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A Study on Stress-induced Hydrogen Diffusion in Zircaloy-4 cladding

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1. Introduction

Zirconium alloy cladding are being widely used at nuclear power plants due to their low neutron absorption cross section and high corrosion resistance. However, cladding inevitably absorbs the hydrogen due to water-side corrosion [1]. The absorbed hydrogen precipitates into a hydride platelet which is considered as one of the limiting factor threatening the integrity of spent nuclear fuel during dry storage. Thus, it is important to understand thoroughly the behavior of hydrogen in the zirconium. In particular, hydrogen diffusion is known to be affected by gradient of temperature, hydrogen, and stress [2]. The influence of temperature and concentration is well known as Soret effect and Fick's law, respectively. However, the effect of stress gradient on hydrogen diffusion is unclear so far. For this reason, understanding of delayed hydride cracking (DHC), which is a time-dependent crack growth mechanism, continues to be a controversial issue [3-6].

Currently, there are two major models to explain the process of DHC. Puls [5] claims it is driven by diffusion of hydrogen towards crack tip due to chemical potential difference which is generated by stress gradient between the crack tip and bulk region. In contrast, Kim [7] explains that the first step of DHC is stress-induced precipitation of supersaturated hydrogen at the crack tip. Then hydrogen migrates towards crack tip due to concentration gradient between the two regions.

Kim [3, 4] has criticized the Puls model by citing the Kammenzind's experiments [2] which did not show the hydrogen diffusion at the isothermal condition despite the stress gradient. In addition, he has emphasized that there is no driving force to cause the hydrogen diffusion at isothermal condition because the system is closed.

In this preliminary study, thus, tensile tests were conducted using radially notched ring specimen to investigate whether the stress gradient cause the diffusion of dissolved hydrogen towards the stressed region in the isothermal conditions, which is one of the critical issues among two major DHC models.

2. Experimental

2.1 Specimen Preparation

The test specimen was prepared with a cold worked stress relieved (CWSR) Zircaloy-4 cladding. The cladding was cleaned and pickled to remove initial oxide layer. Then, hydrogen was charged using hydrogen charging apparatus. Hydrogen content was controlled by pressure drop of the chamber. After charging was finished, the specimen was heat treated to obtain uniform hydrogen distribution. Finally specimen was cut into 6 mm length and radial notch was introduced on the outer surface of specimen using electronic discharge methods. Fig. 1 shows detailed geometry of specimens. The reason why the radially notched ring specimen was used is to maximize the stress gradient along the radial direction when load was applied, so that much more steeper stress gradient than that of Kammenzind [2] can be achieved in this experiments.

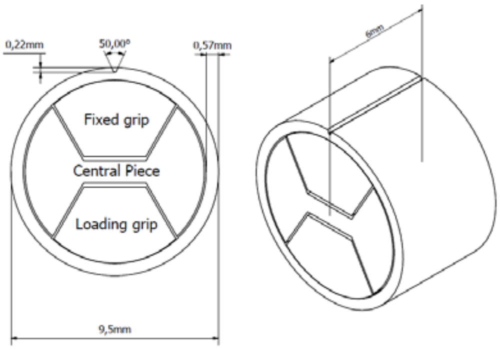


Fig. 1 A schematic illustration of specimen with jig

2.2 Test procedure

The constant load apparatus with 3 piece jig was used for applying the tensile stress to ring specimen. Detailed test conditions and thermal history were shown in Table 1. There are two type of tests, DH and SH, in order to investigate the hydrogen diffusion toward the notch tip in the isothermal conditions. In case of specimens of DH, when the temperature reaches the peak temperature and stabilized, hydrogen is partially or fully dissolved in the zirconium matrix. On the other hand, in case of SH, hydrogen exists in supersaturated state in zirconium matrix without any precipitation due to the hysteresis of the TSS of hydrogen. Thermodynamic state of each specimen was shown in Fig. 2. When the temperature reached the test temperature and stabilized, constant load of 392 ± 0.5 N was applied for a sufficient time to induce the migration of dissolved hydrogen by steep stress gradient. Then, the specimen was water-quenched to prevent the additional migration of hydrogen. Finally, we compared the hydride morphology before and after the test to identify whether the hydrogen diffuses or not.

