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Journal of Nuclear Materials 256 (1998) 114–123

journal of nuclear materials

The effect of hydride on the corrosion of Zircaloy-4 in aqueous LiOH solution

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Received 25 November 1997; accepted 19 April 1998

Abstract

Commercial Zircaloy-4 sheets were charged with 230–250 wppm hydrogen by the gas-charging method and were homogenized at 400°C for 72 h in vacuum. The hydrogen charged specimens were corroded in pure water and aqueous LiOH solutions using static autoclaves at 350°C, and then characterized by measuring their weight gains with the corrosion time and observing their microstructures using an optical microscope (O/M) and a scanning electron microscope (SEM). The elemental depth profiles for hydrogen and lithium were measured using a secondary ion mass spectrometry (SIMS) to confirm their distribution at the oxide/metal interface. As the concentration of Li ions in the aqueous LiOH solution increased to more than 30 ppm, the normal Zircaloy-4 specimens corroded abruptly and heavily, forming more Zr-hydrides by the larger amount of absorbed hydrogen at higher Li ion concentrations. The specimens that had been charged with amounts of hydrogen greater than its solubility limit corroded early with a more rapid accerleration than normal specimens, regardless of the corrosion solutions. At longer corrosion times under 220 wppm Li ion concentration conditions, however, normal specimens showed a rather accelerated corrosion rate compared to the hydrogen-charged specimens. These slower corrosion rates of the hydrogen-charged specimens at longer corrosion times under 220 wppm Li ion concentration conditions may be due to the pre-existent Zr-hydride, which causes the hydrogen pick-up into the specimen to be depressed after the formation of the oxide with an appropriate thickness. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In pressurized water reactors, presently, lithium hydroxide (LiOH) is not only added to the primary coolant to maintain its pH, but also to increase its pH to ranges of 7.2–7.4 for high pH operation, which results in a reduction of circuit activity levels. It has been well known that the addition of large amount of LiOH severly accelerates the corrosion of zirconium-based alloys such as Zircaloy-4, which is used as a fuel cladding material. However, the corrosion mechanism of zirconium-based alloys is still not well understand, irrespective of the numerous researchers who have suggested various theories and models during the past 30 yeas. Of the researchers, Hillner and Chirigos [1] reported that corrosion was accelerated by the increasing anionic vacancies caused by the substitution of the Li^+ ion with the Zr^{4+} ion in the oxide layer. Jeong et al. also found that any significant acceleration of the oxidation kinetics for the zirconium-based alloys in equimolar alkali metal hydroxides, such as NaOH, KOH, RbOH, and CsOH, was absent, except in the aqueous LiOH solution. Thus, they insisted that substitution of the Li^+ ion with Zr^{4+}-sites in the oxide layer occurred easily during the corrosion reaction because of the similar ionic sizes of Li^+ and Zr^{4+} ions, and this accelerated the corrosion [2–4]. Moreover, accelerated corrosion behaviors were observed in specimens with hydrogen concentrations as high as the solubility limit or more [5]. Kido [6] and Blat et al. [7] reported that the corrosion of hydrogen-charged

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PII: S0022-3115(98)00066-X

Zircaloy accelerated when the hydrogen level was higher than the limit of solubility at the corrosion temperature. Simultaneously, the metal–hydride, composed mainly of Zr-hydride, was formed in the metal matrix near the front of the oxide layer by hydrogen absorbed from the aqueous corrosion solution during the corrosion reaction. It was also reported by Garde and Johnson that the hydride in the metal was oxidized more easily compared to the matrix and then metal containing the hydride was oxidized more rapidly than the one not containing it [5,8]. Thus, the zirconium-based alloys having many Zr-hydrides are expected to be rapidly corroded in various corrosion solutions, but how the pre-existent Zr-hydride, already formed in the metal matrix, affects the corrosion behaviors of zirconium-based alloys has not been studied widely yet, especially in an aqueous LiOH solution.

Therefore, there is an ample interest in the accelerated effect of pre-existent Zr-hydride on the corrosion of Zircaloy-4 materials in aqueous LiOH solution at 350°C. In this paper, the corrosion behaviors of the both normal Zircaloy-4 material and hydrogen-charged Zircaloy-4 material with hydrogen concentration at levels greater than the solubility limit (~120 wppm H at 360°C [5]) before the corrosion tests were carried out in detail in pure water and aqueous LiOH solutions with various Li ion concentrations.

