Prospect about hydrogen release at severe accident using mass gain from cladding oxidation

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1. Introduction

The hydrogen produced by chemical reaction between steam and Zircaloy-4 led to a hydrogen explosion during the Fukushima Daiichi accidents. It is an example to show the potential risk of zirconium alloys during accident conditions [1-2]. In order to understand the behavior of the fuel cladding during a severe accident, it is necessary to investigate the behavior of Zircaloy-4 in various conditions. Furthermore the oxidation by steam-nitrogen gas mixtures needs to be focused since severe accident at spent fuel pools such as partial LOCA scenario could make steam contained atmosphere and then causes different results compared to the oxidation by pure air [3-7]. Therefore the experiments were conducted for depicting the Partial LOCA. The experimental condition is established by the acceptable range of experimental device, thermo-gravimetry (TG). This paper is based on a revised and considerably extended presentation given at the 21st International Quench Workshop [8].

2. Methods

Investigations were conducted using 10 mm segments of cladding tube consisting of Zircaloy-4 (Zry-4). A composition of Zircaloy-4 is Cr 0.1%, Fe 0.2%, O 0.12%, Sn 1.4%, and Zr balance. The inside and outside diameters are 9.25 mm and 10.75 mm, respectively. The top and bottom of the sample are open during experiments; therefore oxidation occurred at both, inside and outside. The samples were mounted either vertically in TG experiments.

To have similar oxygen to nitrogen ratio like in air, the ratio between steam and nitrogen was set to 40:60. This allows comparing the oxidation behavior in steam-nitrogen gas mixture and air. Argon was a protective gas and was used either to maintain a partial pressure. The chemical composition of the off-gas released by the experimental apparatus was measured by a mass-spectrometer. Experimental time of isothermal condition was 50 minutes at 850℃ and 20 minutes at 1100℃. The criteria to select the experimental time were the half of maximum percentage of mass gain to prevent severe damage in surface of samples.

To confirm the hydrogen release during oxidation, it is necessary to compare the relation between oxidation and hydrogen release through the general chemical relation as following below.

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2 \qquad (1)$$
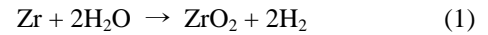
If applying about realistic phenomena based on right side of Eq. (1), oxidation of zirconium, ZrO_2, could be regarded as a mass gain and formation of $2H_2$ could be seen as a by-product of reaction. Taking into account the molar masses of oxygen (15.999 g/mol) and hydrogen (1.0079 g/mol), the relations between mass gain and H_2 release is like following,

$$\text{Mass gain (dioxide, } O_2 \text{)} : H_2 \text{ release (} 2H_2 \text{)} \approx 8:1 \quad (2)$$

In the Thermo-gravimetry (TG) experiments, the thermo-balance measured mass variation of the sample and each composed concentration of the off-gas atmosphere could be evaluated by the mass spectrometer. In order to compare the relationship between mass gain and H_2 release, however, it needs to convert both measured data due to using different units. The argon flow rate was always constant during each experiment. From the experimental data, all of the information could be achieved to obtain hydrogen volume flow rate. The correlation between volume flow rate and volume concentration is given in Eq. (3-1) and Eq. (3-2).

$$V_{H2}\,[l] : V_{Ar}\,[l] = C_{H2} : C_{Ar} \qquad (3\text{-}1)$$

$$\dot{V}_{H2}[l/s] = \dot{V}_{Ar}\frac{C_{H2}}{C_{Ar}}[l/s] \qquad (3\text{-}2)$$

V_x: volume of x component
C_x: concentration of x component
$\dot{V}_x$: volume flow rate of x component

Using both molar mass (2 g/mol) and molar volume (22.4 l/mol) of hydrogen, it is possible to convert concentration unit [-] into hydrogen release rate unit [g/s].

$$\dot{m}_{H2}[g/s] = \frac{H_2\ molar\ mass\ [g/mol]}{H_2\ molar\ volume\ [l/mol]}\dot{V}_{H2}[l/s] \quad (4)$$

After conversion, comparing between mass gain rate and hydrogen release rate was tried to verify theoretical approach.

3. Results

3.1 The flow rate of steam-nitrogen gas mixture of 1 lpm and 10 lpm at 850°C temperature
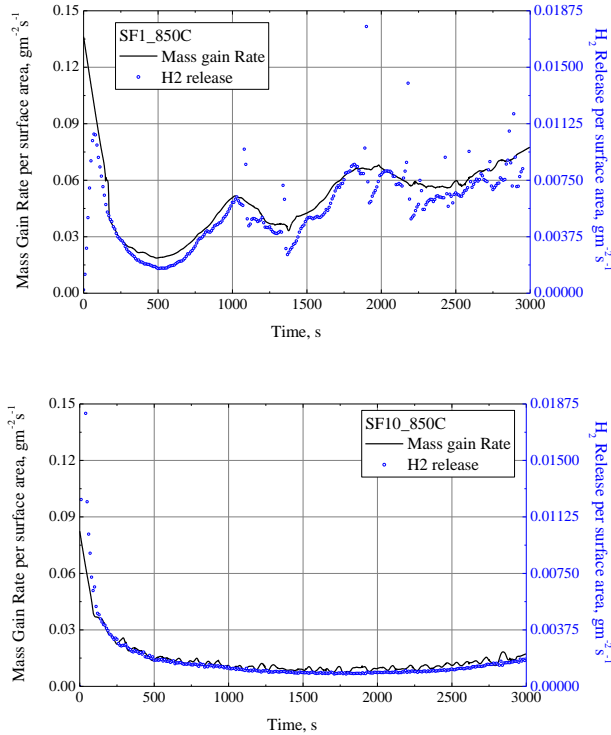

