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Letter to the Editors

Is zirconium oxide morphology on fuel cladding largely determined by lithium hydroxide concentration effects?

B. Cox *

Centre for Nuclear Engineering, University of Toronto, Toronto, Ont., Canada M5S 3E4

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Abstract

The oxide morphology of films on fuel cladding undergoing enhanced corrosion in BR3 is compared with laboratory observations of degradation of zirconium oxide films in concentrated LiOH solutions. It is concluded that such an LiOH concentration process could have caused the enhanced corrosion in BR3. This probably was initiated by crud deposition raising the surface temperature of the cladding above the saturation temperature during the first cycle of operation in BR3. © 1997 Elsevier Science B.V.

The coincidental publication in the same edition of the Journal of Nuclear Materials of two papers (one reporting electron microscope studies on the oxide film formed on a fuel rod irradiated for three cycles in the BR3 reactor [1], and the other presenting a mechanistic study on the effect of LiOH and H_3BO_3 on zirconium oxide films [2]) prompts the inference that the latter provides a framework for a partial explanation of the former. The oxide on the BR3 rod, although only 6–7 μm thick was already showing the beginnings of a degradation process which is typical of those resulting from high concentrations of lithium hydroxide. These features result from the ability of lithium hydroxide that is more concentrated than some critical value (0.1 M $< [\mathrm{LiOH}]_{\mathrm{crit}} < 1.0$ M at 300°C) to dissolve ZrO_2 locally to produce porosity throughout the oxide film [2]. When the lithium hydroxide is well below this critical concentration, as it is in typical PWR primary coolant, this dissolution process is not immediately possible. Thus, in-reactor the normal pre-transition oxide film that is expected to form in high temperature aqueous solutions will form, and remain relatively unaffected by either the water chemistry or the radiation flux [3,4] for some initial period. In another paper in the same edition of this journal, the effects of iron migration under irradiation are demonstrated [5,6] and some difference in the morphology of thin oxides formed in PWRs probably results from this [1].

There is, therefore, little effect on the oxidation kinetics in the pre-transition oxidation period in LiOH solutions of significantly lower concentration than the critical value until porosity begins to develop in the oxide film as the oxidation rate transition is approached [7]. There is evidence of a small amount of dissolution of ZrO_2 even in pure water at 300–350°C; especially of the oxide formed on the intermetallics [7] that will be heavily doped with iron and chromium from the intermetallic phase [5,8]. The effect of irradiation on this doping, as a result of the migration of iron out of the intermetallics, may not occur quickly enough to affect this early stage of the oxidation process [5]. Some evidence has been found [9] that irradiation may enhance the dissolution by water of the thin oxide on the intermetallics, or provide other sites for easy dissolution of the oxide, such as primary knock-on damage tracks.

Once the pre-transition oxide film has developed a small number of pores by such dissolution processes, or by the normal (but not well defined) processes of generating porosity as the oxidation rate transition is approached, then the oxidation reaction will be proceeding at the bottoms of the pores where the thinnest residual oxide barrier will be. Thus, LiOH can concentrate at the bottoms of these pores until a solution that is concentrated enough to dissolve ZrO_2 is achieved [7,10]. This concentration of LiOH can

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* Fax: +1-416 978 4155; e-mail: cox@ecf.toronto.edu

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be effected most efficiently in the presence of a heat flux that permits the saturation temperature of the water to be exceeded within the oxide film. The elevation of the boiling point by LiOH then ensures that the solution in the pores tries to reach the LiOH concentration which has a boiling point equal to the local temperature. Calculations [11] have shown that a local temperature 5 K in excess of the saturation temperature will have an equilibrium concentration of 1.0 M LiOH. In the absence of a heat flux a slower, but still effective concentration mechanism arises from the removal of water from the LiOH solution in the porous oxide by the oxidation process itself. The concentration of LiOH that can be reached by this mechanism will be limited only by the diffusional mixing that occurs between the solution in the pores in the oxide and the bulk solution. That back-diffusion does not prevent LiOH concentration by this mechanism was shown by the enhanced corrosion rates obtained in unheated crevices and DHC (delayed hydride cracking) cracks, both in the laboratory and in in-reactor loops [12]. Porous oxide films would be expected to behave similarly, but more efficiently because of the very small size (1–2 nm) of the smallest pores [13].

