Title: Depth profile of oxide volume fractions of Zircaloy-2 in high-temperature steam: an *in-situ* synchrotron radiation study

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Abstract

To study the steam oxidation behavior of Zircaloy-2, a high-energy synchrotron X-ray diffraction technique was applied to perform an *in-situ* oxidation measurement. The depth profiles of oxide volume fractions were obtained at both 600 and 800°C. Multiple layers, including ZrO₂ scale, ($\alpha + \beta$) Zr matrix with ZrO₂ incursions, and ($\alpha + \beta$) Zr matrix, were mapped according to the volume fraction of each phase. The volume fractions of these phases were observed to change gradually with different distances to the surface, without a sharp edge distinguishing each of the layers. The ZrO₂ consisted of tetragonal and monoclinic crystal structures, which were observed to coexist with different ratios of volume fractions in depth. The higher amount of tetragonal ZrO₂ observed in the very inner region of the oxidizing Zircaloy sample indicates that the tetragonal crystal structure is the *ab initio* phase type, in which new oxide molecules form at the metal-oxide interface.

1. Introduction

Since the beginning of the commercial use of zirconium alloys as fuel cladding materials, the oxidation of zirconium alloys has been extensively investigated in various environments, including water [1-3], air [4], and steam [5-20]. Special interest has been paid to the steam environment due to its similarity to the environment encountered during a loss-of-coolant accident (LOCA). The oxidation mechanisms and kinetics in steam have been widely studied at different temperatures and pressures. [5-20] The recent nuclear accident at Fukushima increased the importance of more fundamental research on the corrosion behavior of zirconium alloys. [21]

Beyond the traditional optical and scanning electronic microscopic (OM and SEM) analyses for determining the oxidation scale, multiple new techniques for studying microstructural characterizations have been applied to the research of oxidation behavior of various zirconium

alloys. Negyesi et al. combined secondary ion mass spectrometry (SIMS), wavelength dispersive spectroscopy (WDS), thermal energy analyzer (TEA), and microhardness measurements in order to investigate the Zr1Nb-O phase diagram [22]. Raman spectrometry was employed by Bouvier et al.[2] and Kadiri et al.[4] in order to study the pressure-temperature phase diagrams of zirconia and its breakaway oxidation phenomenon (which was also examined by atomic force microscopy), respectively. With the recently developed focused ion beam (FIB) slice-and-view technique, the corrosion microstructural characteristics can be preserved for transmission electron microscopy (TEM) analysis. Tejlund et al. [14] and Park et al.[18] have studied the oxide scales using TEM and high-resolution TEM (HRTEM), respectively. In addition to the microstructural characterizations, the study of oxidation kinetics of zirconium alloys, which usually requires time-resolved measurements, has been performed by Moalem and Olander [15] and Baek et al.[9] using a gravimetric method and a thermogravimetric analyzer (TGA), respectively.

In the last few years, synchrotron radiation has been used extensively as a non-destructive technique in material research due to its unique properties, which include its extended spectral range, high intensity, and high degree of polarization [23]. Different synchrotron radiation techniques, including X-ray diffraction [1], X-ray fluorescence [10], and X-ray absorption near-edge structure spectroscopy (XANES) [20] have also been recently employed to characterize the oxidation process of zirconium. The goal of the present study is to use, for the first time, high energy X-ray diffraction to study the steam oxidation behavior of Zircaloy-2, the cladding material used in the Fukushima Daiichi nuclear plants. Beyond the conventional methods used to characterize oxidation microstructural characteristics, such as SEM, TEM, and SIMS, which essentially measure the post-exposure samples, high-energy X-ray diffraction characterizes the Zircaloy during high-temperature steam oxidation. From this *in-situ* measurement, we directly

accessed the depth profile of volume fractions for various phases (α and β zirconium matrix, and monoclinic and tetragonal Zr zirconia) during steam oxidations.

2. Materials and Experimental Procedures

2.1. Materials

A boiling water reactor (BWR) 9×9 type Zircaloy-2 (Zry-2) cladding was employed in the steam oxidation experiment. The cladding has a Zirconium liner on the cladding inner surface (~10% of the wall thickness). This liner is softer than the Zry-2 matrix, and was developed in order to reduce fuel-pellet/cladding mechanical interaction (PCMI) during reactor operations. The outer and inner diameters of the cladding are 10.3 and 8.97 mm, respectively, and the thickness of the liner is ~0.07 mm. More details on the Zry-2 cladding in this study can be found in ref. [24]. In order to fit in the steam apparatus, a ring-shaped specimen with a length of 2.5 mm was cut from the cladding, as displayed in Fig. 1.