Figure 1. Comparing mass gain rate with hydrogen release rate via adjusting scale in case of SF1_850C (the lowest) and SF10_850C (the highest)

Both side of Fig.1 presents a good agreement about the relation between mass gain rate and hydrogen release rate. First of all, the upper side of Fig.1 shows a result of the lowest flow rate of the TG experiment at 850°C. Even though the mass gain rate has fluctuation during experiments, the hydrogen release rate also traces the mass gain rate similarly. Secondly, the lower side of Fig.1 is a result of the highest flow rate in contrast with the left side of Fig.1. It also indicates a good consistency between mass gain rate and hydrogen release rate. To compare both results, the scale of y axis is same. It could be known that the area made by hydrogen release rate of SF1_850C is larger than those of SF10_850C. In the case of 850°C, therefore, as the flow rate is increased, the hydrogen release rate is decreased.

It is confirmed that hydrogen release rate could be anticipated by mass gain rate through cladding oxidation.

3.2 The flow rate of steam-nitrogen gas mixture of 1 lpm and 10 lpm at 1100°C temperature
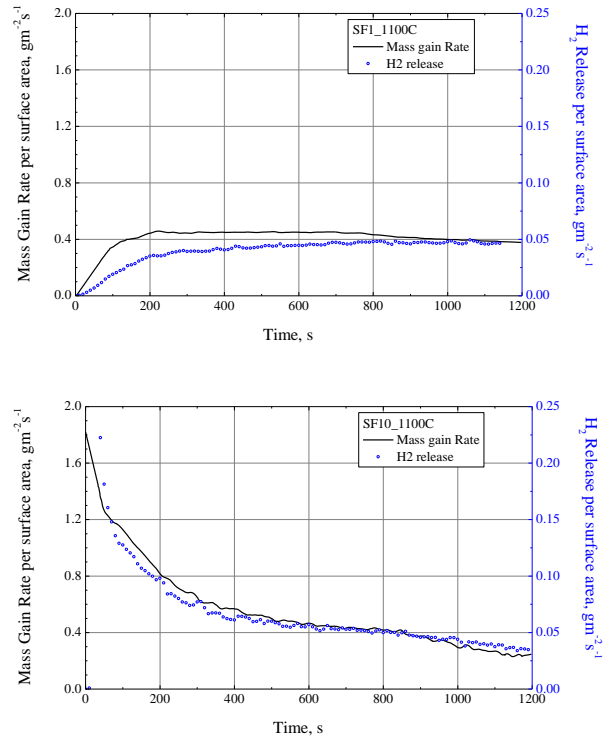

Figure 2. Comparing mass gain rate with hydrogen release rate via adjusting scale in case of SF1_1100C (the lowest) and SF10_1100C (the highest)

In Fig. 2 the mass gain rate and the hydrogen release rate are plotted vs. the oxidation time. It allows comparing the time dependence of the two values. As mentioned before Eq. (2), the ratio between mass gain rate and hydrogen release rate should be compared to confirm the validation of theory. All relations between mass gain rate and hydrogen release rate were similar except for the lowest flow rate (1 lpm). The gap among the mass gain rate and hydrogen release rate in SF1_1100C might be due to absorption of hydrogen by the metal. Hydrogen produced by steam oxidation of zirconium may be released to the environment or absorbed by the metal. The other side, the lower side of Fig.2 shows a good correspondence between the mass gain rate and the hydrogen release rate like before case of 850°C. In the case of comparing the amount of the hydrogen release, the tendency is totally different against to the 850°C experimental results. As confirmed in Fig.2, the case of SF10_1100C has a larger area enclosed by hydrogen release rate, x axis and y axis than the case of SF1_1100C. In other words, the amount of hydrogen release is large as the flow rate of reactive gas is increased.

