The Effect of Dissolved Hydrogen on Zirconium Alloy Oxidation in Air

Yunmock Jung[a] , Kwangheon Park[a]*, Nobuaki Sato[b]
[a]Department of Nuclear Engineering, Kyunghee University, Kyunggi-do 446-701,South Korea
[b]Institute for Advanced Materials Processing, Tohoku University 2-1-1 Katahira, Aoba-Sendai 980-8577, Japan
[*]Corresponding author: kpark@khu.ac.kr

1. Introduction

In high burn-up PWR fuels, Zirconium alloys used as fuel-cladding materials contain hydrogen due to the corrosion of the cladding by water. Zircalloy fuel cladding could be prone to the accidents due to oxidation and corrosion at high temperatures. Hydrogen produced by the corrosion reaction between zirconium and water will be absorbed by zirconium alloys, which can result in the formation of zirconium hydrides. These hydrides lead to dilatational strain and cause the alloy to crack when the hydrogen content exceeds its critical values, and the dissolved hydrogen becomes hydrides when the concentration of hydrogen exceeds the solubility limit at low temperatures. Due to the different mechanical properties of the hydrides, the effect of hydrides on the maintenance of fuel during operation and storage has been a major concern. However, the dissolved hydrogen also affects high temperature oxidation, even though the hydrogen is fully dissolved in the matrix at high temperatures

2. Experiment

2.1 Materials

Zircaloy-4 and Zirlo were used in this study. The plate type samples were cut by a cutter that was 10mm wide, 20mm long, and had a Φ3.1mm hole in the center. Hydrogen absorption experiments were carried out at KAERI(Korea Atomic Energy Research Institute) using a gaseous charge method that is widely used in the hydrogen absorption. The samples were heated to 700℃ in a vacuum chamber and then the highly purified hydrogen was charged into the chamber for hydrogen activation and absorption. The hydrogen activation process took about 10 min, and the hydrogen absorption process lasted for 4 hours. After hydrogen absorption, the chamber was cooled slowly in the hydrogen atmosphere. For the hydrogen desorption process, the samples were heated to a temperature of 400℃ in the tube furnace. The hydrogen absorption amount was confirmed to be about 200ppm. However, there were higher deviation limits.

Table I: Chemical composition of specimen

(wt%)	Zr	Nb	Sn	Fe	Cr
Zry-4	bal.	-	1.35	0.2	0.1
Zirlo	bal.	1.0	1.0	0.1	-

2.2 XRD Characterization

The phase structures of the samples before and after the samples were identified using a Rigaku Type RINT 2000 X-Ray diffractometer (XRD) with Ni filtered Cu Kα irradiation (40 kV and 40 mA) equipped with a curved pyrolytic carbon. The heating rate was 20℃/min until 780℃, and thereafter the heating rate was 5℃/min to make a stable temperature condition. The XRD exposure time was 5 min, and it was done a total of 8 times for 40 min with each sample. After XRD analysis, each sample was cooled to maintain the vacuum condition to prevent unwanted oxidation. The phases of the products were then identified by comparing the obtained diffraction patterns with those from the JCPDS data. However, the apparatus could not identify hydrides because the minimum quantity was about 2% that could be detected.

2.3 Phase Transformation

Zirconia exhibits three polymorphs: cubic, tetragonal, and monoclinic. The tetragonal phase is stable at temperatures above 1430 K and below 2640 K. The monoclinic phase is stable from room temperature to 1430 K. As oxidation proceeds due to an anionic diffusion mechanism, the new oxide molecule always forms at the oxide/metal interface. Thus, every molecule must undergo the tetragonal to monoclinic transformation at a certain distance from the interface. The transformation from tetragonal to monoclinic in the zirconium oxide layer is an important factor in corrosion degradation and crack formation in the outer oxide layer.

