Corrosion characteristics of zirconium alloy with a high temperature pre-formed oxide film

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Abstract

Pre-oxide films were formed on the surface of Zircaloy specimens at high temperatures 700 and 1100 °C and their corrosion characteristics were investigated at 360 °C. The pre-oxides of different thickness were layered with varying annealing times; 0.5–2.3 μm thick films were formed by annealing at 700 °C from 10 to 120 s while oxide layers thinner than 2 μm were not obtained at 1100 °C even with the shortest exposure time 20 s. Cross-sectional studies revealed that the pre-oxides were adherent. Oxidation characteristics of the specimens having pre-oxide layers ranging from 0.5 to 3.7 μm were investigated by measuring weight gain in an autoclave at 360 °C. The specimens with 1–2.3 μm pre-oxide layers exhibited better oxidation resistance than the thinner or thicker oxides. The bare Zircaloy specimen without a pre-oxide layer had the highest weight gain due to the fact that the bare specimen experienced rate transition after 98 days of exposure. Microstructural study showed the possibility that the tetragonal fraction of the pre-oxide affected the weight gain incremental behavior.
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1. Introduction

Zirconium and its alloys are highly active materials. Due to their high reactivity, oxide layers form on their surfaces in the presence of air or water. Accordingly, when Zircaloy (Zry) tubing is placed in pressurized water reactors (PWRs), an oxide layer naturally forms on the outer surface of the Zry tubing. However, the oxide layer that forms on the surface of Zry used in nuclear reactors exhibits the oxidation rate transition (from cubic to linear). Due to this rate transition, the oxide layer thickness increases linearly with time and eventually peels off [1,2]. In addition, in a failed fuel element, oxidation of the cladding inner surface by steam produces hydrogen in the fuel-cladding gap. Hydrogen formation may be enhanced by fission fragment recoil from the fuel into the gap, where water is decomposed into hydrogen and oxygen [3]. Hydrogen eventually penetrates the oxide scale on the cladding inner surface and forms zirconium hydride in the metal. This process can cause secondary cladding failure, manifested by axial splitting due to large hoop stress in the hydrided metal or by hydride blisters or bulges which can lead to small cracks or circumferential breaks that will expose fuel to the coolant [4–6]. Consequently, considerable effort is devoted to development of advanced cladding materials that exhibit both improved waterside corrosion resistance and resistance of internal surfaces to hydriding. Some studies have been done on the corrosion characteristics of prefilmed zirconium alloys [7–9]. However, no systematic study of zirconium alloys with a high temperature pre-formed oxide film has been performed.

The oxide of Zrys in the pre-transition region has been reported to be a mixture of the tetragonal and monoclinic phases in reactors [10–14]. The oxide layer is under high compressive stress and such stress might stabilize the oxide in its tetragonal form, which is normally stable only at temperatures above 1100 °C [15,16]. This compressive stress is relaxed during the growth of the oxide, and the tetragonal phase became destabilized and transformed to the monoclinic phase, thereby inducing the rate transition. Thus, it is believed

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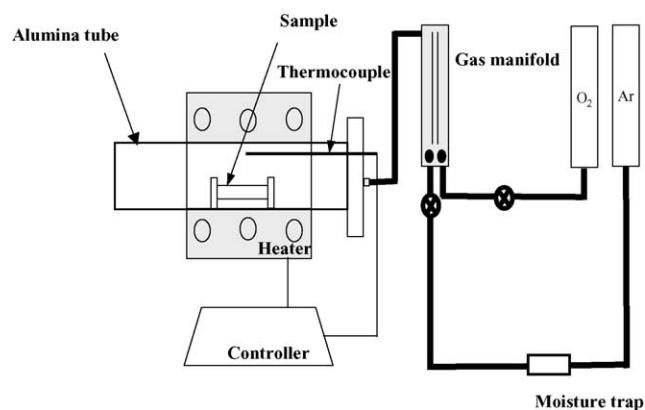*E-mail address:* hshong@iae.re.kr (H.S. Hong).

Fig. 1. Experimental apparatus for Zircaloy oxidation.

that the growth of the oxide on the outer surface of Zry is undesirable in terms of the rate transition and this transition is affected by the reduction of the tetragonal phase in the oxide [12–14,17].