2.2. Experimental Setup for Synchrotron X-ray Diffraction

The *in-situ* steam oxidation measurements with high-energy X-ray diffraction were carried out at the 1-ID beamline at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). The experimental setup is shown in Fig. 2. Similar setups have been used to analyze various metallic materials [25-31], but this setup is unique in that it contains an apparatus that uninterruptedly supplies steam to oxidize the Zry-2 specimen at controlled temperatures. X-ray diffraction measurements were performed continuously during the steam oxidation by using a monochromatic 86 keV ($\lambda = 0.01442$ nm) X-ray beam with a beam size of $10 \times 10 \mu\text{m}^2$. The diffracted X-ray was collected by a GE angio-type area detector. The distance between the sample and the detector was ~2.08 m. In order to measure the local oxidation features, X-ray scans with a step distance of 10 μm were conducted along the Y direction with penetration

through the specimen in the **Z direction** (Fig. 1). Each complete X-ray scan along the thickness direction (i.e. radial scan) consisted of 110 X-ray diffraction measurements, covering a distance of 1100 μm from beyond the outer surface to the inner surface of the Zry-2 cladding. Each X-ray diffraction measurement took 7 seconds for data acquisition, processing, and storage, and a complete X-ray scan took 770 seconds in total.

The temperature control during the experiment is shown in Fig. 3. Before increasing the temperature, a baseline measurement was performed to determine the crystal structure of the Zry-2. Then, the specimen was heated and maintained at 400°C, 600°C, and 800°C for XRD measurements.

3.3. Quantitative analysis of diffraction

The Zry-2 specimen was penetrated with the high-energy synchrotron X-ray, and a large diffraction volume sufficient to represent the bulk properties was attained. The quantitative interpretation from X-ray diffraction for volume fraction of different phases is based on the principle that the total integrated intensity of all diffraction peaks for each phase in a mixture is proportional to the volume fraction of that phase. [32] The volume fraction for each of the phases within the Zry-2 were calculated by:

$$V_i = \frac{\frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_i^j}}{\frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_{\alpha\text{Zr}}^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_{\beta\text{Zr}}^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_{m-\text{ZrO}_2}^j} + \frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_{t-\text{ZrO}_2}^j}}, \quad (\text{Eq.1})$$

where, V_i is the volume fraction of each of the phases; i represents one of four possible phases: 1) α Zr, 2) β Zr, 3) monoclinic ZrO_2 , and 4) tetragonal ZrO_2 , with respective subscripts of αZr , βZr , $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$; I_i^j is the intensity of the reflection of j (for a specific hkl) for the phase i ; n_i is

the number of available reflections for a certain phase; and R_i^j is the material scattering factor for a specific phase (i) and a reflection (j), which can be expressed as:

$$R_{hkl} = \left(\frac{1}{V^2}\right) [F]^2 P \left(\frac{1 + \cos^2(2\theta)}{\sin^2(\theta) \cos(\theta)}\right) e^{-2m} \quad (\text{Eq.2})$$

where V is the crystal cell volume; F is the structure factor; P is the multiplicity factor;

$\left(\frac{1 + \cos^2(2\theta)}{\sin^2(\theta) \cos(\theta)}\right)$ is the Lorentz-polarization factor as a function of θ ; and e^{-2m} is the temperature

factor. Equation 1 enables simultaneous calculation of the volume fraction of α Zr, β Zr, monoclinic ZrO_2 , and tetragonal ZrO_2 in Zircaloy during steam oxidation from a single XRD

scan. One should note that the $\frac{1}{n} \sum_{j=1}^n \frac{I_i^j}{R_{\beta\text{Zr}}^j}$ term is not applicable at lower temperatures (e.g. 600°C)

because the α to $(\alpha+\beta)$ phase transformation only occurs at the higher temperatures for Zry-2. [33]

3. Results and Discussion

3.1. Baseline measurement

The baseline measurement for the Zry-2 was conducted at room temperature. Figure 4 shows a representative X-ray diffraction pattern (quarter of an image plate). Because the Zircaloy sample was placed in a container that slightly attenuated X-rays and induced a noisy background, the diffraction patterns obtained from the panel detector are not as clear as the ones observed in previous studies of iron [25] and Ni-based alloys [34], etc. Nevertheless, all diffraction peaks of the Zry-2 specimen with d -spacings ranging from 1.06 to 3.5 Å were identified and are presented in Table 1. The lattice constants a and c of the Zry-2 were measured to be 3.219 and 5.126 Å, respectively.

