Shadow corrosion

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Abstract

An electrochemical mechanism, based on energetically favored complimentary reduction and oxidation reactions, operating in conjunction with radiolysis is proposed for explaining the shadow corrosion phenomenon observed under BWR conditions. The electrochemical reaction on platinum and nickel alloys (Inconel and X-750) is the oxidation of H_2O_2 to produce a localized enhancement in the concentrations of HO_2 and O_2. Energy level of the conduction band of ZrO_2 matches well with that for the reduction of HO_2 and O_2 regenerating H_2O_2. This reduction of the powerful oxidants, stimulates electron emission in ZrO_2 which then is balanced by increased oxidation of zirconium to generate additional electrons and hence also anion vacancies. A coupling between Zircaloy and platinum or nickel alloy is provided by H^+ transport, the source for initiating shadow corrosion, to Zircaloy-2 (Zircaloy-2 negative relative to platinum or the nickel alloy) in the gap between the materials. An enhanced localized corrosion of Zircaloy-2 occurs, its incidence dependent upon the transport of HO_2, O_2, H^+ and H_2O_2 in the coolant in the gap.
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1. Introduction

In the nuclear industry, the term 'Shadow Corrosion' is used to describe an enhanced in-reactor corrosion of Zircaloy when it is close to or in contact with another metallic component that is usually more noble to the Zircaloy. The enhanced corrosion is localized and mirrors the shape, suggestive of a shadow, of the other noble component. The phenomenon of shadow corrosion is invariably, if not implicitly, associated with observations in BWRs. However, instances of localized enhanced corrosion have also been reported to occur in PWRs, RBMKs and in some specific autoclave tests [1,2]. This had prompted a generalized comprehensive approach to propose mechanisms for localized corrosion that would include the specific case of shadow corrosion.

Additional radiolysis due to energetic β^-, emitted from neutron activated isotopes, resulting in local production of transient species has been suggested as a possible mechanism [1]. In order to double the concentration of species such as H_2O_2, HO_2 and HO_2^- the energy deposited has to increase by about five times [3]; whereas the energy deposited by 2 MeV β^- is calculated to be only about the same as the main energy deposition by γ irradiation in water [1]. Results from a recent investigation in a research reactor using Nitronic 32, a powerful β^- emitter, as the other component did not lead to enhanced corrosion of Zircaloy-2 under simulated BWR coolant chemistry conditions [4]. Shadow corrosion is suggested to be a special case of crevice corrosion, because of the potential difference between Zircaloy and the other metal component under radiolysis in BWR-type environment [2]. The separation between Zircaloy and the dissimilar metal component however, when shadow corrosion is observed is far from what could be classified as a crevice. For example the effect of shadow corrosion is seen at gaps ranging from a fraction of a mm to a few mm, and typical crevices are only tens of nm in width.

Evidence has been obtained for enhanced corrosion, in research reactor experiments simulating the conditions conducive for shadow corrosion [4–6]. There are

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strong indications, from potentials and short circuit currents measured [5], for an electrochemical basis for the enhanced corrosion suggesting the possibility of galvanic corrosion as the mechanism [5,6]. However, there is no direct electrical contact between Zircaloy-2 and the other material producing the shadow effect. Although photo-conductivity of the oxides and increased conductivity of the coolant have been invoked as factors contributing to the current flow between the two metals [5,6], yet the precise mechanism for the enhanced corrosion remains unclear.

Under BWR conditions the radiolysis of coolant water is associated with a number of reactions, and there are electrochemical reactions involving the radiolytic species H_2O_2, HO_2 and HO_2^- which would also be facilitated. An examination of the various reactions shows that generation of HO_2, O_2 and H^+ on platinum and their depletion on ZrO_2 are energetically favored to provide the short circuit current between the two corroding materials. This localized ionic current flow through the coolant, its magnitude dependent on the distance and potential difference between Zircaloy and platinum, depolarizes the ZrO_2 and accelerates the corrosion of Zircaloy. The enhanced corrosion occurs over an area corresponding to the external exposed surface of platinum, thus resulting in a shadow effect. The electrochemical reactions might also proceed on the spinel type oxide on the nickel alloys, dependent on the doping of NiO with Cr and Fe. The details of the proposed radiolytic-electrochemical mechanism for shadow corrosion are presented here.

