore focus on an electric current as mediating the influence of the counter on the Zircaloy surface. (Châtelain et al. (2000) seem to have reached a similar conclusion when analysing their experimental results.)

Note that electrical influence of the counter on the Zircaloy requires either a closed current loop or some radiation effect. This follows from the basic principles of electromagnetism and the conductivity of water. The only way for a counter, not in contact with the cladding, to exert a classical, electrical ‘action at a distance’ is through an electrostatic field in the water separating the counter and the cladding. Of necessity, a current accompanies this electrostatic field. The current, in turn, requires a closed current loop. Thus, if we reject radiation effects there seems to be a strong case for a galvanic mechanism.

Assume, hypothetically, that the counter is in electrical contact with the Zircaloy cladding. We then have the typical set-up of a galvanic cell, as illustrated in Figure 5.

The figure approximates the case of an Inconel spacer in contact with a Zircaloy cladding. In the figure, we have assumed that the oxide is an electronic conductor and closes the current loop. Note that the electronic current and the ionic current in the water are driven by electric fields. However, the ionic current in the oxide is probably driven primarily by a concentration gradient.

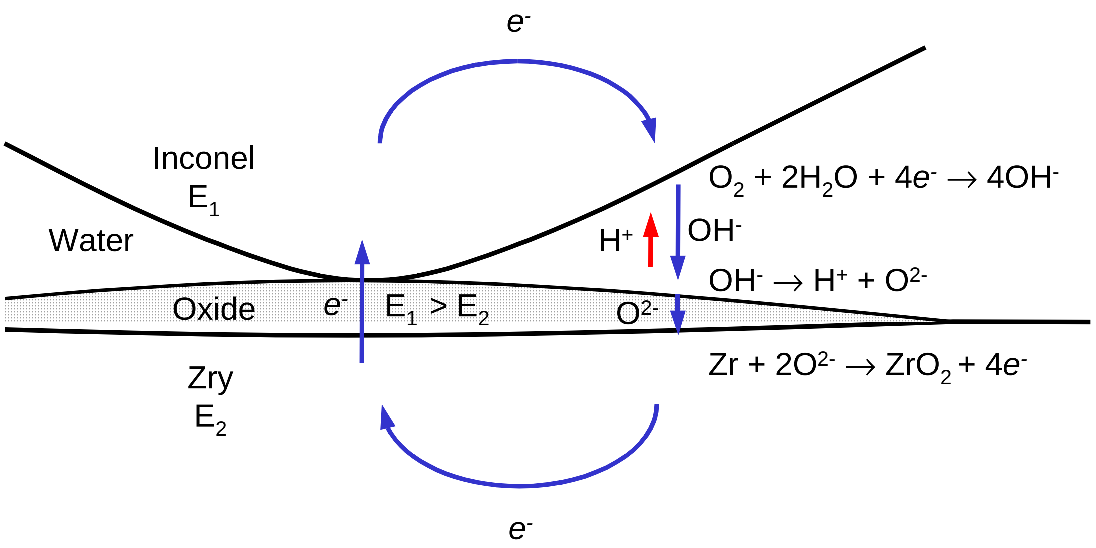

Figure 5: Galvanic corrosion of Zry in contact with an Inconel counter in an oxidising environment.

If the counter has a higher corrosion potential than Zircaloy, i.e. $E_1 > E_2$, an electron current will tend to flow from Zircaloy to counter through the contact point, balanced by an ionic current in the water. By this mechanism reduction of oxidising species at an efficient oxygen electrode (Inconel) may cause an increased oxidation rate of the Zircaloy cladding. If, on the other hand, the corrosion potential of the counter is equal to or lower than the potential of the cladding, there will be no accelerated corrosion of the Zircaloy surface.

Zircaloy is known to have a fairly low corrosion potential in oxidising environments, especially initially when the rate of shadow corrosion is known to be high. We conclude that for the experimental results to be consistent with galvanic corrosion, Pt and Alloy X-750 should have high corrosion potentials and Nitronic 32 a low corrosion potential. This is known to be true for Pt and Alloy X-750. For the case of Nitronic we offer the following argument. Consider the composition of Nitronic 32 shown in table 1.

