The Effect of Corrosion Product Deposit on Corrosion Acceleration of Zr-1.0Nb-1.0Sn Fuel Cladding Materials in High Temperature Pressurized Water

Hee-Sang Shim [a*], Mingyo Seo [a,b], Do Haeng Hur[a], Soon-Hyeok Jeon[a], Sang-Yeob Lim[a], Seong Jun Ha[a], Soo Yeol Lee[b]

[a]*Materials Safety Technology Research Division, KAERI, 989-111 Daedeok-daero, Yuseong-gu, Daejeon 34057, Korea*

[b]*Department of New Materials Engineering, Chungnam National University, 99 Daehak-ro, Yuseong-gu, Daejeon 34134, Korea*

**Corresponding Author: hshim@kaeri.re.kr*

***Keywords: Fuel Clad, Corrosion Product Deposit, General Corrosion, Primary Water, PWR**

1. Introduction

The fuel cladding tubes are mainly made of zirconium alloy, which has low neutron absorption cross-section, excellent thermal conductivity and corrosion resistance. The fuel cladding is 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 ㎛ during three-cycle operation to ensure the fuel integrity.

Many nuclear power plants have been operated recently in power uprate, high burn-up, and long-term operation strategies for economic electricity generation [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 hinders heat transfer from the cladding surface to the coolant and increases the temperature of cladding surface. As a result, heavy 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 developed the methodology to investigate the corrosion acceleration of fuel cladding materials due to heavy crud deposition and evaluated the effect of primary coolant pH on corrosion characteristics of Zr-base alloy fuel cladding tube deposited by thick crud.

2. Experimental

Zirconium base alloy tube, which has the same properties with commercial fuel cladding tube, Zirlo™, 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.

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

The effect of crud deposit on fuel cladding corrosion was in following two-step experiments: 1) thick crud deposition, 2) immersion test under heat flux in primary water of pressurized water reactor (PWR). The Zr-1.0Nb-1.0Sn tube has cut with 550 mm length and one end of the tube specimen was welded with zirconium plug to provide a leak-tight joint. The cladding tube was sequentially degreased in acetone, ethanol, and deionized (DI) water, respectively. A cartridge heater was inserted into the tube and the gap between tube and heater was filled with MgO paste. The simulated PWR primary water is prepared by dissolving LiOH of 2 ppm and H_3BO_3 of 1,000 ppm into the DI water. The dissolved oxygen was controlled to be less than 5 ppb and dissolved hydrogen was maintained 35 cc/kg·H_2O. Crud source for fuel crud deposition was prepared using nickel thethylenediamine tetraacetic acid (EDTA) of 1,500 ppm and iron acetate of 2,000 ppm. Crud deposition were performed using the KAERI crud deposition loop system as shown in Fig. 1. The temperature and pressure of primary coolant in the test section were maintained at 325oC and 13 MPa. The heat flux from clad surface was controlled to 60 W/cm2 to make sub-cooled nucleate condition. The crud source was injected to the bottom of test section by using a metering pump with a flow rate of 1.0 mL/min. The deposition test was conducted for 10 days.

The crud-deposited tube was cut by 100 mm length and welded with non-deposited tube of 100 mm. This welded tube was transported and mounted to the test section of the CATE (CILC Advanced Test Equipment) loop as shown in Fig.2. The corrosion test of crud-deposited fuel cladding was performed in simulated primary coolant under 60 W/cm^2 using the CATE loop for 20 days.

The morphology and thickness of the pre-deposited crud and oxidation layer before and after corrosion test were 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).

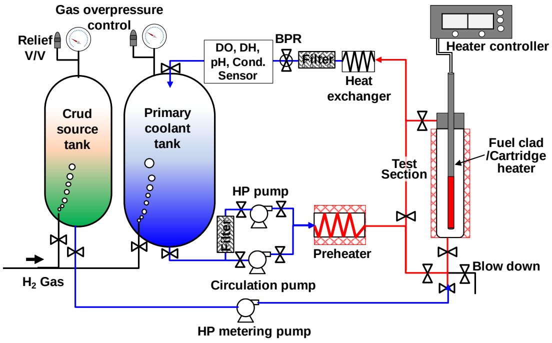


Fig. 1. A Schematic of the simulated crud deposition loop

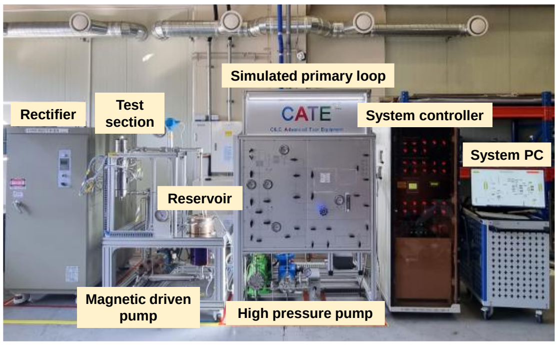
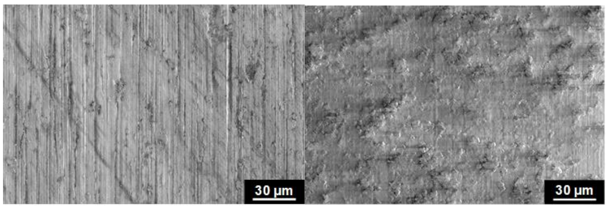