In a preliminary experiment for this study, zirconium oxide was grown to over 100 μm without the rate transition at 1100 °C. It is possible that a thin oxide film formed on the outer surface of Zry during annealing at 1100 °C can be further developed without the rate transition at temperatures found in a nuclear reactor. The aim of this study was to examine the feasibility of introducing a pre-oxide layer on Zry at high temperatures and to see the effect of the pre-oxide on the oxidation characteristics at the low temperature. Accordingly, thin oxide layers with different thickness were prepared on the surface of Zry at high temperatures, and structural characteristics of the oxide layer were investigated. In addition, the oxidation resistance of the specimens having pre-oxide layers was characterized by evaluating weight gain.

2. Experimental

2.1. Pre-oxide formation

Conventional Zircaloy-4 (Zry-4) claddings were used in this study. These claddings were annealed at 700 and 1100 °C to form a pre-oxide film on the surface of Zry-4.

The experimental apparatus for the formation of pre-oxide layer is shown in Fig. 1. The apparatus includes the sample oxidation chamber (an alumina furnace tube) and the gas-supply unit consisting of gas cylinders and gas purifiers. In a preliminary test, the temperature gradient along the sample length was determined by locating two thermocouples at the center and at the axial location corresponding to the end of the sample. The temperature difference was found to be less than 3 °C.

The pre-filming experiment was conducted in a flow mode using O_2-added argon gas (20 vol.% oxygen) instead of steam to avoid hydrogen pick-up. The argon gas was purified with a moisture trap. The experimental procedure was established from the preliminary experiments. Firstly, the temperature was increased to 700 or 1100 °C under pure argon gas and oxygen gas was introduced to the flowing argon gas using the gas manifold. The sample was loaded in the tube furnace by pushing from the glove box with pincers and oxidized for the calculated amount of time. After the oxidation, the oxygen-argon gas mixture inside of the tube furnace was purged and replaced with the pure argon gas.

Five specimens were oxidized at 700 °C and four specimens at 1100 °C, resulting in uniform oxide layers ranging from 0.5 to 13 microns thick. The thickness was determined using an optical microscope. The sample matrix is shown in Table 1.

2.2. Oxidation test and microstructural analysis

Oxidation tests were conducted in autoclaves filled with pure water at 360 °C under a pressure of 180 bar. Oxidation test specimens with the dimension of 20 mm (*L*) × 9 mm (o.d.) were prepared using the pre-filmed specimens at 700 and 1100 °C. The specimens were cleaned with acetone before testing. The test followed the ASTM G2 method [18]. The oxidation behavior was evaluated by the weight gain (ΔW) as a function of exposure time.

Raman spectroscopy was used to identify the crystal structure of the oxide surface. The methods for characterizing the ZrO_2 structure by a Raman spectrometer have been reported elsewhere [19–21]. A Raman spectrometer with 200 mW argon-ion laser source at a wavelength of 488 nm was used.

Table 1
Measured and estimated oxide thicknesses

Sample number	Oxidation time (s)	Temperature (°C)	Measured oxide thickness (μm)[a]	Estimated oxide thickness (μm)[b]
1	10	700	0.5	0.65
2	20	700	1 ± 0.1	1.03
3	30	700	1.3 ± 0.1	1.31
4	60	700	2.3 ± 0.05	1.92
5	120	700	2.5 ± 0.05	2.75
6	20	1100	3.7 ± 0.1	4.3
7	60	1100	6.7 ± 0.1	6.2
8	120	1100	7.5 ± 0.1	7.7
9	600	1100	13 ± 0.1	13
10	None	None	–	

[a] No axial or circumferential oxide thickness change was observed.
[b] From Fig. 2.

A spectral range from 150 to 500 cm^{-1} was used. The Raman measurements were made at room temperature.

3. Result and discussions

Fig. 2 shows the pre-formed oxide film thickness as a function of exposure time to the O$_2$-Ar gas mixture at 1100 and 700 °C. The best-fit curve in Fig. 2 is

$$\delta^3 = At + B \tag{1}$$

where δ: oxide layer thickness (μm); t: time (s).

The fitting coefficients are $A = 3.71$ and $B = 12.1$ for 1100 °C, and $A = 0.17$ and $B = -1.95$ for 700 °C. Results from Fig. 2 show that the fitting of Eq. (1) is quite satisfactory. To calculate a fit, a single rate law was assumed in this study. Combination of rate laws or any single rate law could fit due to few data points, however, the cubic rate law was found to be the best-fit from the regression analysis. For a comparison, the estimated oxide thicknesses from the curve are listed in the last column of Table 1. As shown in Fig. 2, 0.5–2.3 μm thick oxides could be obtained by annealing at 700 °C from

10 s up to 60 s whereas relatively thicker oxides in the range 3.7–6.7 μm were formed at 1100 °C for the same periods. Post-visual examinations showed that the oxides were shiny black. From the cross-sectional study using an optical microscope, it was observed that the oxide was adherent. In all cases, a thin white layer was observed beneath the oxide layer. This white layer was thought to be an oxygen-rich zone that when polished in cross-section generally appears whiter than the rest of metal. Oxygen is thermodynamically more stable in solid solution than it is in an oxide so the high temperature and reduced oxygen partial pressure would have caused dissolution of the oxide film at the oxide/metal interface, thereby resulting in the oxygen-rich zone beneath the oxide layer.