2. Experimental procedures

Rectangular-shaped specimens, 15 by 25 mm in size, were cut from commercial Zircaloy-4 sheet material containing 1.5 wt% Sn, 0.2 wt% Fe, and 0.1 wt% Cr. A typical microstructure of the Zircaloy-4 sheet material is shown in Fig. 1. The specimens were mechanically ground using SiC paper and chemically polished using a pickling solution (a mixture of 5% HF, 45% HNO_3,and 50% H_2O) in the final step. The polished specimens with thickness of 0.6 mm were homogenized at 400°C in a vacuum for 72 h after being charged with hydrogen from a gas phase to concentrations 230–250 wppm. Then, corrosion tests were conducted in both pure water and aqueous LiOH solution with various Li concentrations for different times under static stainless steel autoclaves at 350°C and 17.5 MPa.

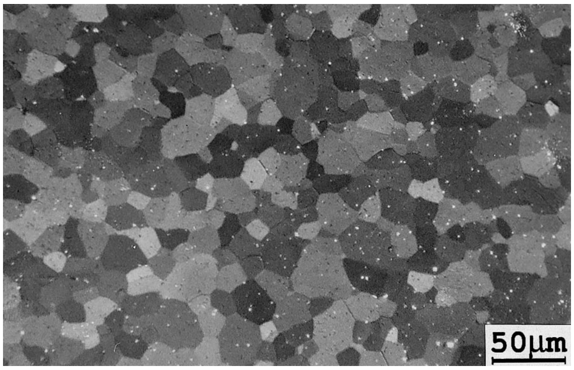

Fig. 1. A typical microstructure for the commercial Zircaloy-4 sheet materials.

The corroded specimens were characterized by measuring their weight gains with the corrosion time. An optical microscope (O/M) and a scanning electron microscope (SEM) were used to observe the thickness and microstructure of the oxide in the corroded specimens. The amounts of hydrogen in the specimen absorbed by the gas-charging as well as the hydrogen contents in the specimens before and after the corrosion test were quantitatively analyzed using the extraction method and a hydrogen analyzer (Leco Co.). The elemental depth profiles for hydrogen and lithium were measured using secondary ion mass spectrometry (SIMS, CAMECA IMS4F) to characterize their distribution at the oxide/metal interface after pre-sputtering for 60 s to remove the surface contaminants. Then, the SIMS was equipped with an oxygen ion (O_2^+) source to scan the specimen area of 50×50 μm^2 with an incident angle of about 60° and was controlled to detect the secondary ion at a direction perpendicular to the scanned area.

3. Results and discussion

Fig. 2 shows the corrosion behavior of the commercial Zircaloy-4 alloy corroded in an aqueous LiOH solution with various Li ion concentrations at 350°C for 550 days. The specimens corroded under pure water or 2.2 wppm Li ion concentration conditions show almost identical cyclic corrosion behaviors with the first transition after about 180 days. For the 30 wppm Li ion concentration, they show also similar behaviors as the pure water over the entire range, but the first transition (at about 120 days) occurs earlier compared to their behaviors for the pure water condition. The difference between the weight gains obtained from pure water and 30 wppm Li ion concentration conditions increases continuously with an increase in exposure time. It was reported that a concentration of 30 wppm Li ions was the critical point to accelerate corrosion for the Zircaloy-4 alloy [9]. Above 220 wppm Li ion concentrations, which may be acquired by local boiling on the surface of the fuel cladding in a nuclear power plant, the alloys corrode very rapidly and heavily, showing very short pre-transition regions. Therefore, it is thought that corrosion of the Zircaloy-4 alloy accelerates heavily with an increase in Li ion concentration in aqueous LiOH solutions.

The absorbed hydrogen and hydrogen pick-up fraction obtained by the corrosion tests under pure water and 220 wppm Li ion concentration conditions are

