Lithium Uptake and the Accelerated Corrosion of Zirconium Alloys


ABSTRACT: The corrosion of zirconium alloys in aqueous lithiated solutions is sensitive to the concentration of the alkali and the temperature. In concentrated solutions, $>10^{-1}$ M in lithium hydroxide (LiOH) (700-ppm lithium) and at temperatures $>573$ K, accelerated corrosion occurs at quite an early stage. Our investigations indicate that the accelerated corrosion is caused by the generation of porosity, rather than the dissolution of lithium, in the growing oxide.

Specimens of standard Zircaloy-4 fuel cladding and Zr-2.5 wt% Nb pressure tube materials were corroded in lithium hydroxide solutions, $10^{-1}$ to 1 M in concentration, at 589 K. Impedance measurements, polarizations in molten lithium nitrate-lithium hydroxide (LiNO$_3$-LiOH) and scanning electron microscopy of the alloy-oxide interface indicated a high level of porosity, right from the initial stages, for oxide films grown in the concentrated solutions. The oxides, when analyzed by atomic absorption spectroscopy, revealed the presence of a few 100 ppm of lithium, too small to account for the accelerated corrosion by a mechanism of solid solution of lithium in zirconia. X-ray powder patterns of the oxides showed peaks for only monoclinic zirconia, but occasionally peaks for LiOH · H$_2$O and LiOH were also observed. The counts for lithium, detected by secondary ion mass spectrometry, decreased when specimens cut from the same corroded samples were leached in nitric acid. It is concluded from these observations that a major part of lithium is physically held in the porous oxide.

Lithium hydroxide is not completely dissociated in aqueous solutions; with increasing concentration and temperature, an increasingly larger proportion of the alkali remains undissociated. It is suggested that the accelerated corrosion in concentrated solutions is caused by the participation of the undissociated alkali in the reactions occurring on the surfaces of the zirconia crystallites. The undissociated LiOH and hydroxyl ions react at an anion vacancy to produce Zr-OLi. These surface -OLi groups could retard the normal recrystallization and growth of oxide crystallites and thus maintain a high intercrystalline grain boundary area for oxygen diffusion to occur. They could also generate porosity in the growing oxide by reacting to form lithium oxide (Li$_2$O), a soluble product.

KEY WORDS: zirconium alloys, corrosion, lithium hydroxide, alkali dissociation, oxide porosity

The alkali, lithium hydroxide (LiOH), is added to the primary coolant of some nuclear reactors for pH control and thereby decrease the activation of out of core components. High concentrations of the alkali are known to increase the corrosion rate of zirconium alloys; these alloys are used as fuel cladding and pressure tube material in the primary circuits of nuclear reactors. Various mechanisms for concentrating the alkali during service, such as

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boiling in the presence of crud, crevice corrosion, and corrosion inside the porous post-transition oxide itself, have been proposed in the literature [1,4,7]. Therefore, information related to the effects of LiOH concentration on the corrosion behavior of zirconium alloys is of importance to the nuclear industry.

Previous researchers have reported data showing the dramatic increase in the corrosion rates of Zircaloy-4 and Zr-2.5 wt% Nb alloy with increasing concentration of the alkali [1–7]. It was suggested that the poor corrosion resistance in concentrated solutions resulted from an increase in the anion vacancy concentration brought about by the substitutional solution of lithium in oxygen-deficient zirconia [2]. Experimental evidence in support of this proposal is provided by the finding of lithium in the oxides grown in concentrated lithiated solutions [5,7]. McDonald et al. have proposed a relation to account for the effect of temperature and lithium hydroxide concentration on the post-transition corrosion rates and suggested that the level of lithium in the oxide could be used as a measure of the extent of accelerated corrosion [7]. Such modelling equations imply that the oxide thickness in its entirety could function as the barrier layer but varying in the concentration of anion vacancies brought about by changes in its composition. However, when the kinetic data are analyzed, it is seen that the rates of accelerated corrosion are much higher than those predicted by the substitutional solution mechanism, and the normal oxidation itself is shown to proceed mainly by the diffusion of oxygen along oxide crystallite grain boundaries rather than bulk diffusion through the zirconia lattice [8]. Moreover, the observations that the accelerated corrosion occurs in concentrated lithium hydroxide solutions but not in concentrated lithium salt solutions [2] or in molten salts containing LiNO₃ and LiOH [9] remain unexplained.

