

The Corrosion Behavior of Zr-Nb-Sn Alloy Fuel Cladding in High Temperature Pressurized Water

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1. Introduction

The fuel cladding tubes, which is mainly made of zirconium alloys, are immersed in the primary water during operation, resulting waterside corrosion [1]. In general, the oxide layer thickness of fuel cladding tube is limited less than 100 μm during three-cycle operation to ensure the fuel integrity.

Many nuclear power plants have been recently employing the economic operation strategies such as power uprate, high burnup and long-term operation [2,3]. Such operation strategies not only accelerate oxidation of fuel cladding, but also accelerate deposition of corrosion product, which is called 'crud', on fuel cladding surface [4]. In addition, increased crud thickness impedes heat transfer from the cladding surface to the coolant and causes the increase in the temperature of cladding surface. As a result, crud deposition again causes accelerated corrosion of fuel cladding [5]. However, the study has been rarely done for accelerated corrosion of fuel cladding due to crud.

In this work, we evaluated the corrosion characteristics of commercial fuel cladding tube for 10,000 hours and analyzed their oxide film, prior to investigating the effect of crud deposit on the acceleration of cladding oxidation.

2. Experiment Methods

Zirconium base alloy tube, which has the same properties with commercial fuel cladding tube, ZirloTM, was used as a test specimen as summarized in table 1. The dimension of the test tube was an outer diameter (OD) of 9.5 mm and inner diameter (ID) of 8.3 mm. The tube specimens were cut to a length of 2 mm and 12 pieces were prepared.

Table 1. Chemical composition and mechanical properties of Zr alloy cladding tube

Chemical composition (wt%)				
Sn	Fe	O	Nb	Zr
1.0	0.1	0.12	1.0	Bal.
Mechanical properties (at RT)				
YS (MPa)	UTS (MPa)	Elong. (%)		
612.5	819.2	15.8		

Prior to the corrosion test, all prepared specimens were pre-characterized by weight and surface area before the test was initiated. The surface area was carefully measured for each specimen by measuring the dimensions of specimen, such as ID and OD, length and wall thickness as well as excluding the holes drilled, using a digital Vernier caliper. The specimens pre-characterized were sequentially degreased in acetone, alcohol and deionized water for 10 min each.

The corrosion test was performed according to the procedure of ASTM G2/G2M-19 [6], which is a standard evaluation method for zirconium and its alloys. Prior to test, the autoclave with a volume of 3.75 L and specimen tree, which were constructed with stainless 316L, were pre-conditioned in deionized water at 360°C for one week after cleaning. After pre-conditioning was completed, the specimens were hung at specimen tree and it was inserted into the autoclave. The deionized water was filled in the autoclave and it was purged with argon gas for 24 hours after covering its lid, to eliminate the dissolved oxygen. Then, the autoclave was gradually heated until the temperature of coolant reached to 360°C. In addition, the weight measurement of the specimens was performed with 500 hours intervals for 10,000 hours to evaluate the corrosion rate.

The morphology and thickness of the oxidation layer for some sampled specimens was analyzed using scanning electron microscope (SEM) equipped with focused ion beam (FIB) machine. In addition, the crystallography of the oxidized specimens was analyzed using X-ray diffraction (XRD). The composition profiles of the oxidized specimens in cross-sectional view were measured using the energy dispersive spectroscopy (EDS) equipped with transmission electron microscope (TEM). Furthermore, the surface zeta potential of as-prepared and oxidized specimens was measured for discussing the reason of change in crud deposition on two-types cladding tubes.