Table 1: Composition of Nitronic 32 (from Châtelain et al. (2000)).

Fe	67%
Cr	18%
Mn	12%
Ni	1.6%
Si	0.5%
N	0.4%
C	0.1%

The only major alloy component of Nitronic that is able to form a stable oxide in the oxidizing environment is Fe. However, Fe is diluted by 18% of Cr and 12% of Mn, both of which are rather soluble under oxidising conditions (the levels of Cr and Mn are low in BWR fuel crud in comparison to their levels in the reactor water). One may therefore expect Nitronic 32 to corrode in a BWR environment and, consequently, to have a lower corrosion potential than e.g. stainless steel or nickel base alloys.

Thus far, the experimental results for the non-contact modules seem to be consistent with the mechanism of galvanic corrosion (ignoring the question of electrical contact). We now turn to the contact modules.

In general, shadow corrosion was not obtained in the cladding-counter crevice. Assuming galvanic corrosion as mechanism, this may be explained as due to reducing crevice conditions. Although oxidising radiolytic species are produced in the crevice water, the volume-to-surface ratio is too small for radiolysis to give oxidising conditions in the crevice. The combined effect of radiolysis and corrosion will instead cause hydrogen to accumulate in the stagnant crevice water and oxidising species to be suppressed (cf. Hydrogen Water Chemistry). Both Zircaloy and counter will therefore have low corrosion potentials and reduced galvanic/shadow corrosion is a reasonable consequence, consistent with PWR experience.

Because of the different levels of oxidising species, the counter will tend to have a high corrosion potential on the exterior surface and a low corrosion potential on the interior surface. The two sides of the counter will then act as the two poles of a shorted galvanic cell. An ionic current will flow in the water from the interior to the exterior side of the counter and the interior and exterior surfaces will mutually polarise each other. Because of the high resistivity of the water, the polarisation will largely be confined to the edges. The edges of the exterior surface will be polarised to a lower-than-normal potential and the edges of the interior surface to a higher-than-normal potential. This will have two consequences.

- The counter exterior will give rise to less-than-normal galvanic cladding corrosion around the edges due to polarisation to less-than-normal potential
- The counter interior will give rise to some galvanic cladding corrosion close to the edges due to polarisation to higher-than-normal potential

Both predictions, based on galvanic corrosion, are in agreement with the experimental results of Châtelain et al.

- The contact modules gave less that half the peak oxide thickness compared to the non-contact modules, despite a smaller counter-cladding gap.
- Curved shadow borders and rounded corners are clearly indicated in the left-hand part of Figure 4 (Alloy X-750).

The experimental results with the contact modules thus strongly suggest that it is the corrosion potential of the counter, and not the counter material *per se*, that controls the formation of shadow corrosion.

What other comparisons can be made between shadow corrosion and galvanic corrosion? A characteristic trait of shadow corrosion is that the counter has to be within a few mm of the Zircaloy surface for a shadow to appear. It is of interest to estimate the potential drop over a water gap of this magnitude in the galvanic corrosion model and relate it to estimated differences in corrosion potential.

The current density in the water is controlled by the equation

$$j = \kappa \cdot E \qquad (1)$$

where j is the current density, κ the conductivity and E the electric field strength. The conductivity of water at BWR temperature is approx. 3 µS/cm. A reasonable order of magnitude estimate for the current density at the rapid corrosion rate experienced in the early phases of shadow corrosion is 10 $\mu A/cm^2$. According to equation (1) this current density requires an electric field strength of 3 V/cm. In other words, a corrosion potential difference of 150 mV will drive a current density of 10 $\mu A/cm^2$ over a distance of 0.5 mm. If the separation increases to 5 mm, the current density will drop to 1 $\mu A/cm^2$. We conclude that the water gap dependence of the rate of shadow corrosion compares favourably with the galvanic corrosion hypothesis.

Galvanic corrosion relies on the existence of a closed current loop. This means that galvanic corrosion will be influenced by resistance to current flow (IR-drop) anywhere in the loop, e.g. in the oxide films. Since the oxide film that develops on Zircaloy has high resistivity, one would expect the importance of galvanic corrosion to be high initially and to decrease with time. This is also the behaviour found in the case of shadow corrosion.