3.2. Oxidations at 600°C

Two sets of X-ray diffraction measurements were conducted once the Zry-2 specimen reached 400°C. No oxidation peak was observed at 400°C. Then, the testing temperature was increased to 600°C and another X-ray diffraction measurement was performed once the temperature had stabilized. Figure 5 shows the diffraction pattern attained from the very outer surface of the Zry-2 specimen, and the reported powder diffraction file (PDF) intensity for hexagonal Zr (α Zr), monoclinic ZrO₂, and tetragonal ZrO₂. All diffraction peaks are identified as belonging to one of these three phases. The diffraction peaks from the ZrO₂ are much weaker than those of the Zircaloy matrix, indicating the oxidation at this stage is not severe. One should note that the only significant peak for tetragonal ZrO₂ is the (101) reflection, which does not overlap with reflections from other phases. Because the volume fraction of tetragonal ZrO₂ is relatively small when compared to the volume fraction of the Zircaloy matrix and monoclinic ZrO₂, many strong peaks of tetragonal ZrO₂, e.g. (211), (112), and (110), cannot be identified and indexed due to their similar *d*-spacings with the reflections of the other two major phases.

Based on the synchrotron X-ray diffraction patterns, the volume fraction of ZrO₂ was calculated by Eq. 1. The inner and outer sides of the Zircaloy specimen developed similar amounts of monoclinic ZrO₂. (Fig. 6) The maximum volume fraction of monoclinic ZrO₂ for the inner and outer surfaces was measured to be ~14.4% and ~13.5%, respectively. At the depth of 65μm from the inner surface, the volume fraction of monoclinic ZrO₂ decreased to ~0.6%, while at the same depth from the outer surface, the volume fraction attained a value of ~1.1%. The observable range for monoclinic ZrO₂ is also slightly larger on the outer side, attaining a depth of ~95μm, at which point a volume fraction of 0.4% is reached.

The difference in the tetragonal ZrO₂ development in the two sides of the specimen is more evident when compared to the difference in the monoclinic ZrO₂ development. The observable

range of the depth of tetragonal ZrO_2 is only $\sim 20\mu\text{m}$ from the inner surface, while this value increases to $\sim 70\mu\text{m}$ from the outer surface. However, the volume fraction of tetragonal ZrO_2 near the inner surface is much higher in its observable range, which is about three times the value for the same depth from the outer surface. This indicates a concentration of tetragonal ZrO_2 in a short range of depth from the inner surface, which is within the Zirconium liner.

3.3. Oxidations and phase transformations at 800°C

After the X-ray diffraction measurement at 600°C, the testing temperature was increased to 800°C in order to conduct another X-ray diffraction scan. More intense diffraction peaks of ZrO_2 were observed from the surface of the specimen (Fig. 7), indicating the development of a thick and condensed oxidation scale during steam oxidation. The depth profiles of the ZrO_2 volume fraction for the inner and outer surfaces of the Zircaloy specimen were calculated and are shown in Fig. 8 (a) and (b), respectively. The oxidation on the inner surface is much more significant than the oxidation on the outer surface. The observable range of depth of ZrO_2 from the inner and outer surface is $\sim 250\mu\text{m}$ and $\sim 150\mu\text{m}$, respectively. This indicates $\sim 60\%$ of Zry-2 in the thickness direction has been oxidized to different extents. (Note that the wall thickness of Zry-2 cladding is $\sim 660\mu\text{m}$.) With a larger observable range of ZrO_2 , the oxidation on the inner side is more severe, and obtains a maximum fraction of $\sim 91\%$ of ZrO_2 (including both monoclinic and tetragonal ZrO_2), which can be compared to the maximum fraction of $\sim 57\%$ for the outer side of the Zry-2 cladding. The development of ZrO_2 for the inner side is observed to be non-monotonous due to the different oxidation mechanisms and dynamics for the Zirconium liner and Zircaloy matrix. Beneath the oxidation of the liner, the development of ZrO_2 in depth is monotonous, which is similar to the outer side of the cladding. One should note that the volume fraction ratio of monoclinic ZrO_2 to tetragonal ZrO_2 is different for both sides of the samples. This ratio for the outer side is around 1, indicating an almost equal volume fraction of the two

types of zirconia. In contrast, this ratio for the inner side shows a strong dependence on the amount of ZrO_2 : for the position with more than ~7% monoclinic ZrO_2 , the ratio is greater than 1, indicating a higher volume fraction of monoclinic ZrO_2 than tetragonal ZrO_2 . And for the position with less than ~7% monoclinic ZrO_2 , the ratio is less than 1, indicating a higher volume fraction of tetragonal ZrO_2 than monoclinic ZrO_2 .