Oxidation characteristics of five specimens with pre-oxide films (annealed at 700 °C, see Table 1) were investigated by measuring incremental weight gains at 360 °C in an autoclave.

The incremental weight gain versus oxidation time curves for six specimens including a bare Zry-4 cladding are represented up to 168 days exposure in Fig. 3. The weight gain generally increased with the exposure time during the oxidation. The weight gain difference between the specimens was not large enough to be clearly distinguished when the exposure time was less than 50 days. However, the bare Zry-4
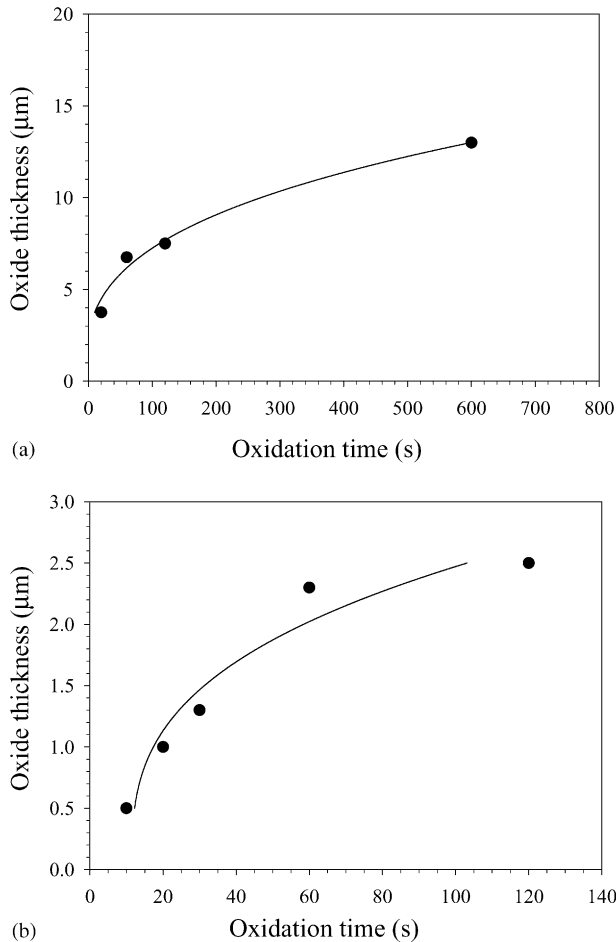

Fig. 2. Oxide thickness variation with time at (a) 1100 °C and (b) 700 °C.
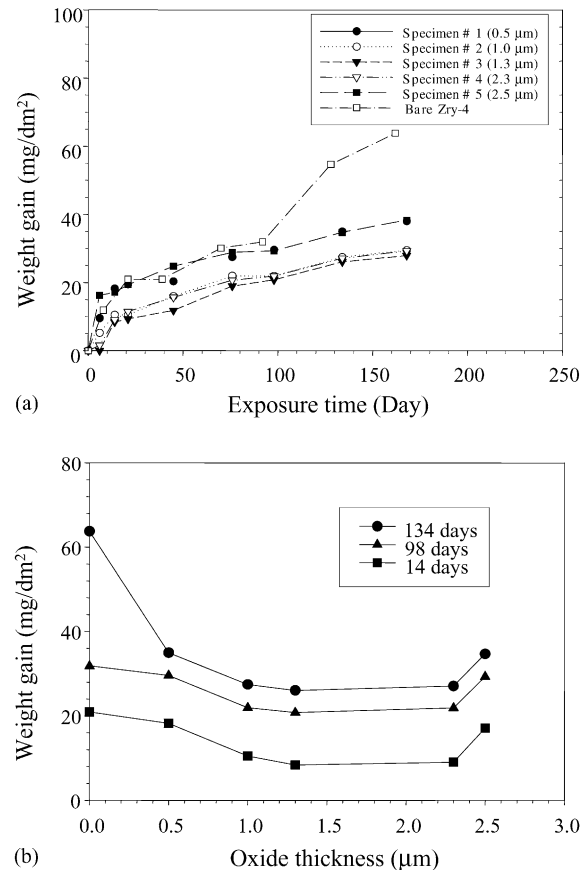