In fact, even the *relative* importance of shadow corrosion decreases with time. Assuming a galvanic corrosion mechanism, this behaviour is also understandable. As passivation improves, the corrosion potential of Zircaloy will increase and the driving force for galvanic corrosion will diminish. We conclude that the time dependence of shadow corrosion seems consistent with a galvanic corrosion mechanism.

The existence of additional resistance to current flow besides the water gap affects the relationship between corrosion rate and water gap in the case of galvanic corrosion. Additional IR-drop reduces the relative importance of the water gap. Oxide thickness should then increase *less* than inversely with clad-counter distance. Conversely, oxide thickness can never increase *more* than inversely with clad-counter distance. This appears to be in agreement with the experimental results. An inverse relationship was the general result in the investigations of Châtelain et al., see Figure 6. However, the shadow effect tends to saturate at separations less than 0.5 mm. In the galvanic corrosion model, this is due to the increasing relative importance of other impedances in the circuit as the water gap is reduced.

Galvanic corrosion relies on a partial separation of anodic and cathodic reactions between the two metals. Galvanic corrosion therefore requires a means for electron transfer between the two electrodes of the galvanic cell. This is in apparent contradiction with the appearance of shadow corrosion in the non-contact modules. With the exception of the missing electron path, the galvanic corrosion mechanism seems to be in excellent agreement with the experimental results of Châtelain et al. A clue as to how the contradiction might be resolved could be to observe that there is another characteristic trait of shadow corrosion: It has only been observed within radiation fields. A reasonable assumption is therefore that a radiation effect provides the missing electron path and makes galvanic corrosion possible.

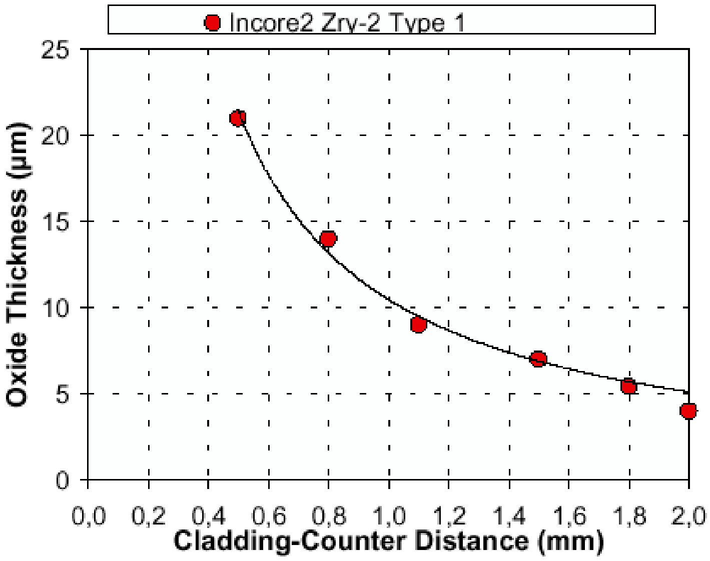

Figure 6: Oxide thickness as a function of clad-counter gap in the non-contact modules. Note that the fitted curve is an almost perfect fit to the 1/d relation (from Châtelain et al. (2000)).

Radiation related part of mechanism

In the absence of a conducting electron path the electrons could, in principle, travel "uphill" against the electric field in the water to complete the galvanic circuit. Radiation might provide the energy required for this process.

During reactor operation intense electromagnetic radiation is present in the reactor core, from visible and UV light (Cherenkov radiation) to hard γ-rays. The energy of this radiation is deposited in the materials in the core and its surroundings. Depending on photon energy, the interaction mechanism is the photoelectric effect, the Compton effect, or pair production. In all cases more or less energetic electrons are produced. The electrons behave like β-rays; within a short distance they transfer their energy to the medium and are captured. High-energy electrons reach up to 1 mm in the structural materials or 1 cm in the coolant.

Closer examination of the radiation effects mentioned indicates that they cannot easily explain the electron transport required for galvanic corrosion. There are several reasons for this. The γ-energy deposition rate is controlled basically by the density of the material and has no relationship to the corrosion potential. Also, emitted electrons have high average energy and cannot be controlled by potential differences of the order of 1 V.