2. Electrochemistry and corrosion-BWR coolant chemistry

The coolant chemistry (corrosion) conditions chosen for illustrating the electrochemical mechanism for shadow corrosion are a temperature of 300 °C, dissolved oxygen at 200 ppb and hydrogen at 10 ppb and a pH_{25} of 7. The Henry's law constant for both oxygen and hydrogen at 300 °C is $\sim 1.2 \times 10^4$ atm mole fraction^{-1}. In terms of partial pressures this will correspond to $\sim 2 \times 10^{-3}$ atm for oxygen and 1×10^{-3} atm for hydrogen. For the radiolytic species the following concentrations in moles per litre are used; H_2O_2 at 10^{-6}, HO_2^- at 3×10^{-9} and HO_2 at 3×10^{-10} [3]. The reactions of interest and their potentials E (all potentials are quoted relative to SHE), corresponding to the coolant chemistry, are listed in Table 1. In computing the potentials standard values E_0 quoted for the reactions in the Handbook of Chemistry and Physics were used. The E_{redox} values are the redox potentials expected for a noble metal under the chosen BWR conditions. A shift of the potentials by $\sim \pm 1$ eV, with respect to the E_{redox} values, due to thermal fluctuations would lead to energy maxima in the Gaussian distribution for the forward and reverse reactions [7]. These are listed as E_{red} for the occupied reduced state and E_{ox} for the unoccupied oxidized state.

On platinum the Fermi energy would adjust to the E_{redox} potential of the reaction. For example it is reported that the potential of palladium, at coolant conditions below the core corresponding to the bottom plenum in a BWR, is quite comparable to that of stainless steel at ~ 0.15 eV [8]. It is seen from Table 1 that E_{redox} potentials of 0.2 and 0.43 eV, for the reactions 9 and 2 respectively, are close to this value and these are the reactions likely to occur on platinum. For example the potential of platinum is likely to be a mixed one, in between the E_{redox} values for the two reactions.

For the reaction to proceed on an oxide, unlike on a metal, an overlap of the energy levels of the conduction or valence band is necessary. For the reduction (reverse) reaction to proceed E_{ox} has to match the energy level of the conduction band; whereas an overlap of E_{red} with the energy level of the valence band is needed for the oxidation (forward) reaction to proceed [7]. In order to discern the possibility of the reactions occurring during

Table 1
Electrochemical reactions and their redox potentials in water at 300 °C with 200 ppb dissolved oxygen and 10 ppb dissolved hydrogen

Reaction	E_0 (Std.)	E_{redox} (eV)	E_{ox} (eV)	E_{red} (eV)
1. $H_2 = 2H^+ + 2e$	0.0	−0.51	0.49	−1.51
2. $H_2O_2 = HO_2 + H^+ + e$	1.495	0.43	1.43	−0.57
3. $3OH^- = HO_2^- + H_2O + 2e$	0.878	1.42	2.42	0.42
4. $OH^- + H_2O = H_2O_2 + H^+ + 2e$	1.362	1.02	2.02	0.02
5. $OH^- + H_2O = HO_2^- + 2H^+ + 2e$	1.706	0.87	1.87	−0.13
6. $2H_2O = HO_2^- + 3H^+ + 2e$	2.119	0.62	1.62	−0.38
7. $2H_2O = H_2O_2 + 2H^+ + 2e$	1.776	0.76	1.76	−0.24
8. $HO_2^- + OH^- = O_2 + H_2O + 2e$	−0.076	0.59	1.59	−0.41
9. $H_2O_2 = O_2 + 2H^+ + 2e$	0.695	0.20	1.2	−0.8
10. $H_2O_2 + 2OH^- = O_2 + 2H_2O + 2e$	−0.146	0.72	1.72	−0.28

Table 2
Electron energy levels for the oxides ZrO_2, SnO_2 and NiO and the matching potentials for the reactions listed in Table 1

Oxide	ZrO_2	SnO_2	NiO
Semiconductor type	n	n	p
Conduction band E_c (eV)	1.2	0	1.8
Valence band E_v (eV)	−3.8	−3.6	−1.2
Reaction number, type and E (eV) (Table 1)	2, reduction, 1.43 9, reduction, 1.2	1, reduction, 0.49	2, oxidation, −0.57 9, oxidation, −0.80

corrosion of Zircaloy-2 and the nickel alloys (Inconel and Alloy X-750), the electron energy levels for the oxides ZrO_2, SnO_2 and NiO are listed in Table 2 [7,9] and compared with E_{ox} and E_{red} values from Table 1. Corrosion of Zircaloy-2 would proceed by the oxidation of zirconium at the metal–oxide interface generating anion vacancies and the migration of oxygen species from the oxide–coolant interface. The electrons released from the oxidation of zirconium charge the metal negative and some also get trapped at the anion vacancies. Tin existing at a high concentration is reported to segregate to the oxide crystallite boundaries, and will form its own impurity conduction band. A good overlap of the energy level for proton reduction, reaction 1 in Table 1, with the conduction band of tin oxide is seen. The cathodic reaction of hydrogen evolution at the oxide–coolant interface would hence be favored at the oxidized tin site [10]. The anodic oxidation of zirconium, at the metal–oxide interface, is balanced by cathodic hydrogen evolution on oxidized tin.