3. Results and discussion

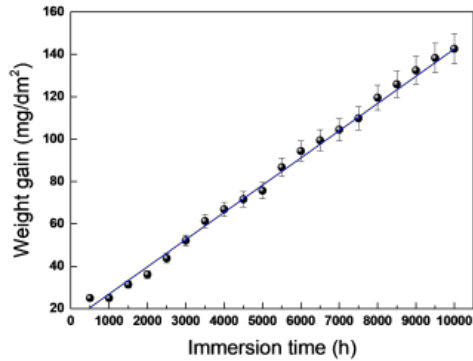
Fig.1 shows the weight gain and the corrosion rate of fuel cladding specimens with increase in immersion time. The weight gain (WG) has linear relationship with immersion time (T) as fitted by followed equation (Fig. 1(a)). This result has similar value to that for equivalent material reported by some researchers [1, 7].

$$WG(\text{mg}/\text{dm}^2)=0.00157+1.4357\times 10^{-6}T$$

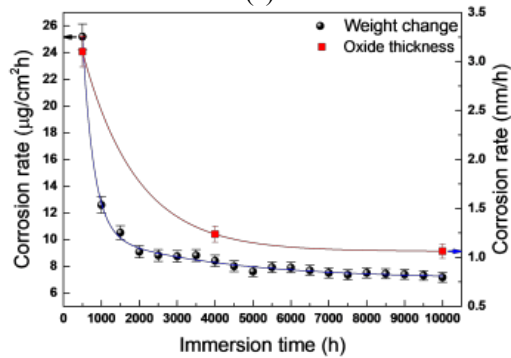
The corrosion rate (CR) as shown in Fig. 1(b) decreases exponentially with increase in immersion time as fitted by followed equation. The corrosion rate was evaluated from the weight gain and the measured thickness value as shown in Fig. 1(a) and Fig. 2, respectively.

$$CR(\text{mg}/\text{dm}^2\text{h})=90.258-79.185(1-e^{-T/296})-3.998(1-e^{-T/3355})$$

$$CR(\mu\text{m}/\text{h})=0.00106+0.00289e^{-T/1426}$$



(a)



(b)

Fig. 1 (a) Weight gain and (b) corrosion rate of fuel cladding specimen through corrosion test for 10,000 hours.

In addition, many circumferential cracks were observed in the oxide layer and the number of cracks increased with increase in immersion time as shown in Fig. 2. The oxide thickness of the specimen corroded for 500 hours is about $1\ \mu\text{m}$ and that corroded for 10,000 hours is about $10\ \mu\text{m}$.

Fig. 3 shows the XRD patterns of the specimens as the test time increases. The characteristic peaks of metallic Zr-1.0Nb, which is referred to JCPDS No. 05-0665, were observed on the specimens corroded for 500 and 2,000 hours. In addition, the characteristic peaks of Zr-1.0Nb disappeared and the characteristic peaks of monoclinic zirconium dioxide ($m\text{-ZrO}_2$), which is referred to JCPDS No. 37-1484. The intensity of the $m\text{-ZrO}_2$ characteristic peaks gradually increased as the test time increased in the range of 4,000 to 10,000 hours.

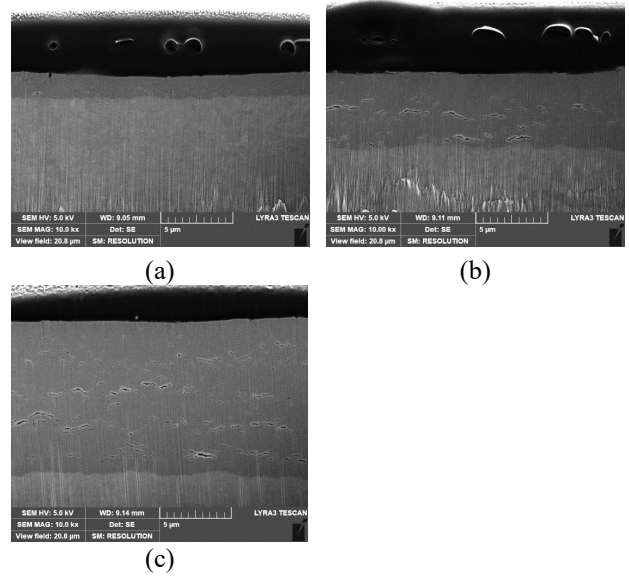


Fig. 2 Cross-sectional SEM images of specimens corroded for 500, 4,000 and 10,000 hours.