The purpose of the present investigation was to study the corrosion behavior of Zircaloy-4, and Zr-2.5 wt% Nb alloy in aqueous and molten salt media containing lithium hydroxide; to characterize the oxide at various stages of growth using techniques, such as impedance and polarization measurements, examination of the metal-oxide interface on the scanning electron microscope, chemical analysis for lithium, Auger electron spectroscopy, X-ray diffraction and secondary ion mass spectrometry and to propose a mechanism for the occurrence of accelerated corrosion in concentrated aqueous alkaline solutions.

Experimental Procedure

Specimens, 1.5 cm long and 14 cm² in area, were cut from standard Zircaloy-4 fuel cladding (cold-worked and stress-relieved tube 1.5 cm in diameter and 0.04 cm in wall thickness); Atomic Energy of Canada Limited (AECL) identification code for this batch of tubes is MLI-3033. The Zr-2.5 wt% Nb specimens, 2 cm by 1 cm and 6 cm² in area, were machined from Canadian Deuterium Uranium (CANDU) pressure tube material (cold-worked and stress-relieved at 673 K for 20 h, 10 cm diameter tube with 0.4 cm wall thickness). The kinetic data were obtained for the cladding material; oxides from both the cladding and pressure tube materials were analyzed by the various techniques. The surfaces were prepared following established procedures of pickling in acid baths. All the corrosion testings were carried out at 589 K in 1-L stainless steel autoclaves; before starting the experiment, hydrogen was bubbled through the solution at room temperature for 10 min, and the autoclave was charged with hydrogen to a pressure of 1.4 MPa (200 psi). Each experiment consisted of corroding a pair of specimens for a period of time to obtain a weight-gain data point on the kinetic curve; this was followed by impedance measurements on one of the specimens and polarization measurements on the other; subsequently, the specimens were cut, cross sections polished and etched to reveal the oxide-alloy interface and examined on the scanning electron microscope.
Impedance measurements were made at room temperature and 1 kHz in a 1-M ammonium nitrate solution. The inside and edges of the tube specimen and a major portion of the spot-welded Zircaloy wire were coated with a thin insulating film of Lacomit (supplied by W. Canning and Company Ltd.; Catalogue 2567A). A cylindrical platinum gauze formed the other electrode. With the specimen held above, the solution in the impedance cell was frozen using a bath of dry ice in acetone, and the cell was evacuated. After warming to room temperature, the specimen was immersed in the solution, and the changes in capacitance were followed for about 2 h; the cell was then opened to atmospheric pressure and a final measurement made. This final reading was constant over a long period of time, usually about an hour.

Specimens were also corroded in molten LiNO₃(95)-LiOH(5) and NaOH(82)-LiOH(18) at 589 K; the numbers listed refer to percentages by weight.

Polarizations of the specimens, corroded in the aqueous solutions and molten salts, were carried out in the molten LiNO₃-LiOH at 589 K. The apparatus and procedure for corrosion and polarization in the molten salts are described in detail elsewhere [9,10]; the only modification was the use of a nickel crucible as a container for the NaOH-LiOH melt. For all the measurements in the molten salts, the cell was evacuated and filled with argon to atmospheric pressure at 589 K.

A Zircaloy-4 tube was machined to a depth of ~25 μm and the turnings were collected, washed, and corroded in the 1 M LiOH solution for 10 days. A piece of Zircaloy-4 tube, plugged at one end with a welded end cap, served as the container for the turnings. The turnings were completely oxidized, and the powdered oxide collected was washed thoroughly and analyzed for lithium by atomic absorption [7], X-ray diffraction, Auger spectroscopy, and secondary ion mass spectrometry (SIMS). Specimens cut from the same corroded specimen were analyzed after a normal washing in water and after leaching in boiling nitric acid solution. A gallium ion beam was used for sputtering during the SIMS analysis.