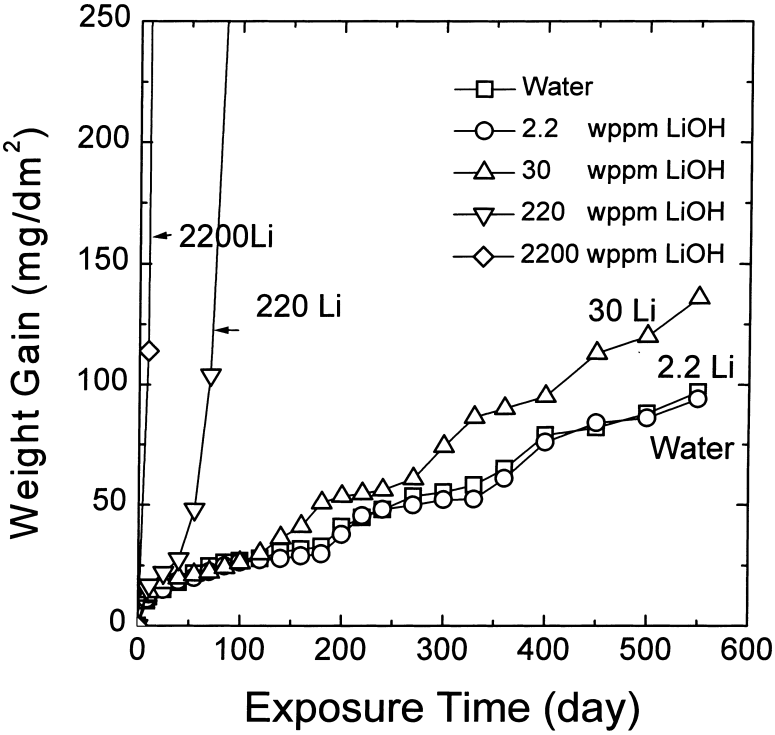

Fig. 2. Corrosion behaviors of the Zircaloy-4 in pure water and the various LiOH solutions at 350°C.

shown in Fig. 3, where the hydrogen pick-up fraction refers to the ratio of the measured hydrogen concentration to the hydrogen amount theoretically generated by the corrosion reaction. In pure water, when weight gain in the post-transition increases up to two times as large as that in the pre-transition, the absorbed hydrogen content almost up to two times that in the pre-transition as well. However, their hydrogen pick-up fractions have no changes regardless of weight gains after the transition. In the 220 wppm Li ion concentration, on the other hand, when the weight gain in the post-transition increases to an amount nine times as large as that in the pre-transition, the absorbed hydrogen content increases by up to 17 times compared to that in the pre-transition. As a result, the hydrogen pick-up fraction in the 220 wppm Li ion condition increases by up to about two times as large as that in the pre-transition. Thus, it can be said that the hydrogen pick-up fraction in the pure water condition does not change with an increase in weight gain but that in the 220 wppm Li ion concentration condition, it increases greatly with weight gain after the transition. It can be also said that an aqueous LiOH solution accelerates the corrosion of Zircaloy-4 alloys and makes them absorb a large amount of the hydrogen during the corrosion reaction.

Absorbed hydrogen at concentrations greater than its solubility limit (~120 wppm H at 360°C) in the Zircaloy-4 alloy at 350°C would precipitate as Zr-hydride in the metal matrix. To investigate in detail the effect of Zr-hydride on corrosion, Zircaloy-4 specimens charged with 230–250 ppm hydrogen were corroded using both pure water and an aqueous LiOH solution with a 220 wppm Li ion concentration at 350°C. The results are shown in Fig. 4. In pure water, all corroded specimens show the same behavior up to 80 days, regardless of the charging of hydrogen into the specimens, but after 80 days, the corrosion of the hydrogen-charged specimens start to slightly accelerate compared to normal specimens (hydrogen-uncharged specimens). In 220 wppm Li ion concentrations, the hydrogen-charged specimens show rapid increase in the corrosion rate after 30 days, whereas normal specimens start such a trend after 43 days, showing severe corrosions compared to those in pure water. After 52 days, the corrosion rates for the hydrogen-charged specimens decrease gradually with an increase in exposure time, and then their corrosion rates become slower than those of normal specimens. Fig. 5 shows photos of the cross-sectional microstructure of a normal specimen corroded in a 220 wppm Li ion concentration for 550 days. In general, oxide grown in 220 wppm Li ion concentration conditions grows ununiformly, like a nodular-type oxide, due to localized accelerated corrosion, as shown in Fig. 5(A). It can be observed from the enlarged SEM micrograph of Fig. 5(B) that many