Metallography is conducted to identify the differences compared to the other cases. Fig.3 shows the results of the post-test samples of SF1_850C and SF1_1100C captured by optical microscope. Although hydrogen absorbed into the Zircaloy metal could not be found by optical microscope, there is a different feature compared to the other case in the bottom side of Fig.3. It is observed that dominant region of gold color, ZrN, is remained in oxide layer of Zircaloy. Also the metallic Zircaloy, which has white color, is remained. For these reasons, it seems that the oxidation reaction is not completely finished. To confirm the hydrogen absorption into the metal phase of Zircaloy or oxide layer of Zircaloy, it needs more precise analysis using other method such as XRD or Raman spectroscopy. SF1_1100C has circumferential cracks in the oxide layer of Zircaloy. These are acted as a block in diffusion. On the other hands, the upper side of Fig.4 has different type of crack. The radial crack can reduce a diffusion path, so it results in a faster reaction than absence of radial crack. The main difference caused by different types of crack is whether the breakaway phenomenon related with oxidation rate appears. Reduced diffusion path could make an accelerated oxidation; therefore the tendency of the oxidation converts a parabolic rate into a linear rate.
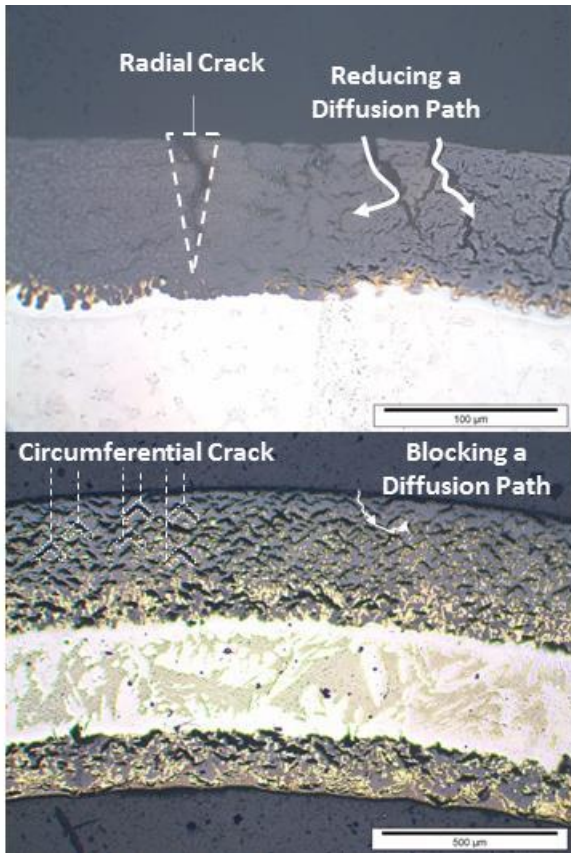

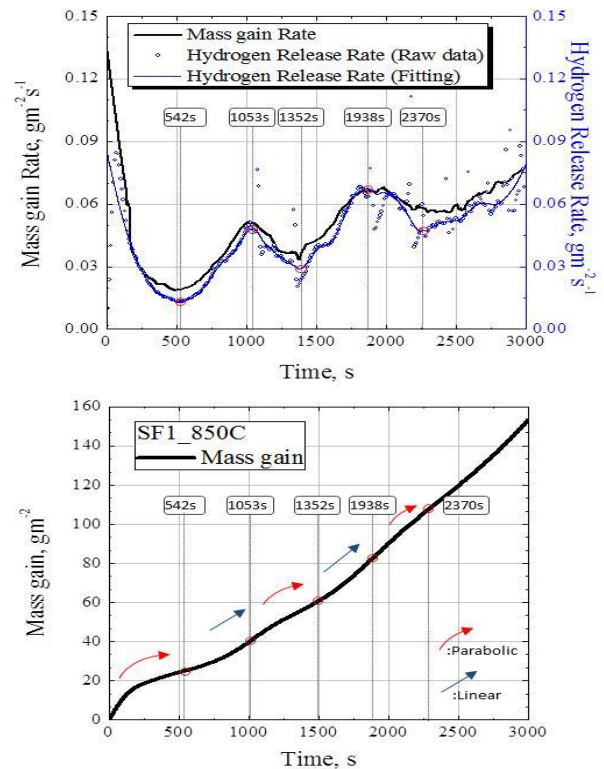Figure 3. Cross section micrographs of the SF1_850C(top) and SF1_1100C(bottom)

Figure 4. The effect of the transition point at hydrogen release rate

To find quantitative analysis of the relation between hydrogen release rate and mass gain rate, it is tried to investigate the effect of the transition points at hydrogen release rate. As shown in Fig.4, there is a good coincidence between transition points at hydrogen release rate and oxidation tendency. Based on the flat slope at the hydrogen release rate, the mass gain tendency varies parabolic to linear or linear to parabolic. It would be treated in later in more detail.

4. Conclusion

Overall, the relation between mass gain rate from Zircaloy oxidation by steam-nitrogen gas mixtures and hydrogen release is described. In the case of 850°C, it is observed that the amount of hydrogen release is increased as the flow rate is decreased. In the case of 1100°C, the hydrogen release is affected by flow rate and the inverse relation in contrast to the tendency at 850°C is revealed. Furthermore the hydrogen absorption is observed in the case of SF1_1100C supplied by the lowest flow rate (1 lpm) of the reactive gas composed by steam-nitrogen mixture. To confirm the role of the hydrogen absorption in the Zircaloy, precise measurement methods for metallography are needed. Through these experiments, it could be contributed to trace the amount of the hydrogen release from the cladding oxidation at severe accident.

ACKNOWLEDGMENTS

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