Results

Oxide Thicknesses from Weight Gain and Capacitance Data

In Figs. 1 and 2, the kinetics of oxide growth, in dilute and concentrated LiOH solutions, obtained from weight gain and impedance measurements are compared. An equivalent oxide thickness was calculated from the final capacitance measured using the formula: thickness (μm) = 19.47/capacitance (n F · cm⁻²) [11]; this oxide thickness was converted to a weight gain using the relation 1 mg · dm⁻² = 67.3 nm. The impedance measurement is thus related to the part of oxide that is impervious to the aqueous solution at room temperature conditions. The ratio of the weight gains obtained from the capacitance and weight-gain data can be used as a rough indication of the extent of porosity of the oxide film. In Fig. 3, the weight gains for the impervious oxide calculated from the capacitance data are plotted against the total weights gained. The solid lines represent pore or leakage-free films, or both, for which the weight gains calculated from the weight gain and capacitance data would be equal. Weight gains calculated from the capacitances measured, initially on immersion and finally after attaining a steady value, are shown by the open and filled symbols, respectively, in the figure. Compared to the oxides grown in the dilute solutions, the porosity of the oxides grown in the concentrated solutions is obvious. Nearly steady readings and occasionally a slight decrease in the measured capacitance, corresponding to a constant or a slight increase in weight gain with time of immersion, were obtained for films grown in the dilute solutions. Whereas large increases in the measured capacitance, indicating decreases in equivalent
FIG. 1—Corrosion of Zircaloy-4 at 589 K in dilute lithium hydroxide solutions; □ and ■ 10⁻³ M and ▽ and ▼ 10⁻¹ M, □ and ▽ weight gain data and ■ and ▼ impedance data.

FIG. 2—Corrosion of Zircaloy-4 at 589 K in concentrated lithium hydroxide solutions; ○ and ● 0.5 M and △ and ▲ 1 M; ○ and △ weight gain data and ● and ▲ impedance data.
weight gains, were common with films grown in the concentrated solutions. An important observation is that even for low weight gains, \( \leq 30 \text{ mg} \cdot \text{dm}^{-2} \) corresponding to the early stages of pre-transition growth, oxides grown in the concentrated solutions are not protective.

**Oxidation and Polarization in Molten Salts**

The kinetics of oxidation in the LiNO\(_3\)-LiOH and NaOH-LiOH melts are shown in Fig. 4; thicknesses obtained from the capacitance data and converted to \( \text{mg} \cdot \text{dm}^{-2} \) are also plotted in the same figure. The oxidation behavior was quite similar to that observed in the dilute lithium hydroxide solutions. In spite of a high concentration of LiOH in the melts, higher than that in the concentrated solutions, a tendency towards accelerated corrosion was absent; the oxide formed in these melts had the protective quality of pre-transition films.

Polarization curves obtained at 589 K in the LiNO\(_3\)-LiOH melt for the specimens corroded in the same melt and corroded in the lithium hydroxide solutions are shown in Figs. 5, 6, and 7. The cathodic and anodic branches of these curves are associated with the ease of electron and oxygen-ion transports respectively, occurring through the oxide films existing on the corroded specimens [8,9,10]. Oxide films formed in the molten salt and in the dilute solutions, \( 10^{-3} \) and \( 10^{-1} \text{ M} \) in LiOH, showed similar characteristics. Currents during anodic polarization, reflecting the oxygen ion transport through the films, decreased, and the rest potential moved in the anodic direction with increasing corrosion in the respective medium. The corrosion films grown in the concentrated solutions, 0.5 and 1 M in LiOH, passed quite large currents and showed extensive hysteresis during anodic polarization. With increasing

**FIG. 3**—Oxide thicknesses obtained from the impedance measurements and expressed in \( \text{mg} \cdot \text{dm}^{-2} \) plotted versus the weight gained: (a) corrosion in the dilute solutions \( \square 10^{-1} \) and \( \vartriangle 10^{-3} \text{ M} \) and (b) corrosion in the concentrated solutions \( \bigcirc 0.5 \) and \( \bigtriangleup 1 \text{ M} \); open and filled symbols, oxide thicknesses from initial and final capacitance readings, respectively.
Lithium Incorporation in the Oxide

The oxide produced by complete corrosion of alloy turnings in 1 M LiOH solution was dissolved and analyzed for lithium [7]. A level of 250 ppm was found by atomic absorption corrosion, the anodic polarization currents stayed high and the rest potential shifted in the cathodic direction.

