Exploring the microstructural difference between circumferential hydride and radial hydride in reactor-grade Zirconium cladding tube

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1. Introduction

Hydride reorientation has been considered to be a main issue for the dry storage of spent nuclear fuels. Under hoop stress, radial hydrides act as a major deteriorating factor of cladding integrity on the macroscopic scale.

Microscopic scale analysis is also essential for understanding the difference between circumferential hydride and radial hydride. In Qin et al.'s theoretical model [1], the assumption that radial hydrides precipitate at the prismatic plane of radial basal pole-textured α-Zr was used. And it was found that this assumption strongly affects the modeling of hydride reorientation [2]. Therefore, a more accurate characterization of the microscopic property of radial hydride is needed for accurate modeling of hydride reorientation.

In this study, microscopic analyses of Electron Back Scattered Diffraction (EBSD), Transmission Electron Microscope (TEM), and Differential Scanning Calorimetry (DSC) were conducted to figure out the microscopic character of radial hydrides.

2. Experiments

2.1. Hydride treatment

In this study, unirradiated reactor-grade Zr-Nb alloy cladding tubes with an outer diameter of 9.5 mm and wall thickness of 0.57 mm were used in the experiment. Prior to the hydrogen charging process, the furnace was vacuumed out to ~10^{-6} torr. And then hydrogen was charged to the cladding at 400 ℃ in the furnace. Various hydrogen concentrations were achieved via variations in hydrogen gas pressure drop.

For hydride reorientation treatment, the specimens were heated up to 400 ℃ for 2 hours and maintained at 400 ℃ for 1 hours. Specimens were then cooled down to 25 ℃ for 16 hours with a rate of 0.396 ℃/min. During the cool-down process, constant internal pressure was applied while the external pressure was maintained at 0.1 MPa. During pressurization process, the multi-axial stress is generated by the difference between internal pressure and external pressure. This stress during cool-down process induces the precipitation of radial hydrides.

2.2. Microstructural characterization

EBSD analyses were carried out to investigate the orientation relationships between the Zr matrix and hydrides. A field emission scanning electron microscope (JEOL JSM-7900F) and EBSD (Oxford instruments Nanoanalysis Symmetry S2) were used and analyzed using orientation imaging microscopy (OIM) analysis software. After EBSD analysis, the hydrogen concentration of each specimen was measured using a hot vacuum extraction determinator (ELTRA ONH-2000).

The crystallographic orientation of the grains of radial was also analyzed using TEM (JEOL JEM-ARM200F). A scanning electron microscope (SEM) equipped with a dual-beam focused ion beam (FEI, Helios 650) was used for TEM sampling.

For DSC analysis, ring specimens of 4 mm length were cut into 3 sub-specimens. Then each sub specimen was polished into 4 mm x 4 mm x 0.5 mm sizes with weight of 40±0.7 mg. Each sample was heated to a target temperature of 600 ℃ at a heating rate of 20 ℃/min using DSC (Netzsch STA 449 F5). The exemplary result of DSC curve of hydrided specimen is shown in Fig. 1 (a). For peak area analysis, the baseline was set as the presented dot lines in Fig. 1 (a). And the difference between the original graph and the baseline was obtained as can be seen in Fig. 1 (b). The stored energy released during dissolution process was calculated as the area under the baseline correlated DSC curve of Fig. 1 (b). In each DSC curve, T_{TSSd} was defined as the maximum temperature as noted in Fig. 1 (b). And the hydrogen concentration of each specimen was calculated using Eq. (1) [3].

$$TSSd = 106446.7 \times exp\left(\frac{35990}{RT}\right) \quad (1)$$

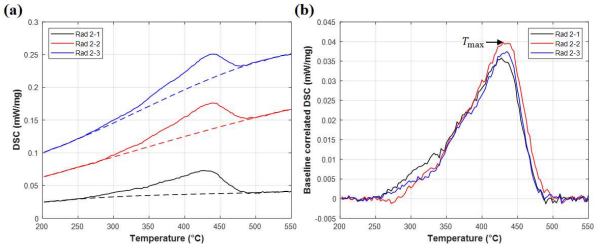

Fig 1. (a) DSC curve during heating, (b) baseline corrected DSC curve

3. Result and Discussion

3.1. Orientation relationship analysis

Four specimens were analyzed using EBSD. One specimen contained 100% circumferential hydride, and the others contained radial hydrides precipitated under the constant pressure of 11, 14, and 18 MPa. Since the specimen with only circumferential hydrides did not undergo the pressurization process, it will be noted 0 MPa specimen from now on. To minimize the effect of hydrogen concentration, specimens with hydrogen contents of ~200 wppm were used in the analysis.

EBSD phase interface relationship was analyzed for 20 different regions in each specimen. Phase maps for circumferential hydrides and radial hydrides precipitated under different internal pressures are presented in Fig. 2.

