Post-quench ductility of Cr-coated (8µm, AIP) Zr-1.1Nb Accident Tolerant Fuel cladding and accident margin analysis

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1. Introduction

After the Fukushima Daiichi nuclear power plant accident in 2011, there has been a growing interest in developing Accident Tolerant Fuel (ATF). The basic concept of ATF is to improve the safety and performance of nuclear fuel by reducing oxidation of the cladding, which results in loss of the ductility of the cladding through oxide(ZrO_2) generation and hydrogen embrittlement. Current Emergency Core Cooling System (ECCS) safety criteria limit Equivalent Cladding Reacted (ECR) at 17% to ensure the ductility of the cladding post Loss of Coolant Accident (LOCA) [1]. In addition, as the burnup of the nuclear fuel increases, the ECR limit decreases due to hydrogen embrittlement of the cladding. In this study, the ECR limit was derived for various specimens including Cr-coated ATF, and the accident coping time for each cladding in high burnup nuclear fuel.

2. Experiments

2.1 Experimental setup

The experimental facility is designed to simulate loss of coolant accident (LOCA). It consisted of a specimen holder, rodless air slide, steam generator and radiant furnace, as shown in Fig. 1. The holder is made of 310S welding rod and the bottom of the holder is composed of 4 hooks. Each hook can hold up to four specimens with a length of 8 mm for each, but in this experiment, up to two specimens were fixed to each hook. K-type thermocouple fixed with dummy specimen to measure temperature of specimens. When the temperature of the experiment facility reaches 1204 °C, the holder with the specimen is inserted into the furnace through an air slide. After that, the temperature of the specimen is maintained at 1204±5°C for a specific time according to the experimental conditions, and steam is entered into the furnace at the same time. The mass flux of steam entering into the furnace was 3.94 $[mg/cm^2s]$. It is consistent with the protocol of the Zircaloy steam oxidation provided by the U.S. NRC's standard guideline(0.8-30$[mg/cm^2s]$)[2-4]

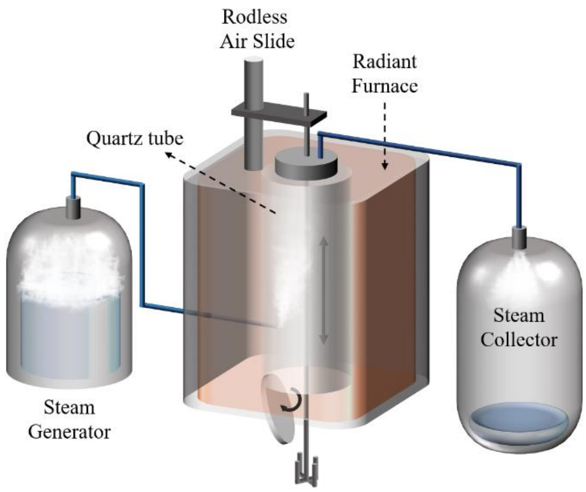

Fig. 1. Schematic of LOCA experiment facility.

After subjecting the specimen to a high-temperature steam environment, it was cleaned with ethanol and allowed to dry completely. The weight of the oxidized specimen was then measured. Subsequently, the specimen was heated to a temperature within 135±3°C, and then the RCT was conducted using an INSTRON-8516 model. Displacement rate of 0.033 mm/s was applied during the test.[2]

2.2 Materials

Two types of Zr-based alloys used in this study. The chemical composition ratio of each alloy is listed in Table I. The specimens used in this study had a length of 8mm, an outer diameter of 9.5mm, and a thickness of 0.57mm. Pure Cr was coated on the outer surface of the Zr-1.1Nb alloys by using Arc Ion Plating (AIP) method and the thickness was 8.3±0.4 [µm].

Table I: Chemical composition of Zr-based alloy.

Alloy	Sn [wt%]	Nb [wt%]	Fe [wt%]	Cr [wt%]	Cu [wt%]
Zircaloy-4	1.3-1.5	-	0.2	0.1	-
Zr-1.1Nb alloy	-	1.1	-	-	0.05

3. Results and Discussion

3.1 Ductile to brittle transition

As shown in Fig. 2, the residual ductility of the specimens decreases with increasing oxidation. Oxygen in the high-temperature steam environment diffuses into the specimens. As a result, the phase of the cladding is divided into ZrO_2, α, and prior-β. with the progression of oxidation, the β layer which exhibits high ductility gradually narrows[5].