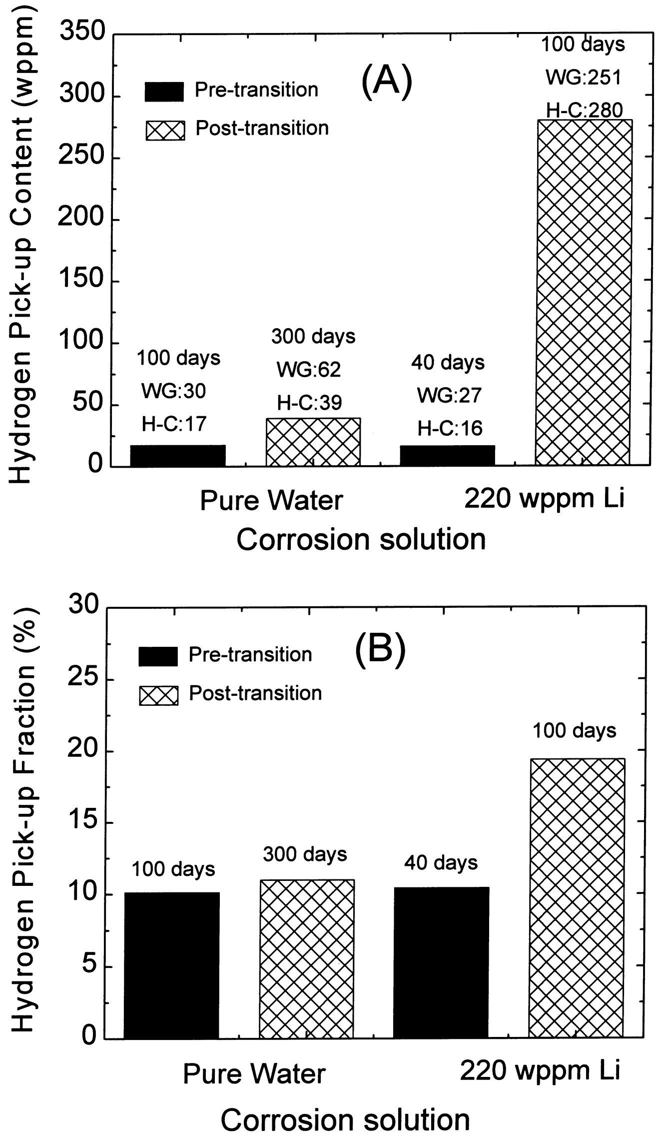

Fig. 3. Comparison of hydrogen pick-up for the Zircaloy-4 alloys in the pure water and the 220 wppm LiOH aqueous solution at 350°C. (WG: weight gain, H-C: Hydrogen pick-up content).

Zr-hydrides formed near the front of the oxide layer during the corrosion reaction. It was also reported that the hydride in the metal was oxidized easily compared to the matrix and then the metal containing the hydride was oxidized more rapidly than the one not containing it [5,8]. Thus it can be thought that the growth of the oxide will be affected and enhanced continuously by the existence of the Zr-hydirde. Therefore, it can be also assumed from the corrosion behaviors that the hydrogen-charged specimens having many Zr-hydride precipitates in the matrix corroded more easily than the normal specimens due to rapid oxidation of the Zr-hydride. As shown in Fig. 4, however, the normal specimen corroded rather more rapidly than the hydrogen-charged specimens at longer corrosion times under 220 wppm Li ion concentration conditions.

To understand the slower corrosion rate of hydrogen-charged specimens at longer corrosion times, the distributions of lithium and hydrogen in the oxide, metal, and oxide/metal interface were measured using SIMS with an oxygen ion source after corrosion tests of hydrogen-charged specimens and normal specimens.

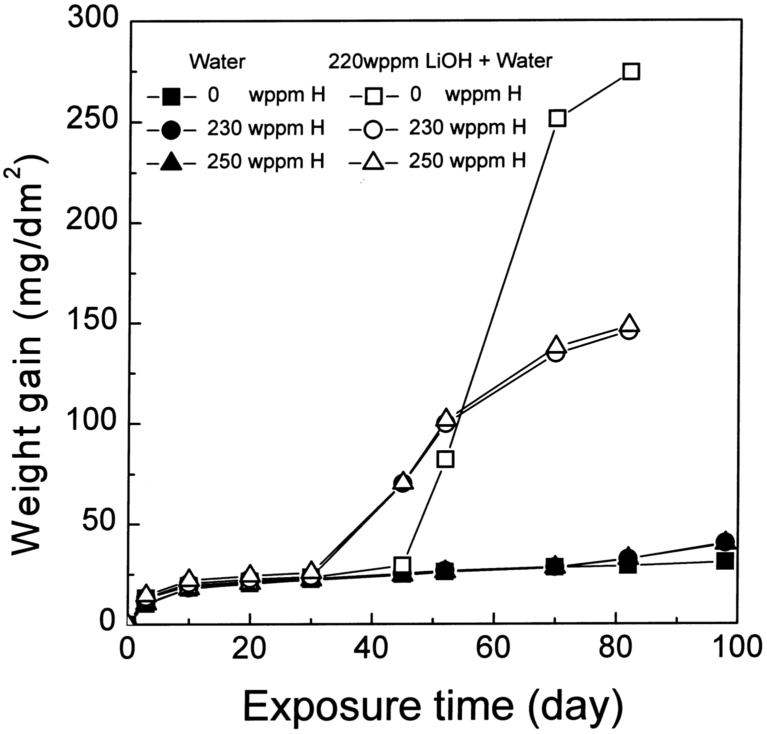

Fig. 4. Corrosion behaviors of the hydrogen charged Zircaloy-4 specimens corroded at 350°C.