Table 1 Test condition of each experiments

No.	H wppm	Peak Temp. (℃)	Loaded Temp. (℃)	Loaded time (day)	Load (N)	Cooling rate	Result
DH-01	~150*	400	400	3	392 ± 0.5	WQ**	X
DH-02	226	400	400	3	392 ± 0.5	WQ	X
DH-03	415	500	500	1	392 ± 0.5	WQ	X
SH-01	~400*	470	400	3	392 ± 0.5	WQ	Diffusion
SH-02	~400*	460	420	2	392 ± 0.5	WQ	X
SH-03	~600*	500	460	1	392 ± 0.5	WQ	Diffusion
SH-04	~600*	500	480	1	392 ± 0.5	WQ	X

* predicted hydrogen content, ** WQ : Water-Quenched

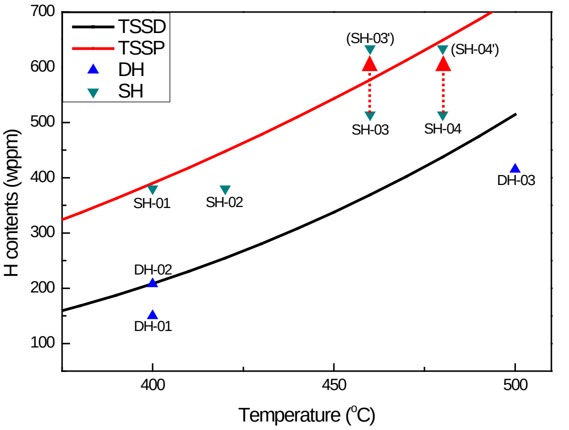


Fig. 2. Hydrogen contents and temperature of each specimen with TSS curves. (SH-03' and SH-04' is not experimental results. These points are marked for explain.)

3. Results and Discussion

Fig. 3 shows the morphology of before and after the DH test. It can be noticed that lengthy circumferential hydrides were precipitated uniformly around notch tip before the test. After the test, uniformly distributed fine hydrides were observed in all cases. That is, no hydrogen diffusion of fully or partially dissolved hydrogen by stress gradient was observed in DH test. In contrast, in some cases of SH containing the supersaturated hydrogen, hydride accumulation can be observed at the notch tip (**Fig. 4**).

Kim argued that hydrogen could not be diffused in the isothermal condition despite chemical potential gradient was applied because the system is internally closed [3]. However, the hydride accumulation at the notch tip observed in this study may be accepted as evidence for hydrogen diffusion by stress gradient.

That phenomenon can be explained as follow. When load was applied, stress gradient was generated between the crack tip and bulk region. Then, hydrogen was diffused toward crack tip. If hydrogen content exceeds the TSSP, hydride was precipitated and accumulated. Otherwise, hydrogen diffusion was not kept. For example, dissolved hydrogen content of SH-03 and SH-04 is 486 wppm and TSSP at 460 °C and 480 °C was 648 wppm and 577 wppm because the hydrogen content follow the TSSD curve when temperature was elevated. We used TSSD and TSSP by average value reported by several researchers [8]. If we assume that chemical potential gradient generates the hydrogen concentration difference of 120 wppm, hydrogen would be diffused toward crack tip to adjust the chemical potential gradient (**Fig. 2** SH-03→SH-03'). But, it was impossible to meet the chemical potential gradient (**Fig. 2** SH-03') because hydride is precipitated when hydrogen concentration exceeds the TSSP curve. Therefore, chemical potential gradient (**Fig. 2** difference between SH-03' and TSSP at 460 °C) was still kept and hydrogen was continuously diffused and accumulated. In contrast, SH-04 could be met to the chemical potential gradient because it was lower than TSSP curve (**Fig. 2** SH-04'). Thus, even if the hydrogen concentration at the crack tip was raised, hydride could not be precipitated. Of course, hydrogen concentration at the crack tip might be higher than bulk region. But it was impossible to determine the hydrogen concentration quantitatively for specific region and we could not observe the hydrogen accumulation in case of SH-04.