Topography of the Alloy-Oxide Interface

Scanning electron micrographs of the alloy-oxide interface exposed after dissolution of the unoxidized alloy are shown in Fig. 8. The schematic included in the figure shows the cross section of a corroded specimen following the acid etch to reveal the alloy-oxide interface and the area examined on the microscope. The micrographs shown in Fig. 8 were obtained for specimens corroded in the dilute and concentrated solutions to similar weight gains of \( \sim 14 \text{ mg} \cdot \text{dm}^{-2} \). Specimens corroded in the concentrated solutions to weight gains of 30, 60, and 90 \( \text{mg} \cdot \text{dm}^{-2} \) were also examined. A pebbly structure of the interface was evident in the early stages of oxide growth in the concentrated solutions and continued to exist all throughout the course of the accelerated corrosion. The oxide crystallites protruding out in relief and giving rise to this type of texture (Figs. 8c and d) are about 250 nm in size. In the case of films grown in the dilute solutions, although the interface was not smooth, a pebble-like structure was not readily evident. The scale of surface roughness, following the etching away of the unoxidized alloy, was larger compared to the films grown in the concentrated solutions. The beginning stages of a pebbly structure were barely visible in the case of specimens corroded in the \( 10^{-1} \text{ M} \) solution for 62 days.

Lithium Incorporation in the Oxide

The oxide produced by complete corrosion of alloy turnings in 1 M LiOH solution was dissolved and analyzed for lithium [7]. A level of 250 ppm was found by atomic absorption
spectroscopy. X-ray diffraction patterns of the oxide showed peaks only for monoclinic zirconia. Similarly, the diffraction patterns from pressure tube specimens corroded in the 1 M solution revealed the presence of only monoclinic zirconia. However, oxide flakes collected from the crevices of sandwiched specimens, corroded in the concentrated solution, when examined by X-ray diffraction, showed characteristic peaks for LiOH · H₂O and LiOH in addition to those of monoclinic zirconia. Auger spectroscopy also indicated the presence of small amounts of lithium in the oxide; a small peak at 47 eV, in the form of a prominent shoulder to the zirconium peak at 38 eV, was distinctly present. Such a shoulder was not detected or was ill-defined in the spectra obtained from the specimens oxidized in steam.

The SIMS analysis of the oxides grown in the concentrated solutions gave a strong signal for lithium. In Figs. 9 and 10, the spectra and lithium maps for an oxide 15 μm thick, grown on the pressure tube material in 1 M solution, are shown. Peaks corresponding to the atomic masses of lithium, calcium, gallium, zirconium, and zirconium oxide (ZrO₂) could be identified in the spectra. Leaching the corroded specimen in boiling nitric acid reduced considerably the amount of lithium detected and eliminated the peak at mass 23. Depth profiles of the surface layers also revealed a lowering of the concentration of lithium by the acid leaching step.
FIG. 6—Specimens corroded in $10^{-1}$ M LiOH solution at 589 K for the periods indicated on the curves and polarized in molten LiNO$_3$-LiOH at 589 K.

**Discussion**

**Presence of the Aqueous Medium**

At 589 K, accelerated corrosion of Zircaloy-4 is observed in 0.5 and 1 M lithium hydroxide solutions in the time period of 8 days but not in $10^{-1}$ and $10^{-3}$ M solutions for exposures up to 60 days. These results are in general agreement with the findings by other workers except for the fact that higher weight gains than those observed in the present study have been reported for corrosion in the $10^{-1}$ M solution [3,7]. When the corrosion data reported by various workers are compared, it is seen that at a concentration of $10^{-1}$ M there is a disagreement in the weight gains at higher temperatures also. For example, at 633 K for 3- to 4-day exposures it varies from $\sim 15$ [5,6] to $\sim 700$ [1,3,7] mg$ \cdot$ dm$^{-2}$; the behavior of Zircaloy-2 is not different from Zircaloy-4 [1]. For Zircaloy-2, corrosion rates at 573 K have been reported over a wide range of concentrations of lithium hydroxide [4]; the data for the $10^{-3}$ M solution are comparable with that obtained in the present investigation.