Instead of passing through the water, the electron path might in principle also pass through the semi-conducting or insulating oxides (ZrO_2 and Al_2O_3). The oxides become more conducting in the radiation field. The reason is that photons at UV and higher energies excite electrons from the valence band to the conduction band where they are free to move. This well-known effect is termed photoconductivity.

In practice photoconductivity is strongly affected by various electron-trapping mechanisms. The trapping effect is specific for a particular type of solid. It must therefore be determined experimentally whether photoconductivity is able to provide the electron path required for galvanic corrosion.

The weak point of the hypothetical mechanism of galvanic corrosion/photoconductivity is the uncertainty whether the photo-induced conductivity will be strong enough. We have not been able to find relevant information in the literature on this point. An experimental investigation therefore seems desirable.

Note that the shortest electric current path through the alumina insulators of the non-contact modules in the experiment of Châtelain et al. is only about 0.5 mm, see Figure 3. (Actually, from an electrical point of view there are two parallel paths.) A current of the order of microamperes will therefore be able to pass through the photo-conducting insulators even if the resistivity is still relatively high.

The mechanism and a generalization

Shadow corrosion seems to always appear in-core when the prerequisites of galvanic corrosion are fulfilled, i.e. when Zry and a noble counter are galvanically coupled in an oxidising environment. A typical example is the shadow of a control blade on the fuel channel shown in Figure 1. In this case the control blade is galvanically coupled to the fuel channel.

As discussed above, shadow corrosion does not occur when the counter has a low corrosion potential, e.g. when the local environment is non-oxidizing (crevice), or when the separation is such that the water gap would give a high IR-drop at typical corrosion current densities. These results support the galvanic corrosion hypothesis. Yet, there are two facts that do not immediately fit in with the galvanic corrosion hypothesis.

- Shadow corrosion appears only within radiation fields.
- Manifest galvanic coupling is not necessary for shadow corrosion to appear.

A straightforward assumption, and in the opinion of the authors the first alternative to investigate, is that both these apparent inconsistencies are due to an in-core radiation enhancement of oxide conductivity.

It seems reasonable to presume that certain other instances of local corrosion enhancement on Zry surfaces could also be due to electrical currents. The mechanism behind the electrical current must not necessarily be galvanic in nature. In a nuclear reactor core, electrical currents arise also as a direct effect of the intense high-energy radiation. A well-known example is the Self Powered Neutron Detector (SPND). Devices of this type are, in principle, also sensitive to gamma radiation. The response depends on the details of the design and on the gamma and neutron spectra (Vermeeren, 2001).

Generally, radiation generated currents are expected to be weak compared to galvanic currents. Under special circumstances, discernible corrosion effects may still result.

Discussion

Knowledge of the mechanism behind a phenomenon is frequently of great help as it allows us to understand trends, to make predictions, and to devise counter-measures. As an illustration, we examine some known results in the light of the proposed mechanism for shadow corrosion.

Enhanced Spacer Shadow Corrosion

The phenomenon of Enhanced Spacer Shadow Corrosion (ESSC) (Andersson and Zwicky, 1999) started off much of the recent work on shadow corrosion. Since the problem required immediate mitigation, an engineering approach was pursued in parallel to a more scientific approach. The engineering approach identified the following recommended steps to ameliorate the occurrence and consequences of ESSC (Schrire 1997).

- Change to a cladding with a different heat treatment to avoid amorphisation of the second phase particles.
- Use autoclaved cladding.
- Avoid an iron deficient fuel crud.

The motivation for modifying the heat treatment was mainly to limit hydrogen uptake, so as to limit the consequences of shadow corrosion. However, the heat treatment could possibly also have a direct effect on shadow corrosion. Amorphisation of the second phase particles is known to enhance cladding corrosion. As the protective oxide layer is degraded oxide resistivity is likely to fall. Furthermore, Zircaloy is not known as a good electrode (i.e. having a high exchange current density) for either the reducing or oxidising agents in the reactor water. The potential of Zry will then be more influenced by the corrosion process. The corrosion potential of the cladding is therefore also likely to fall as the corrosion rate rises. This will increase the driving force of galvanic corrosion, i.e. of shadow corrosion. The general corrosion enhancement, due to amorphisation of the second phase particles, of high burn-up fuel with a low value of the annealing parameter might therefore result in a resurgence of shadow corrosion.