Fig. 2. A picture of the corrosion test loop of crud deposited fuel cladding

3. Results & discussion

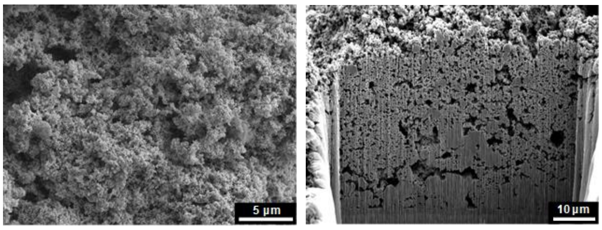
Fig. 3 shows the SEM surface images of non-crud deposited fuel clad welded with crud-deposited clad before and after corrosion test. The polishing marks were only observed on the surface of fuel clad before corrosion test as shown in Fig.3(a) but, small polyhedral particles were observed on that after corrosion test as shown in Fig. 3(b). The polyhedral particles were nickel ferrite as not shown here and those might be migrated from the crud-deposited fuel clad through flowing coolant.



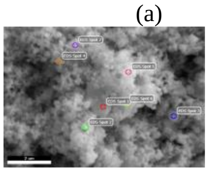
(a) (b)

Fig. 3. SEM surface images of non-crud deposited fuel clad before and after corrosion test

Fig. 4 shows the SEM surface and cross-section images and EDS analysis results of pre-deposited crud. Crud deposited on fuel clad are composed of polyhedral particles with sized of hundreds nanometer to few micrometers as shown in Fig. 4(a). This crud shows the porous structure with 70~90 μm thickness as shown in Fig.4(b). The chemical composition of crud was analyzed with $Ni_xFe_{3-x}O_4$ nickel ferrite as summarized in Fig.(c). The chemical composition of four crud samples was analyzed as a nickel ferrite to be $Ni_{0.7}Fe_{2.3}O_4$.



(a) (b)

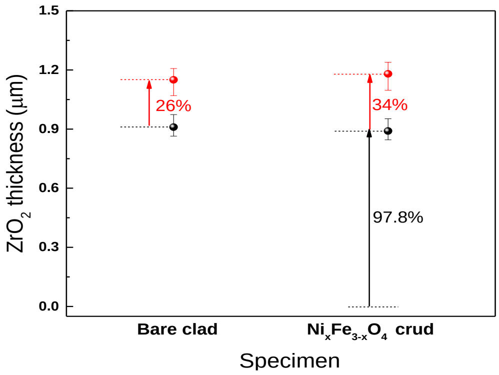


Element (at%)	P1	P2	P3	P4	P5	P6	P7
Ni	19.13	13.88	16.20	12.41	11.09	15.32	10.70
Fe	39.59	32.80	36.49	37.97	34.27	30.98	33.78
O	41.28	53.32	47.31	49.63	54.64	53.70	55.52
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

(c)

Fig. 4. (a) Surface and (b) cross-sectional SEM micrographs and (c) EDS point analysis of pre-deposited crud layer

Fig. 5 displays the comparison graph for zirconium oxide (ZrO_2) thickness of fuel cladding tube with and without crud before and after corrosion test. The ZrO_2 thickness was measured by TEM analysis from FIB-machined cross-section of the samples. The oxidation of Zr-1.0Nb-1.0Sn alloy increased more by 8% in crud deposited cladding than in non-crud deposited cladding. Therefore, this experimental data can support well the theoretical opinion, in which the oxidation of fuel cladding is promoted due to the interference of heat transfer by the crud.



4. Conclusions

We have investigated the effect of crud deposition on the corrosion rate of Zr-1.0Nb-1.0Sn alloy fuel cladding in this work. Some of the crud deposited on fuel cladding was washed and transported on fresh cladding tube surface but, almost crud was maintained on deposited location. In addition, the crud accelerated the corrosion of fuel cladding with about 8%, comparing to that of fresh surface. Therefore, it is proved that the crud promotes the oxidation of fuel cladding and increases the probability of its crud-induced localized corrosion.

Acknowledgments

This work was supported by the National Research Foundation (NRF) grant funded by the Koran government (Grant No. RS-2022-00143316).

REFERENCES

[1] 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
[2] 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
[3] J. Deshon, PWR Axial Offset Anomaly (AOA) Guidelines, Rev. 1, EPRI Report, 1008102, EPRI, Palo Alto, 2004.
[4] D. Hussey, D. Wells, Fuel Reliability Guidelines: PWR Fuel Cladding Corrosion and Crud, Rev. 1, EPRI Report, 3002002795, EPRI, Palo Alto, 2014.
[5] J. S. Lee, G. Kim, Crud and Oxide Layer Modeling for Safety Analysis of a PWR, Trans. KNS Spring Meeting, Jeju, Korea, 2016.