In addition to the oxidation development, the α to β phase transformation of the Zircaloy matrix was observed at 800°C. Figure 7 shows the diffraction pattern from the outer surface of the Zry-2 specimen at 800°C and the reported powder diffraction file intensity for β Zr (PDF#01-089-4916). Different from the hexagonal crystal structure of the α Zr matrix, the crystal structure of the β Zr matrix is body-centered cubic (BCC) with a lattice constant of $\sim 3.61\text{\AA}$. The most distinguishable and intense diffraction peak for the β Zr matrix is the (110) reflection. Figure 9 shows the depth profile of the volume fraction of the α and β Zr matrices for the entire wall thickness of the Zry-2 cladding. Generally, the volume fraction distribution of the α and β Zr matrices is similar in the thickness direction. The amount of either phase decreased dramatically in both sides of the specimen due to the steam oxidation. Similar to the volume fraction ratio of monoclinic ZrO_2 to tetragonal ZrO_2 , the volume fraction ratio of α Zr to β Zr varies with the distance to the surfaces. This ratio is above 1 for most of the in-depth positions of the specimen except for at the very inner surface, where the severe oxidation scale is placed.

Table 2 summarizes the diffraction peaks identified at RT, 400, 600 and 800°C in the Zry-2 sample.

4. Discussion

Two depth profiles of oxide volume fractions of Zircaloy-2 at 600 and 800°C were obtained from the *in-situ* synchrotron measurements. For both temperatures, oxidation was observed to be more severe on the inner side of the cladding. One should note that the X-ray was scanned from the outer to the inner side of the specimen. Even though the delay time in moving from the outer to the inner surface was only about 8 minutes, more oxidation on the inner surface was expected. The difference in ZrO_2 build-up for the inner and outer sides at 600°C was not significant, while the difference at 800°C was substantial, suggesting much higher steam oxidation dynamics at 800°C, where 8 minutes was long enough for Zry-2 to grow an additional oxide scale. Another important factor impacting the difference in oxidization of the inner and outer sides of the cladding is the zirconium liner on the inner surface. During the steam exposure at 600°C, most of the oxidation on the inner side occurred on the zirconium liner, which has worse oxidation resistance, while the zircaloy matrix beneath was almost free of oxides. Particularly, the tetragonal ZrO_2 is concentrated in the depth of $\sim 20\mu\text{m}$ from the inner surface (Fig. 6 (a)), which is within the liner. The influence of the zirconium liner on the depth profile of oxidations is more evident in the measurements at 800°C, where the oxides were not developed monotonously due to different oxidation mechanisms and dynamics for the Zirconium liner and Zircaloy matrix. (Fig. 8 (a))

Figure 10 shows the depth profile of volume fractions of all observable phases for the inner side of the Zry-2 specimen. Three distinguishable regions were defined according to the volume fraction of oxides:

Region I: ZrO_2 scale (containing the oxidized liner) with more than 80% of oxides;

Region II: $(\alpha + \beta)$ Zr matrix with ZrO_2 incursions with less than 80% of oxides;

Region III: $(\alpha + \beta)$ Zr matrix, where no oxides were observed.