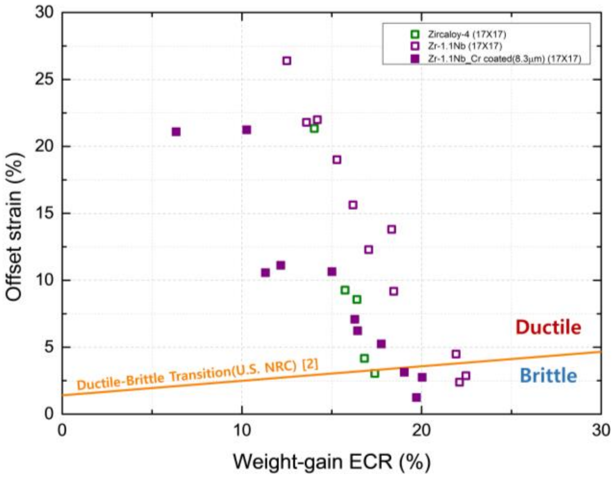

Fig. 2. Offset strain according to Weight Gain Equivalent Cladding Reacted (WG-ECR) and U.S. NRC criteria.

In this study, the ductile-brittle transition was obtained by interpolating the WG-ECR of the specimen with the highest WG-ECR among ductile specimens and the specimen with the lowest WG-ECR among brittle specimens. As a result, the Ductile to Brittle transition ECR was obtained, which is shown in Table II.

Table II: Ductile to Brittle transition WG-ECR.

Type of cladding	WG-ECR[%]
Zircaloy-4	17
Zr-1.1Nb alloy	22
Cr-coated Zr-1.1Nb alloy	19

The ductile to brittle limit of Zircaloy-4 specimen obtained in this study is consistent with the result reported by the U.S. NRC[6]. The difference in residual ductility between the Zircaloy-4 and Zr-1.1Nb alloy would be attributed to various factors such as the influence of alloying elements and the differences in grain size due to the variation in manufacturing process.[7-9]

Alloying elements such as Nb have a significant effect on residual ductility[10-12]. Although the alloy elements are added to improve the corrosion resistance of the material, they have the effect of reducing its ductility. In the case of a Zr alloy containing Nb, the shape of α-Zr phase has acicular structure similar to the martensite in the quenched Fe-C alloys, as shown in Fig. 3.

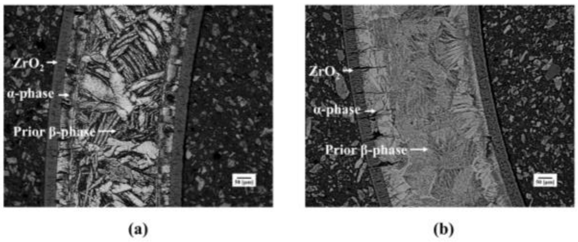

Fig. 3. Cross-section of oxidized specimen (WG-ECR = 17%) (a) Zircaloy-4 specimen (b) Zr-1.1Nb specimen.

For the Cr-coated specimen, the ductility is smaller than that of the uncoated specimen for all ECR ranges (Fig. 2), and the ductile to brittle limit WG-ECR is 18%, which is lower than that of the uncoated specimen (Table II). In the case of coated specimens having the same WG-ECR as uncoated specimens, the thickness of the inner wall oxide layer is thicker than that of uncoated specimens. Also, in the ring-shaped specimen stress distribution, the most stressed parts are the 12 o'clock and 6 o'clock parts of the inner wall, so the ductility of the coated specimen is smaller[4]. However, the point of view of the oxidation time, the Cr-coated Zr-1.1Nb specimen is 24 minutes and 8 minutes for uncoated specimens to reach the ductile to brittle transition limit WG-ECR.

3.2 Safety margin of ATF in LBLOCA without ECCS

Fig. 4 shows the thinned thickness of the specimen resulting from ballooning and burst. For the uncoated specimen, the average thickness thinned by approximately 22%, and about 20% for the Cr-coated specimen.