Figs. 6–8 show the depth profiles for a normal specimen corroded in pure water conditions, and for normal specimens and the hydrogen-charged specimens corroded in a 220 wppm Li ion concentration conditions, for 52 days at 350°C. The specimens corroded in a 220 wppm Li ion concentration for 52 days were selected and analyzed because they had similar weight gains, as shown in Fig. 4. The thickness of the oxide films were measured using SEM. It was also confirmed that the oxide film thickness almost agreed with the location of the interface determined near the starting point of the constant signal for Zr^{++} from the surface to the metal matrix with sputter time. Determining the location of the oxide/metal interface is possible from the different intensities of Zr^{++} due to the sputter yields in the oxide and metal. It is also possible to compare the concentrations of hydrogen and lithium qualitatively when the Zr^{++} intensity in the metal side is assumed to be equal in all environments. Here, the intensities for hydrogen and lithium were measured from the signals of H^+ and Li^+, but the Li intensity in Fig. 8 was just measured from the signal of Li_2^+ due to the high intensity of Li^+ over the limitation of the equipment. Also, very low intensities for Zr^{++}, H^+, Li^+ and Li_2^+ near the surface in all spectra may be generally due to fundamental effects occuring in the pre-equilibrium regions at surfaces [10].

The high intensity of hydrogen near the surface of the oxide film, as shown in Fig. 6, indicates that the hydrogen pick-up occurred from an aqueous solution into the metal during the corrosion reaction. As shown in Fig. 7, the relative amount of the hydrogen at the oxide/metal interface of the normal specimen absorbed under a 220 wppm Li ion concentration condition is larger than that under the condition of pure water (Fig. 6). It is even much larger in the case of the hydrogen-charged specimen (Fig. 8). However, it can be known that the hydrogen pick-up content or rate into the metal interior of the normal specimen regardless of the exposure time is higher than the hydrogen-charged specimen in the corrosion condition of a 220 wppm Li ion concentration, as shown in Table 1. Specially, the hydrogen pick-up rate of the normal specimen increases with the exposure time, whereas that of the hydrogen charged specimen decreases with the exposure time. In the case of the hydrogen-charged specimens corroded in a 220 wppm Li ion concentration, the hydrogen intensity increases in parallel with that for Zr^{++} at the metal side with an increase in sputter time. At the same time, the Li_2^+ intensity decreases abruptly with sputter time in this region. Therefore, as shown in Fig. 8, increases in SIMS intensities in the metal region with sputter time are attributed to the general edge effect by the increase of penetration depth of the SIMS ion source into the metal interior when

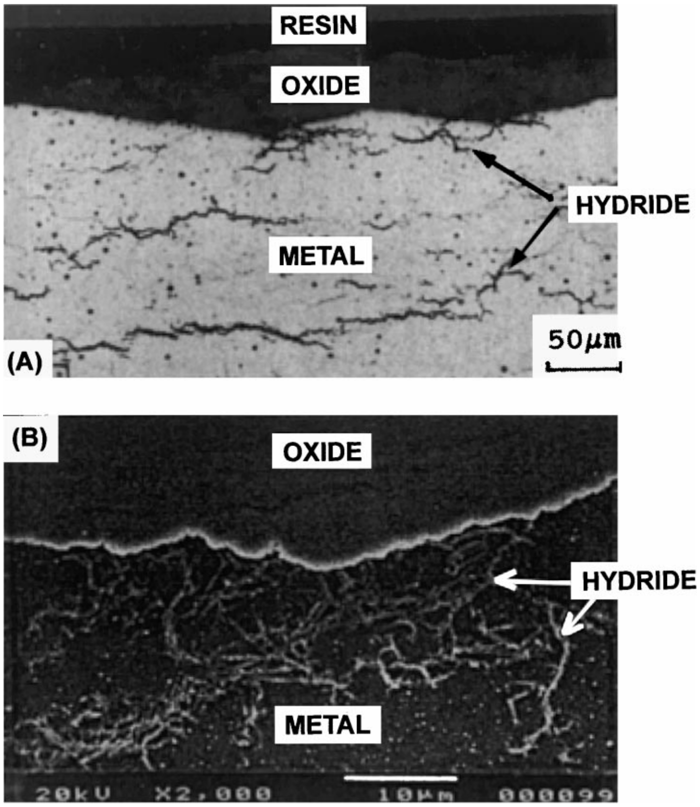

Fig. 5. Optical microscope photograph (A) for many hydrides and nodular-type oxide layer grown in 220 wppm LiOH solution and SEM photograph (B) for the enlarged part of (A) at the oxide/metal interface.

the SIMS ion source has an incident angle of about 60°. From the SIMS data, it can be said that the absorbed hydrogen by the gas-charging method is distributed uniformly, depressing the hydrogen diffusion from the oxide/metal interface into the metal interior with no uptake of lithium at the metal side.