Region I is the ZrO_2 scale (~ 0 to $80\text{ }\mu\text{m}$ from the inner surface), which consisted of the oxidized liner and the oxidized Zircaloy matrix. This region, dependent on the depth, contains about 80 to 90% of the volume fraction of oxides. Due to a weak oxidation resistance, the entire zirconium liner had been oxidized, while the Zircaloy matrix underneath only developed an oxide scale with a thickness of $\sim 10\text{ }\mu\text{m}$. Beneath the ZrO_2 scale, the composition of ZrO_2 decreased significantly in depth, with an increase in the volume fraction of the α and β Zr matrixes. This region, in the depth of ~ 90 to $260\text{ }\mu\text{m}$ from the inner surface, is the $(\alpha + \beta)$ Zr phase with ZrO_2 incursions, i.e. region II. In this region, the volume fraction of monoclinic ZrO_2 is generally less than that of tetragonal ZrO_2 , except for the very outer part. The volume fraction of the monoclinic ZrO_2 is near zero percent in the very inner part ($\sim 250\text{ }\mu\text{m}$) of the region II, while the volume fraction of tetragonal ZrO_2 maintains a few percent. This provides direct evidence that the tetragonal crystal structure is the *ab initio* phase type in which new oxide molecules form at the metal-oxide interface. The current measurements agree well with the study by Kadiri et al. using Raman spectroscopy, atomic force microscopy, and optical microscopy [4]. At lower temperatures, the tetragonal ZrO_2 cannot maintain a stable crystal structure and transforms into the monoclinic structure. [9] Only at temperatures of $\sim 1050^\circ\text{C}$ or higher can the tetragonal crystal structure be stabilized [4, 9]. The innermost layer ($> \sim 210\text{ }\mu\text{m}$ from outer surface), defined as region III, is the $(\alpha$ and $\beta)$ Zr matrix, where no oxide was observed in the X-ray diffraction.

Previous studies on high-temperature steam-oxidized Zr alloys using SEM and OM revealed four major regions with different microstructures : 1) oxide, 2) α -Zr(O), 3) $(\alpha + \beta)$ Zr, and 4) prior β -Zr/ β -Zr. [5, 6, 8, 22, 35] Depending on the temperature (particularly above the $(\alpha + \beta)/\beta$ transformation temperature) and the time of steam exposure, the region of $(\alpha + \beta)$ Zr may not be

observed in the SEM examinations. [6, 8] In the current study, we did not see the α -Zr(O) region, where the α -Zr phase is dominant over the β Zr phase, or the prior β -Zr region, where β -Zr is the major phase. In contrast, both the α and β Zr phases were observed in the entire sample. The difference in microstructure is due to a lower study temperature in this study. Although the temperatures of the $\alpha/(\alpha + \beta)$ and $(\alpha + \beta)/\beta$ phase transformations depend on the concentration of elements, e.g. O, Nb, and Tin, etc. (mainly oxygen in the oxidation studies, [22]), the higher temperature generally promotes the transformation and stabilization of the β phase. Since the temperature of this study was 800°C, which is in the middle of the $\alpha + \beta$ range, the extended distribution of both phases can be expected.

Another important observation from the depth profiles of both 600 and 800°C is the continuity of the oxidation phase development in depth. We do not see a sudden drop (an edge) of the amount of oxide phase in depth direction, although the SEM/OM metallography shows different microstructures in different layers/ regions. [5, 6, 8, 22, 35] The observation in the current study is the *in-situ* X-ray diffraction measurement when the specimen was under steam oxidation was different from the SEM/OM examinations on the post-oxidized specimens, which were often quenched or natural-cooled from the high-temperature exposure. Moreover, the X-ray diffraction measurement provides volume fractions of each phase in depth, which could hardly be interpreted using SEM/OM, especially to distinguish the monoclinic and tetragonal ZrO₂.

This study shows a significant amount of β phase at 800°C, while the α to β phase transformation was estimated to be ~810°C. [33] This difference may attribute to the temperature gradient within the ring specimen. Unlike the regular electric heating furnace that provides wide range of uniform heating zone, the radiation heating by infrared furnace may produce temperature gradient depending on the local thermal mass. In this experiment, the thermal couple connecting

to one side the specimen measured the surface temperature of the Zry-2 tube. With oxide buildup on the sample surface at high temperatures, the thermal couple was measuring the temperature of the sparse oxide, while the matrix temperature can be higher due to the larger thermal mass. In addition, the isothermal temperatures to stabilize α , $(\alpha + \beta)$ and β are elementary dependent, and may decrease if the compositions of β stabilizers, e.g. iron, chromium and nickel etc., are a little higher within the Zry-2.

The current *in-situ* experiment is the first attempt to use high-energy synchrotron diffraction to conduct layer-by-layer measurements for an oxidizing Zry-2. The results prove the feasibility for this technique to attain depth profiles of different phases during steam oxidation. Based on this method, further experiments, for example, oxidation dynamics study with isothermal temperature control or stage temperature control (the latter simulates the temperature development in a LOCA scenario [5]) can be performed in an *in-situ* manner, better reflecting the actual oxidation process than the post-exposure microscopic analyses.