In the concentrated solutions, the accelerated attack asserts itself right in the early stages of oxidation when the total weight gained is less than 10 mg$ \cdot$ dm$^{-2}$. Another equally important finding is that the accelerated corrosion is not observed in molten salts containing a much higher concentration of lithium hydroxide than the concentrated solutions. In fact, the corrosion in the molten salts proceeds at a slightly slower rate initially than even in the dilute solutions. Therefore, not only a high concentration of the alkali is essential, but also the presence of water as the medium is necessary to bring about the accelerated attack.
Porosity of the Oxide Films

The formula used for calculating the oxide thickness from the measured capacitance is derived by modeling the behavior of the oxide film in terms of an equivalent circuit. Any part of the film penetrated by the contacting electrolyte solution is considered to contribute a resistive component in series with the impervious part, which is taken to function mainly as a capacitive component. Also, no allowances are made for surface roughness, and the dielectric constant is assumed to be 22 [11]. Thus the true thickness of the barrier layer controlling the corrosion at 589 K cannot be defined from the capacitance measured at room temperature conditions. However, the capacitance measurements do indicate how pervious the oxide films are to the electrolyte solution and therefore could be used to compare their relative porosity.

Oxides grown in the concentrated solutions are highly porous. It is seen from Fig. 3b that even for films in the early stages of pre-transition growth, at weight gains of ~10 mg·dm⁻², nearly half of the thickness is quickly penetrated by the ammonium nitrate solution. Then with continued immersion, there is a further large increase in the capacitance caused by ingress of the solution into small pores. The impervious part of the oxide is a small fraction, about 20% or less, of the total oxide thickness for weight gains up to 100 mg·dm⁻². The pre-transition films grown in the dilute lithium hydroxide solutions, and molten salts are relatively nonporous. The almost steady capacitance readings correspond to an impervious portion of 70% or more of the total thickness. This difference of 30% between the weight gain and capacitance data could partly be ascribed to factors such as surface roughness and leakage in the capacitive component caused by intermetallics rather than to porosity.
Evidence for the porosity of the corrosion films grown in the concentrated solutions is also provided by their polarization behavior in the molten salt. These films grown to weight gains of up to 100 mg·dm⁻² pass anodic currents similar to that of a protective oxide grown in the molten salt to ~5 mg·dm⁻² (Figs. 5 and 7). The molten salt is therefore able to penetrate a major portion of these films to give such high currents. The area of charge transport is likely to be less compared to the protective oxide of uniform thickness; therefore, the oxide controlling the charge transport in the porous films could be even thinner than that corresponding to 5 mg·dm⁻². Also because of the porosity and the easy access of the molten salt to the metal-oxide interface, the anodic currents exhibit a large hysteresis.

Protective oxide growth occurring under the porous oxide films, during forward polarization, reduces the current during the reverse step. The extent of hysteresis decreases, with successive polarizations, because of the increase in thickness of this protective oxide growth. The highly negative rest potentials in the melt, obtained for these specimens corroded in the concentrated solutions, also reflect the easy access of the molten salt to the alloy-oxide

FIG. 8—Scanning electron micrographs of the alloy-oxide interface, AOI, for specimens corroded in the dilute and concentrated lithium hydroxide solutions to weight gains of 14 ± 1 mg·dm⁻²; specimens corroded in (a) 10⁻³ M, (b) 10⁻¹ M, and (c) and (d) 1 M LiOH solutions; (d) circled area in (c) magnified.
interface. The rest potentials for pickled specimens are highly negative in these melts, and they shift in the anodic direction with increase in oxide thickness. With the specimens corroded in the concentrated solutions, a similar shift in the rest potentials is seen with time of immersion and anodic polarization. The polarization behavior of oxides grown in the dilute solutions and molten salts is typical of protective pre-transition films; the anodic currents decrease with the decrease in corrosion rate and the rest potentials shift in the anodic direction to steady values.

The scanning electron micrographs show subtle differences in the structure of the alloy-oxide interfaces for specimens oxidized in the dilute and concentrated solutions. When the cross section of a corroded specimen is etched, the unoxidized alloy is dissolved preferentially but the oxide at the interface is also attacked, although to a much less extent than the alloy. The vivid roughness of the interface, in the case of specimens corroded in the concentrated solutions, is similar to that observed for the post-transition films. It appears that on the basis of structural similarity of the oxides, corrosion in the concentrated solutions, from the beginning, proceeds like a post-transition growth. Frequent renucleation sequences resulting in the formation of fine oxide crystallites 5 to 50 nm in size at the interface and porosity in the columnar bulk oxide are considered to be responsible for the accelerated kinetics during post-transition [12]. Thus, the corrosion in concentrated solutions seems to be characterized by the renucleation step setting in at the interface earlier on and persisting throughout the rest of the oxide growth. These fine crystallites are dissolved during the acid etch leaving in relief the protruding grains of the bulk oxide.
Lithium Incorporation in the Oxide