Fig. 3. Weight gain as a function of (a) exposure time and (b) oxide thickness at 360 °C.

specimen showed a rate transition from the cubic oxidation rate to the linear oxidation rate after the 98 days exposure as shown in Fig. 3(a) and the weight gain was rapidly increased. Thus, in the long-term oxidation of 168 days, it is obvious that the weight gain of the bare Zry-4 specimen was much larger than the others. Although the specimens with 0.5 and 2.5 μm thick pre-oxide layers had the similar incremental weight gain to the bare Zry specimen, these specimens did not show the rate transition up to 168 days. The different oxide structure before the transition might be responsible for the different transition behavior. Fig. 3(b) shows that specimens having an oxide layer which ranged from 1 to 2.3 μm exhibited the better resistance to the oxidation at 360 °C water than the thinner or thicker oxides; the weight gains of the specimens with the 2.5 μm oxide film or with 0.5 μm oxide film were higher than the specimen with 1 μm oxide film by about 35%. It is thought that the incremental weight gains are less on a pre-oxidized specimen that is following a cubic rate law, and depend on the pre-oxide thickness of the pre-oxidized specimen. The existing adherent film would slow the delivery of oxygen to the inner interface. For a fixed interval of time, the weight gain will be larger when the oxide film is thin than for the same time interval when the film is thick. However, too thick films may have a higher incremental weight gain due to the proximity to the transition. In this study, it was intended to form pre-oxide films with the same thickness at the different temperatures 700 and 1100 °C resulting in different microstructure to see the effect of oxide structure on the weight gain change. As shown in Fig. 2, 0.5–2.3 μm thick oxides could be obtained at 700 °C within 60 s. However, at the higher temperature 1100 °C the oxidation rate was so fast that it was impossible to obtain an oxide layer less than 2 μm thick. At the shortest exposure time of 20 s, the thinnest oxide layer was 3.7 μm thick. Thus, it was not possible to obtain the same oxide thickness less than 2 μm at the two different temperatures.

The crystal structure of the oxide formed during annealing at 700 °C was analyzed by Raman spectroscopy to examine its effect on the weight gain change. The quantitative evaluation of the amount of the tetragonal phase in the oxide was done with the equation

$$\% \text{ tetragonal-ZrO}_2 = \frac{I[(280)_t)]}{I[(180)_m + (189)_m + (280)_t]} \qquad (2)$$

where I represents the intensity of the Raman lines and the subscripts m and t represent the monoclinic and tetragonal phase, respectively.

The oxide was found to be a mixture of the tetragonal and monoclinic phase. Tetragonal fraction of the oxide ranged from 30 to 33%. Fig. 4 shows the relationship between the tetragonal fraction of the pre-formed oxide film and the incremental weight gain obtained from the oxidation at 360 °C. There was an inverse relationship between weight gain change and the fraction of the tetragonal phase in this study. When the weight gain was higher, the tetragonal fraction was lower and this relationship was consistent
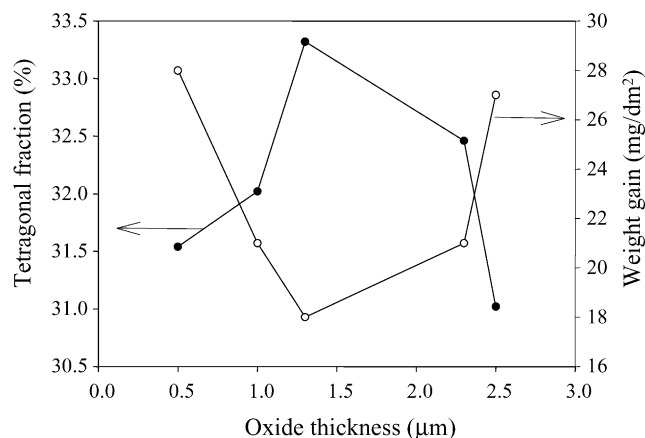

Fig. 4. Comparison between tetragonal phase and weight gain.

throughout the specimens. Not enough specimens were analyzed to correlate accurately the weight gain change with the tetragonal fraction. Available data suggest that the weight gain change is inversely proportional to the tetragonal phase fraction showing the possibility that pre-oxides that consist mostly of a tetragonal phase might have improved oxidation resistance.