On the other hand, the Li content measured in the oxide layer is higher for the hydrogen-charged specimen than the normal specimen. This indicates that the preexistent Zr-hydride attracts larger amounts of Li ions into the oxide layer, together with depressing the hydrogen pick-up from an aqueous LiOH solution. Jeong et al. [2–4] reported that any significant acceleration in the oxidation kinetics for Zirconium-based alloys in equimolar alkali metal hydroxide solutions, such as NaOH, KOH, RbOH, and CsOH, was absent, except in the aqueous LiOH solution. Therefore, it is likely that the hydrogen-uptake by the negative potential at the oxide/metal interface obtained by the Zr oxidation causes the formation of Zr-hydride near the front of the oxide/metal interface, and then again the hydride attracts a lot of Li-uptake in the oxide layer. Then, the Li-uptake may be accomplished by the easy substitution of a Li^+ ion with a Zr^{4+} -site because of the similar ionic sizes of the Li^+ and Zr^{4+} ions in the oxide layer, as reported by Jeong et al. and Hillner et al.

Fig. 9 shows SEM photographs for the cross-sectional surfaces of specimens corroded in both pure water and a 220 wppm Li ion concentration for 52 days at 350°C. The normal specimen corroded in a 220 wppm Li ion concentration has a relatively uniform oxide layer compared to the hydrogen-charged specimen. The hydrogen-charged specimen (Fig. 9(C)) has a more locally and rapidly corroded oxide layer than the normal specimen (Fig. 9(B)) and even shows a thickness of the thinnest oxide part which is almost the same as that of the normal specimen (Fig. 9(A)) corroded in pure water. It was observed that these trends for the oxide layer thickness were maintained continuously, even after 82 days. Therefore, it can be said that although the hydrogen-charged specimen has locally a thicker oxide layer than the normal specimen due to oxidation of the pre-existent Zr-hydride, the average thickness of its oxide layer becomes smaller than that of the normal specimen at longer corrosion times. It may be that the additional hydrogen pick-up can be depressed because the amount of hydrogen in the hydrogen-charged specimens is larger than the solubility limit (~120 wppm H

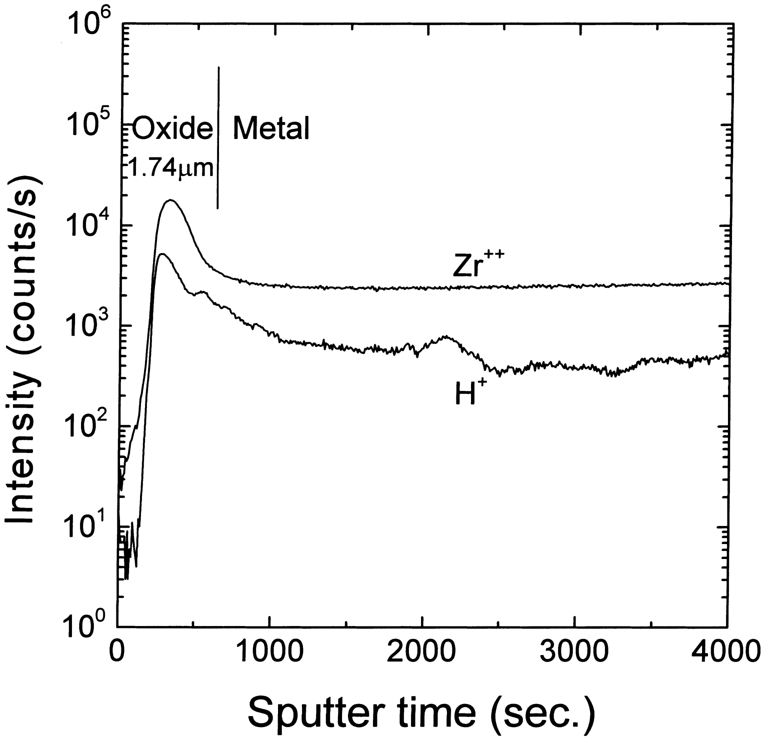

Fig. 6. SIMS depth profiles for the Zircaloy-4 specimen corroded in pure water for 52 days at 350°C.