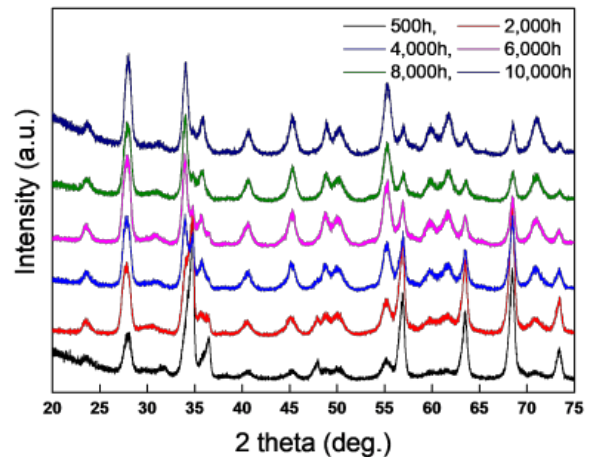


Fig. 3 XRD patterns of oxidized specimens as the test time increases.

The zirconium content in oxide layer of Zr-1.0Nb alloy specimen gradually increased from water-side to metal-side in TEM-EDS results as shown in Fig. 4. While the oxygen content in oxide layers gradually decreased from water-side to metal-side.

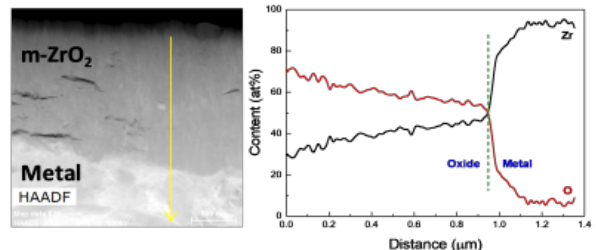


Fig. 4 STEM image and EDS profile of fuel cladding corroded for 500 hours.

4. Conclusions

We have investigated the oxidation behavior of Zr-1.0Nb alloy fuel cladding. The weight gain increases linearly with increase in immersion time. In addition, the corrosion rate evaluated from the weight gain and the oxide thickness decreases exponentially with increase in immersion time. Many circumferential cracks were observed in oxide layer and its density increases with increase in immersion time. Therefore, it is expected that the oxidation characteristics of Zr-1.0Nb alloy can affect to the crud growth and the accelerated corrosion for crud-deposited fuel cladding.

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REFERENCES

- [1] A. T. Motta, A. Couet, R. J. Comstock, Corrosion of Zirconium Alloys Used for Nuclear Fuel Cladding, *Annu. Rev. Mater. Res.* 45(2015) 311-343.
- [2] J. Deshon, D. Hyssey, B. Kedrick, J. McGurk, J. Secker, and M. Short, Pressurized Water Reactor Fuel crud and corrosion modeling Nuclear Reactor Power Monitoring, *Journal of Materials*, 2011.
- [3] G. Wang, W.A. Byers, M.Y. Young, J. Deshon, Z. Karpitas, and R.L. Oelrich, Thermal conductivity measurements for simulated PWR crud, *International Conference on Nuclear Engineering*, 2013.
- [4] J. Deshon, PWR Axial Offset Anomaly (AOA) Guidelines, Rev. 1, EPRI Report, 1008102, EPRI, Palo Alto, 2004.
- [5] D. Hussey, D. Wells, Fuel Reliability Guidelines: PWR Fuel Cladding Corrosion and Crud, Rev. 1, EPRI Report, 3002002795, EPRI, Palo Alto, 2014.
- [6] ASTM G2/G2M-19, Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680°F(360°C) or in Steam at 750°F(400°C), 2020, ASTM.
- [7] Water chemistry and clad corrosion/deposition including fuel failures, *Proc. Tech. Meeting, IAEA*, 2010.