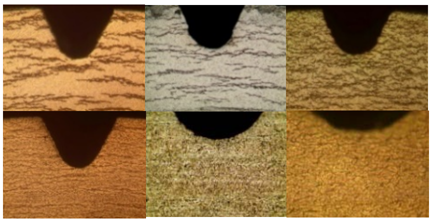
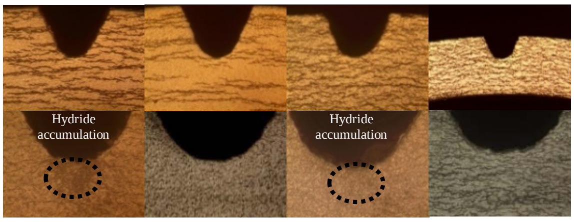

DH-01 DH-02 DH-03

Fig. 3. Before (upper) and after(lower) morphology of DH test



SH-01 SH-02 SH-03 SH-04

Fig. 4. Before (upper) and after(lower) morphology of SH tests

In addition, although same load was applied for all tests, hydrogen diffusion was observed only for SH-01 and SH-03. In particular, the difference between SH-03 and SH-04 was only loaded temperature. This makes the difference of gap between TSSP and hydrogen content of specimen. It finally causes the different results. Therefore, it can be speculated that there is a certain threshold condition to cause the hydrogen diffusion.

4. Conclusions and Future Plans

This study was conducted to confirm whether the hydrogen can diffuse induced by stress gradient in the isothermal conditions. So far the following conclusions were drawn:

- Hydrogen can be diffused by stress gradient in the isothermal conditions.
- Certain threshold condition may exist on hydrogen diffusion.

Additional tests will be conducted.

REFERENCES

[1] M. B. Elmoselhi, B. D. Warr, S. Mcintyre, **"A Study of the Hydrogen Uptake Mechanism in Zirconium Alloys"**, *Zirconium in the Nuclear Industry: Tenth International Symposium*, ASTM STP 1245, A.M. Garde, E.R. Bradley Eds., American Society for Testing and Materials, Philadelphia, 1994, pp. 62-79.
[2] B. F. Kammenzind, B. M. Berquist, R. Bajaj, E. H. Kreyns, D. G. Franklin, **"The Long Rang Migration of Hydrogen Through Zircaloy in Response to Tensile and Compressive Stress Gradients"**, *Zirconium in the Nuclear Industry: Twelfth International Symposium*, ASTM STP 1354, G.P. Sabo, G.D. Moan Eds., American Society for Testing and Materials, West Conshohocken, PA, 2000, pp. 196-233.
[3] Y. S. Kim, Author's reply to "Review of the thermodynamic basis for models of delayed hydride cracking rate in zirconium alloys, M.P. Puls in J. Nucl. Mater. 393 (2009) 350–367", Journal of Nuclear Materials, 399 (2010) 240-247.
[4] Y. S. Kim, Author's 2nd reply to comments on author's reply to "Review of the thermodynamic basis for models of delayed hydride cracking rate in zirconium alloys," M.P. Puls in J. Nucl. Mater. 393 (2009) 350–367, Journal of Nuclear Materials, 399 (2010) 259-265.
[5] M. P. Puls, Review of the thermodynamic basis for models of delayed hydride cracking rate in zirconium alloys, Journal of Nuclear Materials, 393 (2009) 350-367.
[6] M. P. Puls, Comments on author's reply to "Review of the thermodynamic basis for models of delayed hydride cracking rate in zirconium alloys", M.P. Puls in J. Nucl. Mater. 393 (2009) 350–367, Journal of Nuclear Materials, 399 (2010) 248-258.
[7] Y. S. Kim, Comments on the Dutton–Puls model: Temperature and yield stress dependences of crack growth rate in zirconium alloys, Materials Science and Engineering: A, 527 (2010) 7480-7483.
[8] J. S. Kim, Y. S. Kim, Effect of thermal history on the terminal solid solubility of hydrogen in Zircaloy-4, International Journal of Hydrogen Energy, 39 (2014) 16442-16449.