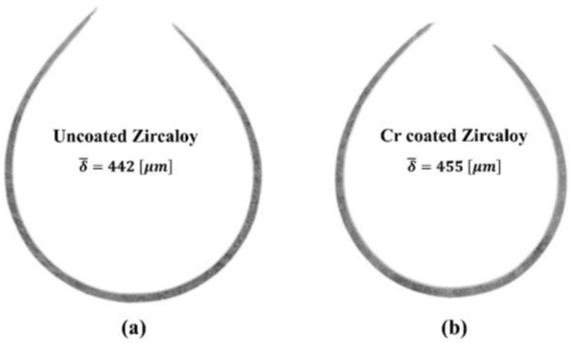

Fig. 4. Cross section of the thinned thickness of the specimens.

In the case of high burnup fuel, as the effect of hydrogen embrittlement on the cladding increases, it is necessary to apply an appropriate ductile to brittle criteria, which is reported in 10CFR50.46. The amount of hydrogen content in the cladding was calculated using Eq. (1)-(3), and the ductile to brittle limit was then determined[13].

Ductile to Brittle transition ECR[%]

$$\begin{cases} 18 - 0.03\mathrm{H}_{\mathrm{Zr\_Nb}}\ (\mathrm{H}_{\mathrm{Zr\text{-}Nb}} < 400[wppm]) \\ 6 - 0.01(\mathrm{H}_{\mathrm{Zr\_Nb}} - 400)\ (\mathrm{H}_{\mathrm{Zr\text{-}Nb}} > 400\ [wppm]) \end{cases} \quad (1)$$

$$\mathrm{H}_{\mathrm{Zr-Nb}}\ (peak)[wppm]$$
$$\mathrm{ZrO}_{2,\ \mathrm{Zr\text{-}Nb}} \times 0.175 \times 54.27\ [\mu m] \quad (2)$$

$$\mathrm{ZrO}_{2,\ \mathrm{Zr\text{-}Nb}}(peak)[\mu m]$$
$$\begin{cases} 2.02 \times 10^{-2} Bu_d^2 + 0.0118 Bu_d\ (Bu_d \le 86.5) \\ 150\ (Bu_d > 86.5) \end{cases} \left[\frac{\mathrm{MWd}}{\mathrm{kgU}}\right] \quad (3)$$

In an accident, Cr-coated Zircaloy brings a great benefit in accident coping time because of one-side oxidation. However, it should be noted that eutectic melting occurs at around 1310℃ for Cr-coated Zircaloy, which is approximately 500℃ lower than the melting point of conventional Zr alloys[14]. Therefore, to estimate the accident coping time more precisely, the eutectic melting should be taken into account.

Fig. 5 shows the accident coping time of each cladding in the Large Break LOCA (LBLOCA) scenario where the ECCS is non-functional [15]. The burnup was assumed as 60[MWd/kgU] and four cases were analyzed and compared based on the presence of Cr coating and/or thinning of the thickness of cladding.

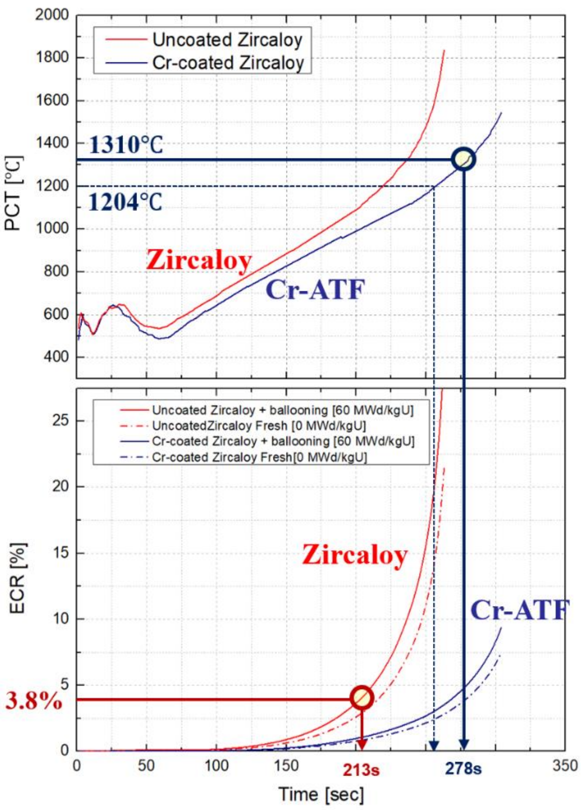

Fig. 5. Accident coping time during LBLOCA without ECCS.