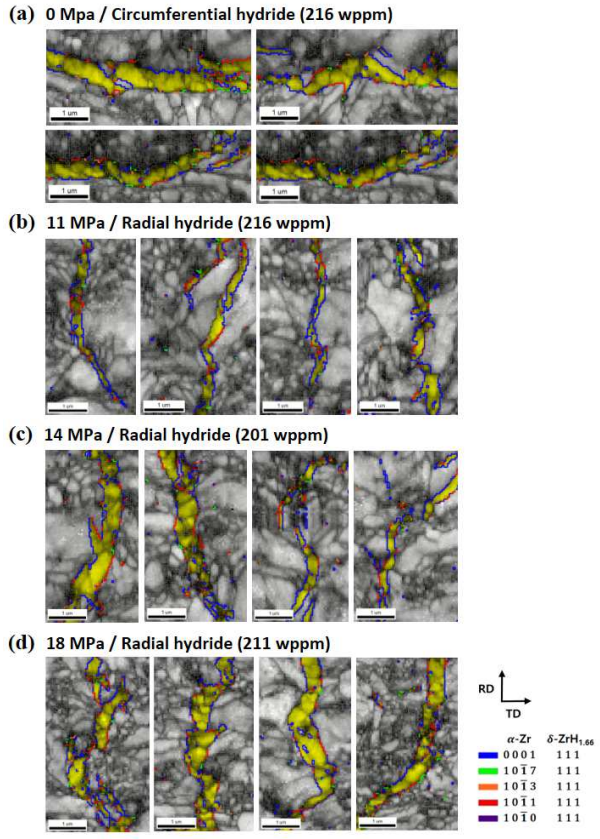

Fig 2. Phase map images (x20k) of different regions in specimen containing (a) circumferential hydride, (b) radial hydride of 11 MPa, (c) radial hydride of 14 MPa, (d) radial hydride of 18 MPa

The average fractions of orientation relationships are listed in Table 1. It was found that the orientation relationship of $\{0001\}_\alpha//\{111\}_\delta$ is still dominant in radial hydrides. The traditional assumption that radial hydrides precipitate at the prismatic plane which reveals $\{10\underline{1}0\}_\alpha//\{111\}_\delta$ would have been reasonable for annealed cladding or Zircaloy-4 cladding whose grain sizes are larger than recently used Zirconium cladding of Zr-Nb alloy [4]. In this analysis, high-quality EBSD images allowed us to investigate the orientation relationship of radial hydrides under various pressures. Other than the $\{0001\}_\alpha//\{111\}_\delta$ relationship, there were no significant differences between all specimens for other orientation relationships.

Table 1. Average fraction of 20 different regions depending on the internal pressure (Orientation of ZrH is fixed for $\{111\}_\delta$, unit: %)

	0 MPa	11 MPa	14 MPa	18 MPa
$\{0001\}_\alpha$	61.1	71.3	67.5	60.5
$\{10\underline{1}7\}_\alpha$	6.7	3.6	4.3	5.1
$\{10\underline{1}3\}_\alpha$	4.7	3.7	3.5	4.2
$\{10\underline{1}1\}_\alpha$	23.4	16.6	20.0	22.1
$\{10\underline{1}0\}_\alpha$	4.1	4.8	4.0	4.1

The orientation relationship between the Zr matrix and radial hydride precipitated under 18 MPa was investigated using TEM analysis (FIg. 3). SAED pattern of Fig. 3 (c) indicates the Zr matrix with zone index of <11$\underline{2}$0> and (d) indicates the ZrH with zone axis of <110>. The interface presented in Fig. 3 (e) indicates the orientation relationship of $\{0001\}_\alpha//\{111\}_\delta$. This supports the result of Table 1 that not all radial hydrides are precipitated at the prismatic plane.

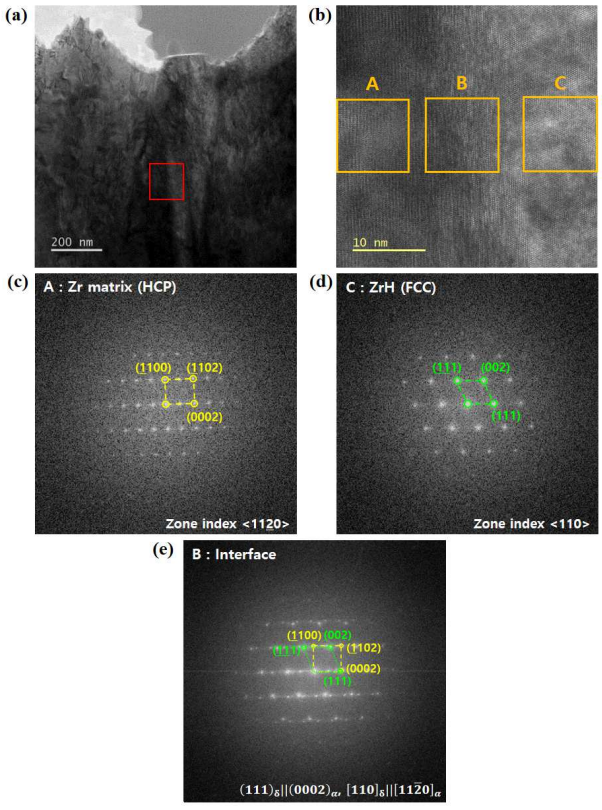

Fig 3. (a) x30k TEM image, (b) x800k TEM image of the region marked by red box. (c), (d), and (e) are SAED patterns of region A, C, and B, respectively.