Once the LiOH solution at the bottoms of the pores in the oxide has become concentrated to above the critical value that causes rapid local dissolution of ZrO_2 films [2,7] then a concentration gradient both in lithium hydroxide and in dissolved ZrO_2 will have been established between the mouth of the pore (oxide/environment interface) and the bottom of the same pore (near to the oxide/metal interface). These concentration gradients will result in a gross attack on the oxide film at the oxide/metal interface to give both accelerated corrosion and the growth of a highly porous, degraded oxide film. Some of the ZrO_2 dissolved during this process will be re-deposited hydrothermally on the pore walls (carrying with it whatever lithium concentration is determined by the partition coefficient for lithium between the local solution concentration and hydrothermally deposited ZrO_2). However, much of the dissolved ZrO_2 will be carried out to the oxide surface where the low LiOH concentration in the bulk solution (and hence the low solubility for ZrO_2) will cause its rapid deposition. Some will probably be deposited elsewhere in the reactor primary circuit, or in the loop or autoclave system depending upon the local thermal hydraulic conditions. The hydrothermal deposition of roughly equiaxed ZrO_2 crystallites on specimen surfaces and the transfer of ZrO_2 to the autoclave walls has been observed in autoclaves in concentrated LiOH solutions [2,7].

In addition, the oxide formed close to the metal/oxide interface consists of a mixture of the monoclinic (m-ZrO_2) and tetragonal (t-ZrO_2) phases, the latter being stabilised by different processes including compressive stresses, chemical doping, lower interfacial energy or very fine grain size. Such a two-phase microstructure is basically out of equilibrium and the solubility of each phase in a concentrated LiOH solution will not be the same. This will be the driving force for higher dissolution of the tetragonal phase compared to the monoclinic and thus the enhanced hydrothermal dissolution and re-deposition kinetics.

Thus, these studies predict that ZrO_2 films that become degraded as a result of either high heat fluxes or very long exposures in non-heat flux conditions to low concentrations of LiOH should have at least a three-layer morphology. An outer porous layer of equiaxed, m-ZrO_2 crystallites resulting from hydrothermal re-deposition of ZrO_2 dissolved by the concentrated LiOH solution that develops at the metal/oxide interface. A second layer in the middle of the oxide film, that usually will be comparable to the normal columnar ZrO_2 structure and which represents relatively unaffected oxide still present within the degraded oxide film, and a third porous layer extending up to the oxide/metal interface that consists of equiaxed crystallites of m-ZrO_2 produced by severe corrosion in the high concentration of LiOH present in this region of the oxide. The thickness of this degraded oxide will be determined by the fraction of oxide growth that has taken place during the period of accelerated corrosion caused by the LiOH concentration mechanism. The thickness ratio of the outer porous layer (produced by hydrothermal re-deposition) to the inner porous degraded layer (resulting from attack by concentrated LiOH) may vary depending upon the precise concentration gradients set up within the oxide. However, when extensive oxide growth has taken place by this LiOH concentration mechanism it would be expected that the outer porous layer would be relatively thin compared with the inner porous layer. Thus, under such conditions the remains of the initial columnar oxide should be visible (in oxide sections) near to, but not at, the oxide/environment interface. Similar oxide morphologies cannot be produced in dry steam, where the oxide dissolution mechanism would not be available.

The three-layer oxide morphology is precisely the one that was seen on Zircaloy-4 specimens from a fuel rod exposed for three cycles in the BR3 reactor [14]. It appears that at the maximum oxide thickness of 6–7 μm present on this rod the LiOH concentration process, and the resulting degradation of the oxide near the oxide/metal interface were just beginning. Sufficient hydrothermal transport of ZrO_2 to the oxide surface had already occurred to create a thin layer of porous equiaxed ZrO_2 at the oxide/environment interface by hydrothermal deposition. During the fourth cycle in BR3 it appeared that a rapid acceleration of the oxide growth had occurred; producing ~ 23 μm of oxide in this cycle alone [14]. However, since oxide thicknesses were measured only at the end of the irradiation, it cannot be concluded that the difference in oxide thickness between the 3 and the four-cycle rod occurred in the fourth cycle, because it is not known what the oxide thickness was on the four-cycle rod at the beginning of the fourth cycle. Because of the low power of this rod during the fourth cycle it is most probable that these differences arose during an earlier cycle when the power was high

[14]. Most of this difference in oxide thickness between the three- and four-cycle rods resulted from the production of degraded oxide in concentrated LiOH solution, so that most of the oxide thickness on the four-cycle rod comprised such a degraded layer.