3. Results

Figure 1 and Figure 2 show the results of the XRD analysis of ZrO_2 oxide at 800℃ for 20 min and 40 min in air. As can be seen, the shape and position of the peaks is almost same, but the counts are a little different. In order to analyze the ratio of the tetragonal ZrO_2 to the monoclinic ZrO_2, this study used Origin pro 8.6 ver.
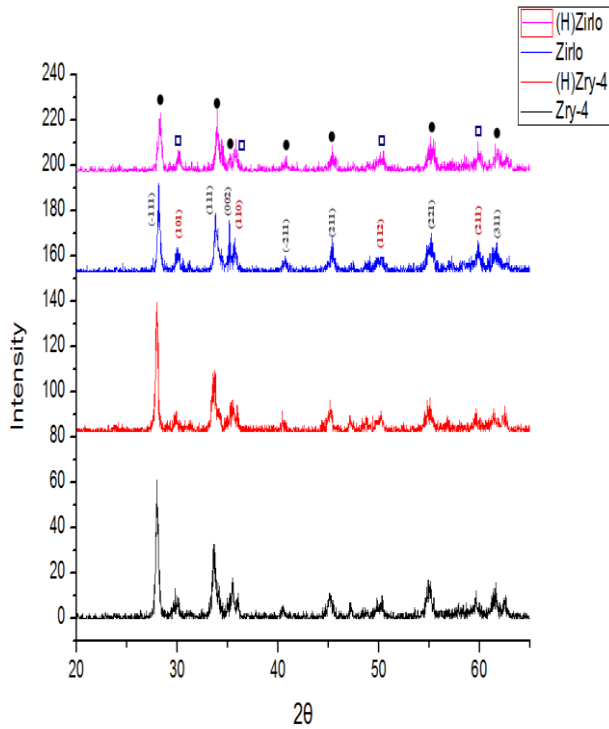
Fig. 1. X-ray diffraction patterns(20°-70° in 2θ) of ZrO₂ oxidize at 800°C for 20 minute in air. ;
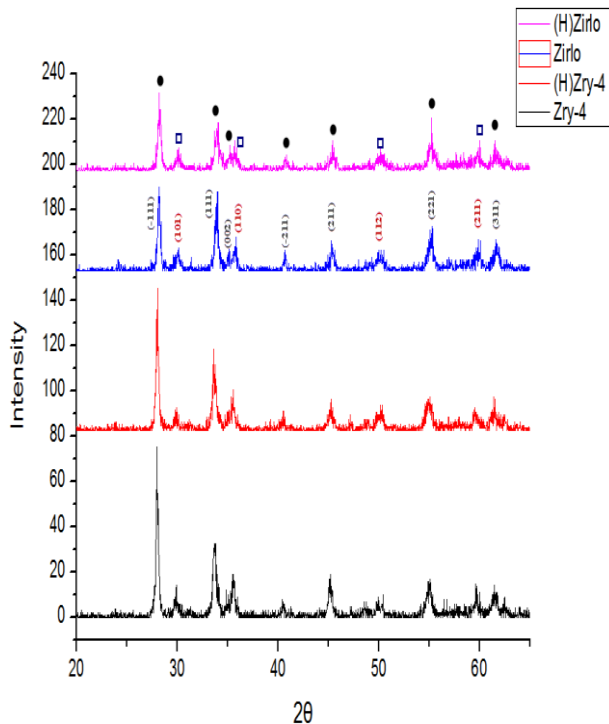(●) monoclinic phase of ZrO₂ (□) tetragonal phase of ZrO₂.

Fig. 2. X-ray diffraction patterns(20°-70° in 2θ) of ZrO₂ oxidize at 800°C for 40 minute in air. ;
(●) monoclinic phase of ZrO₂ (□) tetragonal phase of ZrO₂.

Table II shows the ratio of tetragonal ZrO$_2$ to monoclinic ZrO$_2$, and the weight gains were compared for hydrogen-charged and non-charged zirconium alloys at 800℃ in air.

Table II: The ratio of tetragonal ZrO2 to monoclinic ZrO2 and the weight gain for each sample.

	20 min $\left(\frac{I(101)_t + I(112)_t}{I(\bar{1}11)_m + I(111)_m}\right)$	40 min $\left(\frac{I(101)_t + I(112)_t}{I(\bar{1}11)_m + I(111)_m}\right)$	Weight Gain $\left(\frac{mg}{dm^2}\right)$
Zry-4	0.133	0.138	302.213
(H) Zry-4	0.110	0.101	340.726
Zirlo	0.163	0.166	343.496
(H) Zrilo	0.113	0.101	433.397

4. Conclusions

The weight gain and ratios of the hydrogen-charged samples were higher than for non-charged samples. The effect of accelerated oxidation by hydrogen was about 13% (Zry-4) and 26% (Zrilo). The oxidation enhancing effect of hydrogen-charged cladding is due to the hydrogen on the metal layer affecting the formation of the protective oxide layer. The creation of the sound monoclinic phase zirconium alloy oxidation has a major impact on the reinforcement of corrosion-resistance in the oxide layer. When the phase transforms from tetragonal to monoclinic, the hydrogen in the metal layers decreased the surface free energy. Finally, the total free energy was decreased, and this had an adverse effect in creating the sound monoclinic phase. The complex phenomena of oxidation and hydrogenation must be well understood and described in order to predict early failure following sudden accidents such as LOCA and RIA, and it is necessary to design a special oxide layers elastic and solid at elevated temperatures.

REFERENCES

[1] Keys LH, Johanson G, Malin AS. The physical metallurgy of high strength zirconium alloys. Journal of Nuclear Materials 1976;59(2):137e48.
[2] Northwood DO. The development and applications of zirconium alloys. Materials & Design 1985;6(2):58e70.
[3] Wongsawaeng D, Jaiyen S. High-temperature absolute hydrogen desorption kinetics of zirconium hydride under clean and oxidized surface conditions. Journal of Nuclear Materials 2010;403:19e24.
[4] Chao Zhao, Hydrogen absorption cracking of zirconium alloy in the application of nuclear industry. International journal of hydrogen energy 38(2013) 1 0 9 0 3 -1 0 9 1 1
[5] Kim YS, Ahn SB, Cheong YM. Precipitation of crack tip hydrides in zirconium alloys. Journal of Alloys and Compounds 2007;429:221e6.
[6] Yamanaka S, Yoshioka K, Uno M, Katsura M, Anada H, Matsuda T, et al. Thermal and mechanical properties of zirconium hydride. Journal of Alloys and Compounds 1999;293e295:23e9.