3.2. Stored energy analysis via DSC

Total 8 specimens were analyzed in this section: 4 specimens containing 100% circumferential hydrides and 4 specimens containing radial hydrides precipitated under 18 MPa. All specimens were cut into 3 sub-specimens and each of them was analyzed. The baseline corrected DSC curves of all specimens are presented in Fig. 4 (a). In Fig. 4 (a), 3 lines with the same color presented in various line styles indicate sub-specimens in one ring specimen.

If stored plastic strain induced by hydride precipitation is different according to the orientation of the hydride, it is expected that the stored energy calculated in DSC curve would reveal a significant difference. The calculated stored energy is shown in Fig. 4 (b). For both circumferential and radial hydrides, the stored energy proportionally increases with the hydrogen contents, which is axiomatic. And comparing the stored energy of circumferential and radial hydrides, it seems that there is no significant difference between them. It would be consistent with the result of Table 1 that the orientation relationship (misfit strain) between Zr matrix and ZrH is not that different between circumferential and radial hydrides.

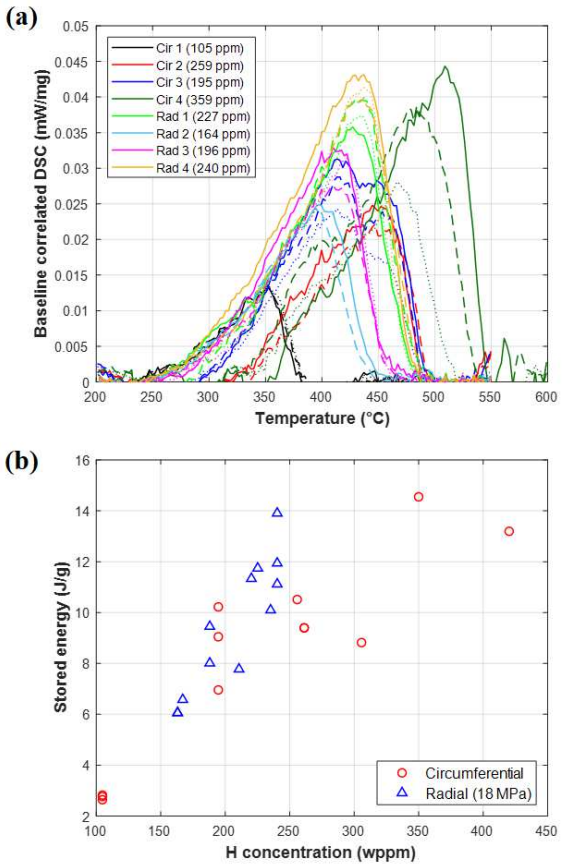

Fig 4. (a) Baseline corrected DSC curve of specimens, (b) Calculated stored energy of each specimen

4. Conclusion

In this study, the microscopic difference between circumferential and radial hydrides was figured out using EBSD, TEM, and DSC analyses. The result indicated that $\{0001\}_\alpha//\{111\}_\delta$ orientation relationship is dominant even for radial hydrides and there is no significant difference between circumferential and radial hydrides in terms of the average fraction of various orientation relationships and stored energy. It might be consistent with the past study that hydride orientation has a limited effect on the axial mechanical behavior of Zircaloy-4 cladding [5].

Based on the pieces of evidence that we discussed in this study, the microscopic behavior of radial hydride in reactor-grade Zr-Nb cladding tube shows somewhat different results from the existing literature that radial hydride is precipitated in the prismatic plane. It implies that the existing concept that assigns energetical penalty on radial hydride of prismatic precipitation may not be applicable to cladding tubes with complex fine grains and that the formation of radial hydride should be discussed with other theories such as grain boundary activation theory. Since misfit strain according to the orientation relationship is essential for theoretical modeling, these results can play a very important role in the development of radial hydride modeling.

This study presented the basic results in analyzing the difference between radial and circumferential hydride, and more specific experiments should be conducted in the following studies.

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REFERENCES

[1] W. Qin, J.A. Szpunar, J. Kozinski, Hydride-induced degradation of hoop ductility in textured zirconium-alloy tubes: A theoretical analysis, Acta Mater. 60 (2012) 4845–4855.

[2] D. Kim, J.H. Kang, Y. Lee, Accurate prediction of threshold stress for hydride reorientation in Zircaloy-4 with directly measured interface orientation relationship, Materialia. 21 (2022).

[3] G. Sabol, G. Moan, Zirconium in the nuclear industry: twelfth international symposium, (2000).
[4] A.P. Nimishakavi, A.P. Nimishakavi, Hydride formation in Zirconium alloys, (2011).
[5] S. Bang, H. a. Kim, J. soo Noh, D. Kim, K. Keum, Y. Lee, Temperature-dependent axial mechanical properties of Zircaloy-4 with various hydrogen amounts and hydride orientations, Nucl. Eng. Technol. 54 (2022) 1579–1587.