Hillner and Chirigos proposed a solid solution model to explain the accelerated corrosion in concentrated LiOH solutions. Empirical equations relating concentrations of lithium in the solution to that in the oxide and rates of oxidation to the amount of lithium in the oxide were derived [2]. The mechanism involved is considered to be the substitution of lithium for zirconium in the oxide generating 1.5 anion vacancies per atom dissolved. The accelerated corrosion was interpreted as due to this increase in vacancy concentration because the corrosion of zirconium alloys proceeds by the diffusion of oxygen. Recently, Sabol et al. have proposed improvisations relating the rate of corrosion to the concentration of lithium in the solution and temperature. The frequency factor and the activation energy associated with the diffusion of oxygen are suggested to be functions of the lithium hydroxide concentration [7]. A large increase in the concentration of anion vacancies, resulting in a chemical concentration gradient, is thus presumed to be brought about by the dissolution of lithium in the oxide. But a major difficulty with the solid solution model is its incompatibility with the fact that oxygen diffusion occurs mainly along short circuit paths during corrosion [8]. The question also arises as to how lithium substitutes for zirconium in oxygen deficient zirconia crystallites where cation diffusion is negligible.

There are other difficulties. First, for the vacancy concentration to increase significantly over that already existing because of thermal generation, a doping level >1000 ppm of
lithium is required [2]. But large increases in the corrosion rates are observed for only a few 100 ppm of lithium analyzed to be present in the oxide. Second, the amount of lithium in the oxide does not correlate with the extent of accelerated corrosion. For example, McDonald et al. report an acceleration factor, during the post-transition stage, of 132 at 589 K for 187 ppm of lithium in the oxide and a factor of only 4 at a higher temperature of 633 K for 146 ppm of lithium in the oxide [7]. Hillner and Chirigos’ data indicate an acceleration factor of 94 at 633 K for 4500 ppm of lithium in the oxide [2], whereas McDonald et al. found an accelerative factor of 347 for 576 ppm of lithium at the same temperature [7]. It is also reported that the lithium concentration in the oxide, during corrosion in the concentrated solutions, does not attain a saturation level despite the high weight gains in the post-transition stage [7]. As a result, the linear post-transition rate had not been affected, but the amount of lithium in the oxide had increased steadily by nearly three times. The obvious conclusion, therefore, is that the lithium in the oxide, even if it is in solid solution, is not affecting the corrosion rate proportionately.

The results from the SIMS analyses, reported here, indicate that all the lithium in the oxide is not existing as an insoluble component, in solid solution in zirconia. A considerable part, as a rough estimate nearly half, can be leached in an acid solution. Although it is claimed that lithium zirconate could form during corrosion in the 1 M solution [2], the X-ray diffraction patterns did not show its characteristic high intensity reflections [13]; all the observed reflections were identified with those of monoclinic zirconia and lithium hydroxide. These results in conjunction with the porosity of the films suggest that a major part of lithium analyzed to be present in the oxides grown in the concentrated solutions exists as lithium hydroxide in the pores. The accelerated corrosion is thus likely to be associated with the porosity generated rather than the lithium found in the oxide. A model is proposed to account for pore generation and accelerated corrosion in concentrated lithium hydroxide solutions.

**Accelerated Corrosion in Lithium Hydroxide**

With increase in concentration at \(>10^{-1}\) M in LiOH, the changes in pH, measured at room temperature, become increasingly less than the expected theoretical values indicating that increasing amounts of alkali remain undissociated. It is also known that even in dilute solutions, at \(\leq 10^{-3}\) M, the dissociation of LiOH decreases with increasing temperature [14]. When the degree of ionization is calculated using the dissociation constants given in Ref 14 it decreases from 0.95 to 0.45 with increase in concentration of LiOH from \(10^{-4}\) to \(10^{0}\) M. The effect of temperature and concentration on the corrosion rate can thus be related to the increase in concentration of and possible reactions with the undissociated alkali during the corrosion. The normal corrosion proceeds mainly by the diffusion of oxygen via vacancies along the zirconia crystallite boundaries. In aqueous solutions, the anodic half of the corrosion process at the oxide-solution interface is the reaction of water or hydroxyls, or both, with an emerging anion vacancy; the subsequent dehydroxylation step provides the oxygen ion for diffusion. These reactions can be written as