5. Conclusions

Synchrotron X-ray diffraction was applied to study steam oxidation behavior of the Zircaloy-2 at temperatures up to 800°C. With the synchrotron X-ray scan, the depth profiles of different phases were obtained. The following conclusions were reached:

1. From the side-to-side X-ray diffraction scan, we observed different depth profiles of oxides in the inner and outer surfaces of the Zry-2 sample. The differences can be attributed to 1) the time of delay due to the X-ray scan, and 2) the zirconium liner within the inner side of the Zircaloy sample. Due to the higher oxidation dynamics, the difference is more significant at 800°C than 600°C.

2. The tetragonal crystal structure is the *ab initio* phase type in which new oxide molecules form at the metal-oxide interface. There was a greater amount of tetragonal ZrO₂ than monoclinic ZrO₂ in the very inner side of the oxidizing Zry-2. The highest study temperature, 800°C, is not able to stabilize the tetragonal ZrO₂ that continuously transforms to monoclinic ZrO₂. This process causes a much higher concentration of monoclinic ZrO₂ near the oxidation surface.
3. During steam oxidation, multiple layers, including ZrO₂ scale, ($\alpha + \beta$) Zr matrix with ZrO₂ incursions, and ($\alpha + \beta$) Zr matrix, were mapped according to the volume fraction of each phase. The decrease in ZrO₂ from the surface in depth is gradual without a sharp edge distinguishing each of the layers.

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Table 1. The diffraction peaks in the Zry-2 sample measured at room temperature

<i>hkl</i>	<i>d</i> -space (Å)	<i>hkl</i>	<i>d</i> -space (Å)
100	2.791	112	1.364
002	2.567	201	1.346
101	2.451	004	1.284
102	1.888	202	1.225
110	1.609	104	1.165
103	1.459	203	1.081
200	1.394		

Table 2. The diffraction peaks identified at RT, 400, 600, and 800°C in the Zry-2 sample.

Temperature	RT & 400°C	600°C			800°C			
Phase	<i>a</i> Zr	<i>a</i> Zr	Monoclinic ZrO ₂	Tetragonal ZrO ₂	<i>a</i> Zr	β Zr	Monoclinic ZrO ₂	Tetragonal ZrO ₂
<i>h k l</i>	100	100	100	101	100	110	100	101
	002	101	-111		101	200	-111	
	101	102	111		102	211	111	
	102	110	-211		110	220	-211	
	110	103			103	310		
	103							
	200							
	112							
	201							
	004							
	202							
	104							
	203

Fig. 1. Ring-shaped Zry-2 specimen for steam oxidation experiment

Fig. 2. Schematic of the synchrotron experimental setup

Fig. 3. Temperature control during steam oxidation measurement

Fig. 4. Representative X-ray diffraction pattern (quarter of an image plate) for Zry-2. All Debye rings are identified as belonging to Zircaloy matrix.

Fig. 5. The diffraction pattern from the outer surface of the Zry-2 specimen at 600°C, and reported powder diffraction file (PDF) intensity for hexagonal α Zr (PDF#04-008-1477), monoclinic ZrO_2 (PDF#04-013-4343), and tetragonal ZrO_2 (PDF#04-005-4208).

(a)

(b)

Fig. 6. (a) depth profile of ZrO_2 volume fraction starting from inner surface, and (b) depth profile of ZrO_2 volume fraction starting from outer surface. The volume fraction of ZrO_2 was calculated by Eq. 1 using synchrotron X-ray diffraction patterns. The diffraction measurement for the ZrO_2 was conducted at 600°C with steam exposure.

Fig. 7. The diffraction pattern from the outer surface of the Zry-2 specimen at 800°C, and reported powder diffraction file intensity (PDF) for β Zr (PDF#01-089-4916).

(a)

(b)

Fig. 8. (a) depth profile of ZrO₂ volume fraction starting from inner surface, and (b) depth profile of ZrO₂ volume fraction starting from outer surface. The diffraction measurement for the ZrO₂ was conducted at 800°C with steam exposure.

Fig. 9. Depth profile of volume fractions of the α and β Zr matrices for the entire thickness of the Zry-2 specimen. The diffraction measurement was conducted at 800°C with steam exposure.

Fig. 10. Depth profile of the volume fractions of all observable phases (α and β Zr matrix, and monoclinic and tetragonal ZrO_2) for the inner side of the Zry-2 specimen. The diffraction measurement was conducted at 800°C with steam exposure.