Autoclaved cladding is likely to have a higher oxide resistivity and a lower initial corrosion rate and therefore also a higher corrosion potential. Well autoclaved fuel may consequently be expected to develop somewhat less shadow corrosion than fuel with a ground surface finish, since the initial period with a high rate of shadow formation is partly eliminated.

The mechanism behind the effect of iron deficiency is not known. We note only that a *qualitative* effect of iron-deficiency is to promote dissolution of surface penetrating, iron-rich second phase particles. Hematite is normally stable in the oxidising BWR environment, in contrast to chromium and nickel oxides. In Isobe, Murai, and Mae (1996) it is shown that the intermetallic compound $Zr(Fe_{0.66}Cr_{0.33})_2$ is able to provide anodic protection for pure zirconium. The possible electrochemical effects of the second phase particles should be further investigated.

In conclusion, the theoretical understanding provided by the galvanic corrosion/photo-conductivity mechanism seems to support the mitigation measures identified by the engineering approach applied by Schrire (1997).

Prefilmed Inconel

The shadow formed by a pre-filmed Inconel spring was studied in shadow corrosion tests in the Halden Reactor (Anderson et al., 2001). It was found that prefilming the Inconel did not reduce shadow corrosion.

The result of this experiment is self-evident in the light of the galvanic corrosion mechanism. Prefilming the Inconel will raise the already high corrosion potential, and thus the potential difference, and will tend to increase shadow corrosion somewhat.

To reduce the driving force of shadow corrosion the Zry must be prefilmed, not the Inconel.

Zry-Zry shadows

Prefilming of Zircaloy may raise the corrosion potential relative to unfilmed Zircaloy. Prefilmed Zircaloy may therefore be able to induce shadow corrosion on unfilmed Zircaloy. Similarly, Zry with good corrosion properties may be able to induce shadow corrosion on Zry with a higher corrosion rate.

Chen and Adamson (1994) report that a welded Zircaloy specimen exposed in-core caused shadow corrosion on two adjacent Zircaloy specimens. The oxide on the weld was found to be black and thin. A reasonable interpretation is that the welding operation modified the corrosion properties of the Zry material, so that less corrosion and a higher corrosion potential resulted.

Andersson et al. (2001) studied the effect of different zirconium alloy counters in the Halden reactor. It was found that a ZrSnFeCrNi counter produced some shadow corrosion, but not a ZrSnFe counter. In the latter case, however, the cladding seemed to produce a shadow on the counter. This reversal of shadow corrosion with essentially the same alloy composition may be seen as clear evidence against a local radiolysis mechanism. On the other hand, the effect is clearly compatible with a galvanic mechanism.

An important conclusion from these reported results is that the corrosion potential of Zircaloy in a BWR environment seems to be sensitive to the fine details of alloy composition, e.g. intermetallics.

Other experiments and observations

Most other observations and experimental results regarding shadow corrosion also seem compatible with the galvanic corrosion and photoconductivity hypothesis.

For example, in the experiments in the Halden reactor by Shimada et al. (2000) it was found that Pt, but not Hf, gave a distinct shadow, while the effects of neutron flux and heat flux were weak. The test rods are reported to have been electrically insulated from the flow channel tube that supported the Pt and Hf rings, but no details are given. The results are in agreement with a galvanic corrosion/photoconductivity hypothesis, given the reasonable assumption that the corrosion potential of Hf is similar to that of Zr.

Graphic evidence for the galvanic nature of shadow corrosion is given in Lysell, Nystrand, and Ullberg (2001). An electrostatic field can have no component parallel to the surface of a conductor. Therefore, the electrostatic field must vanish at a corner, and so must the current density in the water. The shadow oxide thickness is shown to also vanish at a corner.

An exception to the rule is an experiment described by Adamson, Lutz, and Davies (2000) where a hafnium plate inserted between two Zircaloy plates seemed to cause shadow corrosion on the outside of the Zircaloy. One possibility is that the shadow in this case was due to currents caused directly by the radiation.