\[
\begin{align*}
\text{ZrO}_{z-\frac{1}{2}+} + 2x(\text{OH})^- & = \text{ZrO}_2 + x\text{H}_2\text{O} \\
\supseteq \text{Zr} \square \text{Zr} \ll + 2 \text{OH}^- & \supseteq \text{Zr-OH HO-Zr} \ll = \supseteq \text{Zr-O-Zr} \ll \\
+ \text{H}_2\text{O} &
\end{align*}
\]
When undissociated LiOH is present, it can react with the hydroxyl at an anion vacancy to give surface OLi groups.

\[ \text{Zr-OH} + \text{LiOH} = \text{Zr-OLi} + \text{H}_2\text{O} \]

These surface OLi groups, when produced in sufficiently high concentrations, retard the normal recrystallization and growths of oxide crystallites. During oxide growth the OLi groups can also react to produce Li_2O in the crystallite boundaries.

\[ 2 \text{Zr-OLi} = \text{Zr-O-Zr} \leq + \text{Li}_2\text{O} \]

The lithium oxide so produced, by dissolving in the corroding solution, not only generates porosity in the growing oxide but also localizes the concentrating of the alkali in the pores of thick oxides accelerating the corrosion even further. Thus during corrosion in concentrated lithium hydroxide solutions, a porous bulk oxide and a high density of fine crystallites near the oxide-alloy interface, similar to that existing during post-transition growth, lead to an acceleration in rate.

The model proposed is able to account for a number of observations reported here and in the literature. In lithium salt solutions and molten salts containing lithium hydroxide, the absence of undissociated LiOH explains the normal corrosion behavior observed in these media. The extent of accelerated corrosion and the amount of undissociated alkali are both functions of temperature and concentration of lithium hydroxide in the solution. In dilute solutions, long-term exposures are thus necessary for the porous post-transition oxide to concentrate the alkali and for accelerated corrosion to occur. Large differences in the amount of lithium analyzed to be present in the oxides under similar corrosion conditions and the lack of a proportionality to the acceleration in corrosion result from the fact that a major part of lithium is held in the pores and can be leached out. Because the concentrating mechanism involves the dissolution of Li_2O produced during the corrosion, an apparent saturation level for lithium in the oxide is attained more readily in concentrated solutions at lower temperatures. When a specimen corroded in the concentrated solution is cross-sectioned and etched, the fine crystallites at the oxide-alloy interface are also dissolved along with the unoxidized alloy, and the pebbly structure observed in the scanning electron micrographs is that of the interface between these fine crystallites and the bulk oxide. The results from the SIMS analysis are qualitative; but there are indications of evidence for the proposed model. The spectra include peaks that could be assigned to OLi and ZrOLi species.

**Conclusions**

At 589 K, Zircaloy-4 undergoes accelerated corrosion, from the very beginning, in 0.5 and 1 M solutions but not in dilute 10^{-3} and 10^{-1} M solutions or in molten salts containing a higher concentration of lithium hydroxide than the concentrated aqueous solutions. Impedance and polarization measurements indicate a high degree of porosity for the oxides formed in the concentrated solutions. X-ray diffraction, atomic absorption, Auger and secondary ion mass spectrometric analyses, indicate the presence of small quantities of lithium in the oxide. A major part of the lithium in the corrosion films is soluble and can be leached out in acid.

A solid solution of lithium in the zirconia matrix cannot explain the accelerated corrosion. An alternative mechanism is proposed.

The amount of alkali remaining undissociated rapidly increases with concentration and
temperature. In concentrated solutions \(\approx 10^{-1}\) M in LiOH, the reaction between this undissociated alkali and the oxygen deficient zirconia, produced by the corrosion, leads to the formation of OLi groups on the surfaces of the oxide crystallites. These surface groups retard their recrystallization and growth and react to form Li₂O. The Li₂O produced accelerates the corrosion by dissolving and generating porosity and at the same time concentrating the solution in the porous oxide to regenerate OLi and Li₂O and sustain the accelerated corrosion.

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**References**