The primary aim of the study is to form a thin oxide film consisting mostly of a tetragonal phase on a Zry matrix and to assess the benefit of the intentional formation of a tetra-ZrO₂ film by measuring weight gain at a designed temperature of PWRs. From the Raman study, the oxide formed at 700 °C was found to have a relatively low tetragonal fraction of 30–33%. Thus, in order to obtain correlations between the tetragonal fractions, annealing temperature and weight gain, a systematic study of the oxides formed at higher temperatures than 700 °C is necessary. Additional studies are currently underway investigating how to form a thin oxide layer at high temperatures and how to avoid unnecessary microstructural changes in Zry matrix by employing techniques such as a laser surface treatment and rapid thermal processing (RTP) using a W-halogen lamp.

4. Conclusions

1. Black, adherent oxides were formed on the outer surface of Zircaloy specimens after oxidation at 700 and 1100 °C. In terms of the oxidation time, it was easier to control the oxide thickness when the temperature was lower. In the case of annealing at 700 °C, 0.5–2.5 μm thick oxides could be obtained up to 120 s whereas the oxide grew fast at 1100 °C so that an oxide layer less than 2 μm could not be obtained in the present experiment.
2. In autoclave tests for 168 days exposure at 360 °C, the optimum pre-oxide thickness was found to be in the range 1–2.3 μm. The weight gains with the oxide film in this range were lower than those with thicker or thinner oxides.

3. The Zry-4 specimen without the pre-oxide layer had much higher weight gain than all the pre-oxidized specimens at 700 °C for 168 days exposure. The bare Zry-4 specimen showed a rate transition from the cubic oxidation rate to the linear oxidation rate after the 98 days exposure whereas the other specimens with the pre-oxide did not show the rate transition up to 168 days. The initial black oxide in the pre-transition region changed to a porous white or gray oxide after the rate transition.

4. The pre-oxide formed at 700 °C was a mixture of the tetragonal and monoclinic phase. There was an inverse relationship between weight gain change and the fraction of the tetragonal phase in this study. There is the possibility that pre-oxides that consist mostly of a tetragonal phase might have improved oxidation resistance.

References

[1] E. Hillner, in: Third International Symposium on Zirconium in the Nuclear Industry, ASTM-STP, vol. 633, 1977, p. 211.

[2] T. Ahmed, L.H. Keys, J. Less-Common Metals 39 (1975) 99.

[3] C.Y. Li, D.R. Olander, Rad. Phys. Chem. 54 (1999) 301.

[4] J.C. Clayton, in: Eighth International Symposium on Zirconium in the Nuclear Industry, ASTM STP, vol. 1023, 1989, p. 266.

[5] D.R. Olander, S. Vaknin, Secondary hydriding of defected Zircaloy-clad fuel rods, EPRI TR-101773, 1993.

[6] R.L. Yang, O. Ozer, S.K. Yagnik, B. Cheng, H.H. Klepfer, N. Kjaer-Pedersen, P. Rank, EPRI.

[7] S. Kass, Corrosion 23 (1967) 374.

[8] D.E. Thomas, S. Kass, J. Electrochem. Soc. 103 (1956) 478.

[9] J.N. Wanklyn, D.W. Silvester, J. Electrochem. Soc. 105 (1958) 647.

[10] H.S. Hong, S.J. Kim, K.S. Lee, J. Nucl. Mater. 238 (1996) 211.

[11] H.S. Hong, S.J. Kim, K.S. Lee, J. Nucl. Mater. 273 (1999) 177.

[12] H.S. Hong, J.S. Moon, S.J. Kim, K.S. Lee, J. Nucl. Mater. 297 (2001) 113.

[13] H.S. Hong, S.J. Kim, K.S. Lee, J. Nucl. Mater. 304 (2002) 8.

[14] J. Godlewsky, J.P. Gros, M. Lambertin, J.F. Wadier, H. Weidinger, in: Ninth International Symposium on Zirconium in the Nuclear Industry, ASTM-STP, vol. 1132, 1991, p. 316.

[15] G.L. Kulcinksi, J. Am. Ceram. Soc. 51 (1968) 582.

[16] C. Roy, G. David, J. Nucl. Mater. 37 (1970) 71.

[17] T. Arima, T. Masuzumi, K. Furuya, K. Idemitsu, Y. Inagaki, J. Nucl. Mater. 294 (2001) 148.

[18] ASTM G-2, Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680°F or in Steam at 750°F, 1993, p. 47.

[19] D.R. Clark, F. Adar, J. Am. Ceram. Soc. 65 (1982) 284.

[20] R.C. Gavie, P.S. Nicholson, J. Am. Ceram. Soc. 55 (1972) 303.

[21] V.G. Keramidas, W.B. White, J. Am. Ceram. Soc. 57 (1974) 22.