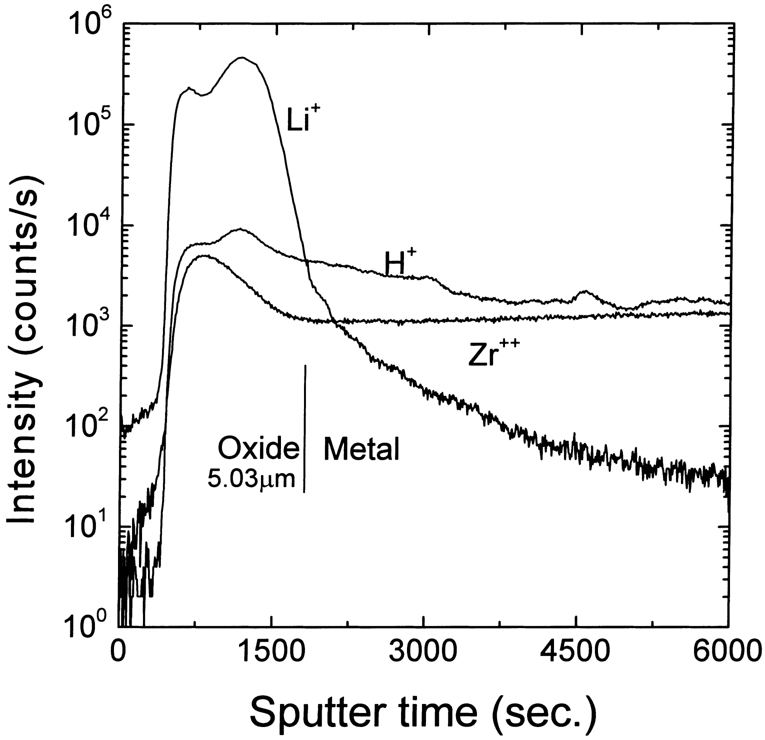

Fig. 7. SIMS depth profiles for the Zircaloy-4 specimen corroded in 220 wppm LIOH aqueous solution for 52 days at 350°C.

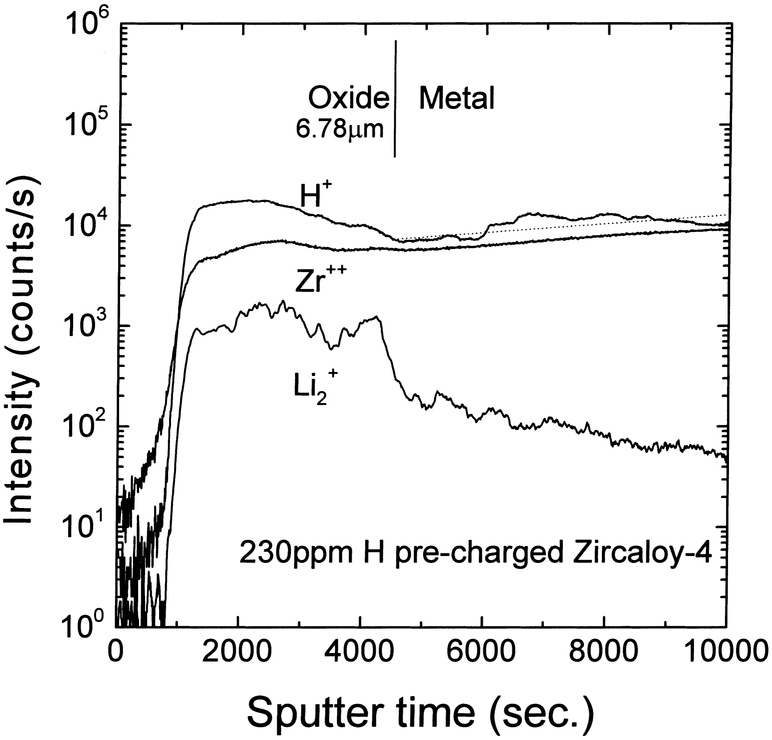

Fig. 8. SIMS depth profiles for the Zircaloy-4 specimen corroded in 220 wppm LIOH aqueous solution for 52 days at 350°C after charging with 230 wppm H.

at 360°C) in the metal. In summary, the pre-existent Zr-hydride in the matrix causes the hydrogen pick-up to be depressed through the oxide layer into the metal at longer corrosion times and then the corrosion rate decreases gradually, although a thick oxide was formed in a short time by the rapid oxidation of the Zr-hydride.

4. Conclusions

Commercial Zircaloy-4 sheets were charged with 230–250 wppm hydrogen by the gas-charging method and homogenized at 400°C for 72 h in a vacuum. The hydrogen-charged specimens were corroded in pure water and aqueous LiOH solutions using static autoclaves at 350°C. The following conclusions can be drawn.