Is shadow corrosion possible in out-of-core autoclaves?

In principle, galvanic corrosion may occur in an out-of-core autoclave under galvanically coupled conditions. The fact that shadow corrosion does not seem to occur in autoclaves (Garzarolli, Hoffmann, and Seibold, 2001) may be due to accelerating factors present in-core, but not out-of-core. Important factors could be γ radiation, which facilitates electron transport through the oxide film, and a more strongly oxidising environment, giving a higher potential difference. Experimental evidence for a higher potential difference in-pile is given in Lysell, Nystrand, and Ullberg (2001).

A weak shadow effect could very well develop in autoclaves under favourable conditions, i.e. galvanic coupling, poorly insulating oxide, high corrosion rate, and a strongly oxidising environment.

Recommended future work

A decisive test of the galvanic corrosion hypothesis of shadow corrosion is clearly desirable. A conclusive experim0ent would be to show that shadow corrosion is prevented if there is no electron-conducting path from Zircaloy to counter. The fact that the recent experiments of Châtelain et al. (2000) and Shimada et al. (2000) both produced shadow corrosion under nominally electrically insulated conditions may rather result from the fact that eliminating electron conductors in-core is a non-trivial problem.

A conclusive experiment would be to investigate the effect of a free-floating counter. In practice, such an arrangement could be based e.g. on the principle of a rotameter, using a Zircaloy ‘sight tube’ and a stainless steel ‘float’.

A mechanically less demanding experiment could rely on sufficiently thick insulators between Zircaloy and counter. With appropriate design of the order of 100 mm of insulation can be accommodated in the limited space in a research reactor loop. The insulating material should be chosen on the basis of in-core measurements of the high-temperature resistivity.

At a more general level, there are two important themes that should be studied further. These are the electrochemistry of Zircaloy and the mechanisms behind the impact of intermetallics on Zircaloy corrosion. In particular, the possibility that the electrochemistry is influenced by the intermetallics, as suggested by Isobe, Murai, and Mae (1996), should be explored further. Such a connection could offer new and highly interesting possibilities to relate the corrosion behaviour of Zircaloy to water chemistry and crud composition.

Conclusions

The experimental evidence in connection with shadow corrosion is, with few exceptions, remarkably consistent with a galvanic corrosion mechanism. The galvanic mechanism has also the attraction of great simplicity in comparison to other proposed mechanisms (e.g. Ozaki (1999), and previous papers in the series). The evidence pointing against the galvanic hypothesis should therefore be examined to see if natural explanations can be found.

There are two main arguments against a galvanic mechanism for shadow corrosion.

- Shadow corrosion develops in-core, even when Zircaloy and counter are nominally electrically insulated.
- Shadow corrosion does not develop out-of-core, even when Zircaloy and counter are galvanically coupled.

Problematic as these facts may seem, there may still be a simple and natural explanation. We propose, as a first step, to investigate if conductivity induced by γ-radiation (photoconductivity) could be the explanation needed. This hypothesis is based on the following logic.

- Out-of-core the electrical resistance of the Zircaloy oxide film may be too high for galvanic corrosion to have any noticeable impact.
- In-core, radiation may reduce the resistivity of not only the Zircaloy oxide film, but also of intentional insulators.

Thus, only one simple and well-known effect of radiation seems necessary, in addition to the galvanic corrosion mechanism, to explain most experimental facts and observations in connection with shadow corrosion. Note, in particular, that it is the photon flux, not the neutron flux, which is responsible for the photoconductivity effect. This might explain why significant shadow corrosion was also obtained 60 cm above the core in the experiment of Châtelain et al. (2000).

In the authors’ opinion, there is little doubt that shadow corrosion is caused by an electrical current that is in most cases galvanic in origin. The uncertainty concerns mainly the mechanism for closing the current loop in the instances where Zry and counter are nominally electrically insulated. The photoconductivity hypothesis is an obvious candidate and should be straightforward to test in a research reactor. Shadow corrosion should be prevented if electron-conducting paths from Zircaloy to counter are all but eliminated.

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