3. Shadow corrosion

Under circumstances when Zircaloy-2 is in close proximity to platinum field-assisted transport of H^+ to Zircaloy-2 would be facilitated (platinum noble to Zircaloy-2). This would lead to oxidation of H_2O_2 (reactions 9 and 2 in Table 1) on platinum and an increase in the concentrations of HO_2 and O_2 locally in the gap between the two materials. The extent of the oxidation would depend on the rest potential of platinum, the field-assisted transport of H^+ and the migration of HO_2 and O_2 under their concentration gradients to Ziracloy-2. The oxidizing potential of HO_2 and O_2 induces their reduction on ZrO_2. A comparison of the E_{ox} energy levels for the reduction reactions 9 and 2 with the conduction band of ZrO_2 shows a reasonably good overlap (Table 2). This increased reduction of HO_2 and O_2, over and above that required for normal corrosion of Zircaloy-2, stimulates emission of electrons trapped at the anion vacancies, and is ultimately balanced by a corresponding increase in oxidation of zirconium at the oxide–metal interface generating additional anion vacancies and electrons. Unlike during normal corro-

sion, the continual increase in anion vacancies at the interface might also induce sustained nucleation of fresh oxide crystallites and impart increased porosity to the growing corrosion film. The resulting enhanced corrosion of Zircaloy-2 is localized to the region of transport from platinum. The increase in gap width would be reflected as a corresponding decrease in the enhanced corrosion, and the area of enhanced corrosion reflects the shape, a shadow, of platinum. The reduction reactions on ZrO_2 regenerate H_2O_2, which becomes available for continued oxidation on platinum. According to the mechanism proposed here the initiation is by H^+ transport in the gap between the two materials and shadow corrosion would occur right from the beginning.

In the case of galvanic corrosion the electrical connection between the two metals would short-circuit the electron current and also transfer the reaction from one to the other metal. This is not the case during shadow corrosion, where the coupling of the two dissimilar metals is via complimentary redox reactions; essentially oxidation of H_2O_2 on platinum and reduction of the resulting products on Zircaloy regenerating H_2O_2. Radiolysis is essential, so as to maintain a steady state concentration of radiolytic species so that the electrochemical reactions result in changes in the concentrations.

Instead of platinum when a nickel alloy is the other dissimilar metal, corrosion of the nickel alloy will produce a spinel-type oxide. Normally NiO is a p-type oxide with a predominantly hole conduction involving Ni^{3+} and Ni^{2+}; however, doping it with higher valence Cr or Fe could impart electron conduction as well involving Ni^+ and Ni^{2+} [11]. Unlike platinum where the Fermi energy adjusts to the E_{redox} potentials, the energy levels of the oxide has to match the E_{ox} and E_{red} values for the reactions to proceed. It is seen from Table 2 that the electron energy level E_v of the valence band in NiO has a reasonable overlap with E_{red} for the oxidation of H_2O_2. And the conduction band E_c shows a good overlap for a number of reduction reactions listed in Table 1. The doped NiO could function as platinum in bringing about the shadow corrosion of Zircaloy-2. For example, stainless steel, where the oxide film will also be a spinel-type oxide, has been shown to mimic noble metal for its electrochemical potential [8].

4. Conclusions

When Zircaloy-2 is in close proximity to platinum or nickel alloys under BWR conditions:

1. Shadow corrosion is initiated by proton transport to Zircaloy-2 assisted by the potential difference between the two materials.
2. Electrochemical reactions involving oxidation of H_2O_2 occurring on platinum and nickel alloys result in a localized increase in HO_2 and O_2 concentrations.
3. Reduction of HO_2 and O_2 is energetically favored on ZrO_2 that results in electron emission in the oxide, and a localized increased oxidation of zirconium at the oxide–metal interface generating more anion vacancies and electrons. H_2O_2 regenerated by the reduction is available for continued oxidation on platinum and the nickel alloy.
4. Coupling of the two materials is via ionic transport in the coolant in the gap, which is facilitated by the potential difference between the two metals, and the transport of species under their concentration gradients.
5. Radiolysis is a requirement for the proposed electrochemical mechanism to operate, so that a minimum concentration of radiolytic species exists.

Acknowledgements

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