In the case of uncoated Zircaloy, the time to reach the ECR criteria of 3.8%, which guarantees ductility at a burnup of 60[MWd/kgU], was faster at 213s than the time to reach the Peak Cladding Temperature (PCT) criteria of 1204 ℃. In the case of Cr coated cladding, the time to reach the eutectic melting point was faster than the time to reach ECR limit, which guarantees ductility, at about 278s. Through the above results, it can be confirmed that the Cr coated Zircaloy can secure more accident coping time of about 1 min than the conventional Zircaloy.

4. Conclusions

Zr-1.1Nb cladding has a ductile to brittle limit of 22% and is more ductile in high temperature steam environment than Zircaloy-4 cladding, which has a limit of 17%. This is expected to be a complex effect of various factors such as alloy elements and grain size of the specimen. In the case of the Cr coated specimens, compared to the uncoated specimens, the ductility tends to be lower in a high temperature steam environment, which is due to the thicker thickness of the inner wall Zr oxide layer. In a study that assumed high burnup fuel, Cr coated Zircaloy have a greater accident coping time about 1 min compared to the conventional Zircaloy. It is because the effect of the Cr coating that protect the oxidation occurred at the outer wall of the cladding. However, since the peak temperature of the cladding and duration of accidents vary depending on the accidents, research on various accidents seems necessary and will be studied in the future.

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REFERENCES

1. *"Acceptance criteria for emergency core cooling systems for light water cooled nuclear power reactors," and Appendix K to 10 CFR 50. "ECCS Evaluation Models, U.S. Federal Register 39 (3).* 10 CFR 50.46.
2. *USNRC. Regulatory Guide 1.223-Determing post quench ductility*. 2018, Washington. D.C., USA.
3. Yook, H. and Y. Lee, *Post-LOCA ductility assessment of Zr-Nb Alloy from 1100 degrees C to 1300 degrees C to explore variable peak cladding temperature and equivalent cladding reacted safety criteria*. Journal of Nuclear Materials, 2022. 567.
4. Yook, H., et al., *Post-LOCA ductility of Cr-coated cladding and its embrittlement limit.* Journal of Nuclear Materials, 2022. 558.
5. Brachet, J.C., et al., *High temperature steam oxidation of chromium-coated zirconium-based*

alloys: Kinetics and process. Corrosion Science, 2020. 167.

6. *NUREG/CP-6967-Cladding Embrittlement During Postulated Loss-of-Coolant Accidents* 2008, U.S.NRC.
7. Park, J.H., et al., *High temperature steam-oxidation behavior of arc ion plated Cr coatings for accident tolerant fuel claddings.* Surface & Coatings Technology, 2015. 280: p. 256-259.
8. Michau, A., et al., *High-temperature oxidation resistance of chromium-based coatings deposited by DLI-MOCVD for enhanced protection of the inner surface of long tubes.* Surface & Coatings Technology, 2018. 349: p. 1048-1057.
9. Fazi, A., et al., *Cold sprayed Cr-coating on Optimized ZIRLO™ claddings: the Cr/Zr interface and its microstructural and chemical evolution after autoclave corrosion testing.* Journal of Nuclear Materials, 2022. 560: p. 153505.
10. Baek, J., et al., *Oxidation behaviors of Zr-xNb and Zr-xSn alloys in LOCA.* 2003.
11. Jeon, C.-J., Y.-H. Jeong, and S.-J. Kim, *Study on corrosion characteristics of Zr-Sn and Zr-Nb-Sn alloys.* Korean Journal of Materials Research, 1999. 9(4): p. 378-385.
12. Kang, S., et al., *Study on the standard establishment for the integrity assessment of nuclear fuel cladding materials.* 2008.
13. Kim, D., et al., *TRANOX: Model for non-isothermal steam oxidation of zircaloy cladding.* Journal of Nuclear Materials, 2021. 556.
14. Chaari, N., et al. *The behavior of Cr-coated Zirconium alloy cladding tubes at high temperatures*. in *Zirconium in the Nuclear Industry: 19th International Symposium*. 2021. ASTM International.
15. Gurgen, A. and K. Shirvan, *Estimation of coping time in pressurized water reactors for near term accident tolerant fuel claddings.* Nuclear Engineering and Design, 2018. 337: p. 38-50.