As the concentration of Li ions in the aqueous solution increased, the normal Zircaloy-4 specimens corroded rapidly in more than 30 wppm Li concentrations. This is due to the rapid oxidation of many Zr-hydride precipitates formed by the large amount of absorbed hydrogen, as well as the enhanced oxidation resulting from the increased substitution of Li^{++} ions with Zr^{4+}-sites in the oxide with increases in Li ion concentrations. The

Table 1
Hydrogen pick-up content and rate of the corroded Zircaloy-4 alloy measured after removing the oxide layer

	Intial hydrogen content, W_i (wppm)	Hydrogen content at 52 days, W_{52} (wppm)	Hydrogen content at 82 days, W_{82} (wppm)
		Rate = $(W_{52} - W_i)/52$	Rate = $(W_{82} - W_i)/82$
H not charged specimen	6	89	232
(in 220 wppm LiOH solution)		1.60	2.76
250 wppm H charged specimen	250	312	329
(in 220 wppm LiOH solution).		1.19	0.96

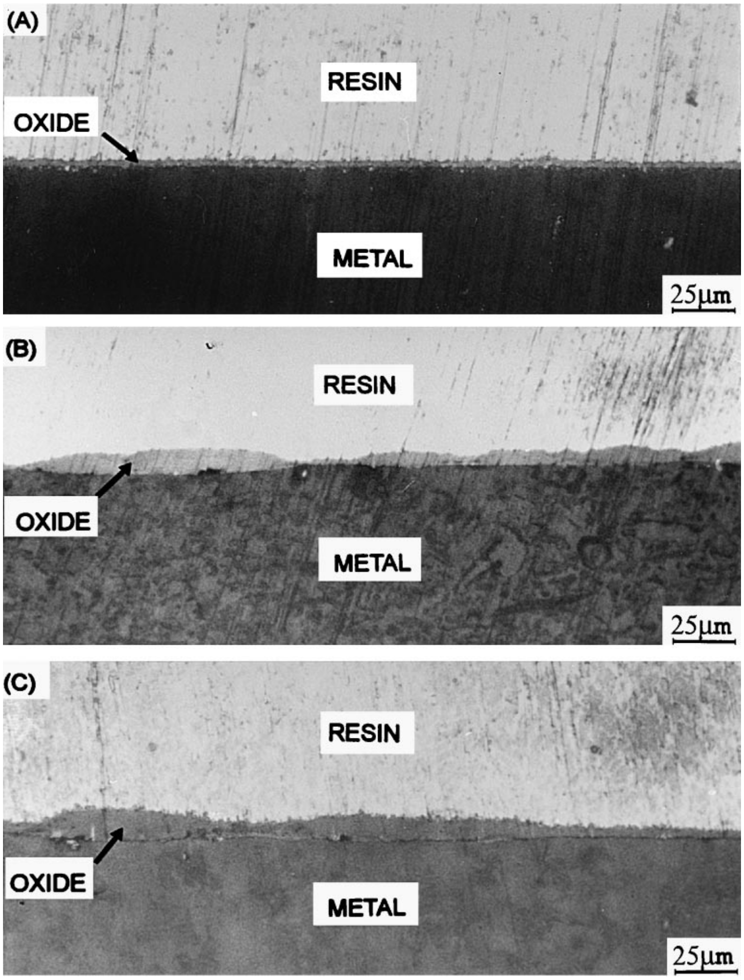

Fig. 9. Optical microscope photographs for the cross-sectional surfaces of the corroded Zircaloy-4 alloys at 350°C for 52 days: (A) the normal specimen in the pure water conditions; (B) the normal specimen in the 220 wppm Li ion concentration conditions; and (C) the hydrogen charged specimen with 230 wppm H in the 220 wppm Li ion concentration conditions.

specimens charged with more hydrogen than their solubility limits (~120 wppm H at 360°C) were corroded earlier with more acceleration than the normal specimens, regardless of the corrosion solutions. At longer corrosion times under 220 wppm Li ion concentration conditions, however, the normal specimens showed a rather more accelerated corrosion rate than the hydrogen-charged specimens. It can, therefore, be thought that the corrosion of the hydrogen-charged specimens accelerated relatively easily with the rapid oxidation of the Zr-hydride in a short time, but the slower corrosion rates of these specimens at longer corrosion times would be due to the pre-existent Zr-hydride, which causes the hydrogen pick-up into the specimen to be depressed after the formation of oxides with appropriate thicknesses.

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