If we examine the operating conditions in BR3 during the cycles when these rods were present, it appears that both the three- and four-cycle (and only these) rods had their first exposure in cycle 4B of BR3. During this cycle severe crud induced corrosion and fuel cladding failures occurred [15]. Although neither rod failed in this cycle their surface temperatures were probably affected by crud in this cycle, with the highest power (four-cycle) rod suffering the most. Although crud may have raised the surface temperature, LiOH concentration will still be the mechanism that caused degradation, rather than overheating, since the oxide morphology is not typical of what would be obtained at high temperatures. It appears that degraded oxide layers may consist of ZrO_2 that is considerably more hydrated than that produced in steam, so that dehydration and recrystallisation in the electron microscope become very evident [1,14]. It also appears that the degraded layer consists of alternate sublayers of the large crystallite size degraded oxide, and more normal appearing columnar oxide. This suggests that the processes leading to LiOH concentration may be unstable and give rise to cycles of oxide degradation and regrowth of protective oxide. For instance, compressive stresses in the oxide may lead to higher concentrations of tetragonal zirconia during growth that will be easier to dissolve. Once the dissolution/re-deposition process has occurred, the compressive stresses would be lowered and mainly monoclinic zirconia would grow, resulting in a more dense columnar layer. The growth of this layer will build up the compressive stresses again, increasing the tetragonal to monoclinic ratio, and leading to a further increase in oxide dissolution. Thus, a cyclic oxide growth rate and a layered structure of the thick oxide layer could develop.

Most of the features seen in these oxide films, and the differences between them and oxides formed in the laboratory in steam at 400°C, could be explained by an effect of LiOH alone, without a major contribution from irradiation effects. However, even in their first cycle in BR3 the three- and four-cycle rods may have needed some crud deposition to elevate the temperatures in the oxide above the saturation temperature in order to achieve the required LiOH concentration. Nevertheless, the irradiation induced migration of iron out of the precipitates [5,6,16,17] and the effect of the doping of the ZrO_2 crystallites by this iron might be expected to have some effect on the corrosion process. We have seen [2,7] that some dissolution of the oxide formed on the intermetallics takes place even in water at 300°C, and for unirradiated material, perhaps because of doping with iron. As irradiation redistributes the iron in the matrix [5,6,16,17] and hence in the oxide, then more ZrO_2 crystallites doped with Fe may be produced on an irradiated matrix than on an unirradiated one. Although a conclusion cannot be reached now, many experimental facts support a higher t-ZrO_2 fraction due to Fe doping of the zirconia [14]. Whatever, the mechanism, however, it seems that oxides formed on highly irradiated Zircaloy surfaces could be more susceptible to local dissolution even in pure water and hence to accelerated corrosion. The severe oxide degradation effects observed in concentrated LiOH solutions would not be expected under such conditions, but some increase in corrosion should result.

This appears to be precisely what is observed [14]. Small increases in post-transition corrosion rates are observed for pre-irradiated specimens corroded in laboratory autoclaves in 350–360°C water [18,19], and the magnitude of these increases in post-transition corrosion rates increases with prior radiation dose, and hence extent of iron redistribution in the zirconium matrix. When such post-irradiation testing was done in 400°C steam, where no zirconium oxide dissolution contribution would appear to be possible, a shorter time to transition was observed for the pre-irradiated specimens, but no significant difference in post-transition oxidation rate was seen (Ref. [14], fig. 5). This would appear to show that there are two stages at which the redistribution of iron can affect the oxidation kinetics. Firstly, whatever the oxidation environment (steam or water) redistribution of iron, perhaps by increasing the proportion of t-ZrO_2 in the pre-transition oxide film, appears to be able to reduce the time to transition by generating cracks on pores at an earlier stage in the oxidation, possible by a t-ZrO_2 → m-ZrO_2 transformation [20]. Changes in the proportion of t-ZrO_2 in the oxide film have been reported [21] to accompany the cyclic transitions often seen during the oxidation of the Zircaloys. Secondly, during post-transition oxidation the redistribution of iron in the zirconium matrix (by increasing the amount of Fe-doped or t-ZrO_2 being produced at the oxide/metal interface) can increase the extent of ZrO_2 dissolution in water [18,19], but not in steam [14], to give an increased post-transition oxidation rate. It appears unlikely that the small temperature difference between the steam [1] and water [18,19] tests could result in a major change in this iron distribution.

Thus, it appears that the overall morphology of the oxides produced on Zircaloy-4 during accelerating corrosion in-reactor could be ascribed to an effect of LiOH concentration in the oxide, perhaps during periods of reactor operation (e.g., at the end of each cycle) when the protective boric acid concentration has been reduced below some critical value [7,10], or during periods when surface boiling resulting from crud deposition [15] reduced the local concentration of boric acid, which is volatile in steam. Effects of irradiation may result in small increases in corrosion rates compared with a precisely analogous experiment in an out-reactor loop [22], but visible evidence of this appears to be restricted to some changes in crystallite nucleation and growth [1,14]. The degraded oxide structures caused by LiOH concentration ultimately eliminate most of the evidence for such effects [14]. LiOH would probably act as an accelerator of the dissolution re-deposition process that we might expect anyhow in a high temperature aqueous environment because of the formation of oxide crystallites high in iron. Very similar oxide microstructures would be expected, and have been seen [22], in out-reactor loop tests under heat flux in low concentration LiOH solutions. Comparisons of such oxide structures with those formed in reactor may permit the identification of those effects ascribable to irradiation alone.

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