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Behavior of Zinc, Silica, and Zeolite-forming Impurities on Fuel Crud in a Simulated Primary Water of PWRs

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1. Introduction

Corrosion products are released as both soluble and insoluble species from the surfaces of structural materials into the primary coolant of pressurized water reactors (PWRs). Corrosion products transported with coolant to core are deposited on the fuel and become activated. In addition, the activated corrosion products are released back into the coolant and deposited on out-of-core surfaces, resulting increase of radiation dose. A part of corrosion products is remained as the deposit on fuel cladding tubes, which is called as a crud, and often results the accumulation of boron in its porous structure or the increase of local temperature of fuel surface [1-3]. The increased boron content within the crud can cause a shift in the core neutron flux along the length of the fuel assemblies [4-6]. In addition, the increase of local surface temperature often induce localized corrosion and fuel failure [7,8]. Therefore, it is important to decrease the released corrosion products in order to minimize the radiation build-up, neutron flux shift and fuel failure.

Zinc injection has been proposed as an effective way to mitigating PWSCC in steam generator tubing and reactor vessel head penetrations. In addition, it is also well known that zinc is beneficial in reduction of out-of-core dose rates and fuel deposits [9]. This is considered to be because the release of corrosion products into the coolant is suppressed by stable passivation layer such as $ZnFe_2O_4$ and $ZnCr_2O_4$ formed by zinc replacing divalent ions such as nickel and cobalt in the oxide layer of steam generator tubing [10-12]. This phenomenon leads the reduction of fuel deposits. However, concerns about fuel integrity were raised as compounds in which zinc combined with silica or zeolites including calcium, magnesium, and aluminum were observed in fuel crud of some nuclear power plants applying zinc addition, although those were low concentration [13]. Deposition of zinc-silicate and -zeolites on fuel cladding surfaces can potentially increase cladding surface temperature, and lead to increased cladding corrosion rate and possibly failures [14].

Since it was first introduced to US Farley unit 2 in 1994, zinc injection has been widely applied to PWRs around the world, including US and Korea, due to its many positive advantages. It is reported that the zinc concentration in the coolant is enough in 5-10 ppb level for reducing the dose rate, but is more effective in 15-40 ppb level for PWSCC mitigation [13]. In Korea, zinc injection is currently applied to seven plants and there are plans to expand to all PWR plants in the future. Zinc concentration in domestic PWR plants is currently 5 ppb but an increase to 10 ppb is being considered. Therefore, it is necessary to evaluate the effect of the presence of silica and zeolite-forming ions in primary coolant on fuel crud layer during zinc injection in terms of fuel integrity evaluation for the increase of zinc concentration.

In this study, we made thick porous crud on a zirconium alloy cladding tube using simulated PWR primary coolant loop. In addition, the crud-deposited fuel cladding was tested in simulated PWR primary water under constant zinc concentration with injecting silica and zeolite-forming impurities at 328°C. The physical and chemical properties of fuel crud was discussed through various analysis before and after immersion test.

2. Experimental

2.1. Preparation of specimen and test solution

The presence effect of silica and zeolite-forming-ions such as calcium, magnesium and aluminum in primary coolant on crud deposited on fuel cladding surface was analyzed in following two-step experiments: 1) thick crud deposition, 2) immersion test in PWR primary water containing different zinc content, with or without injecting mixed solution of silica, magnesium, calcium, aluminum in constant rate.

A zirconium alloy tube having characteristics equivalent to commercial tube was used as a fuel cladding material. Its chemical composition and mechanical properties are summarized in Table 1. This tube has a dimension of 9.5 mm in outer diameter (OD), 8.3 mm in inner diameter (ID), and 550 mm in length, respectively. The cladding tube was sequentially degreased in acetone, ethanol, and deionized water after welding one end with zirconium plug. A cartridge heater was inserted into the tube and the gap between tube and cartridge heater was filled with MgO paste.

Table 1. Chemical composition and mechanical properties of fuel cladding tube.

Composition (wt%)					**Mechanical properties**		
Sn	Fe	O	Nb	Zr	YS (MPa)	UTS (MPa)	Elong. (%)
1.0	0.1	0.12	1.0	Bal.	612.5	819.2	15.8

The simulated PWR primary water is prepared by dissolving LiOH of 2 ppm and H_3BO_3 of 1,000 ppm into the deionized 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 ethylenediamine tetraacetic acid (EDTA) of 1,500 ppm and iron acetate of 2,000 ppm.

2.2. Thick crud deposition test

Thick crud deposition were performed using the KAERI crud deposition loop system as shown in Fig. 1 [15]. The primary coolant recirculated via a high pressure pump, preheater, test section, and heat exchanger with a flow rate of 280 mL/min. The temperature and pressure of primary coolant in the test section were maintained at 325°C and 13 MPa. The heat flux from clad surface was controlled to 65 W/cm^2 to make sub-cooled nucleate condition [16]. The crud source was injected to the bottom of test section by using a metering pump with a injection rate of 1.0 mL/min. The deposition test was conducted for 10 days to be crud layer thicker than 30 μm.

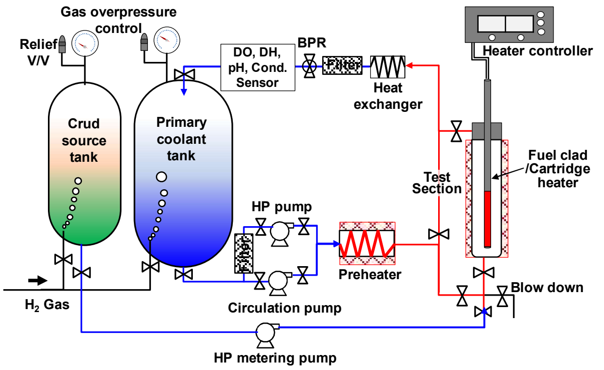

Fig. 1 Schematic of the test loop for thick crud deposition.

2.3. Immersion test of fuel cruds

The immersion test of fuel crud was performed using the simulated primary loop system as shown in Fig. 2. The crud-deposited cladding tube prepared by using the crud deposition loop was transferred and mounted to test section of the immersion test loop. A depleted zinc acetate (DZA) was used as a zinc source and dissolved directly into the solution tank. The zinc concentration was 10 ppb and 60 ppb in simulated primary coolant in this work. Two solution tanks of 200 L and 50 L were switched in order to maintain consistently the zinc concentration during experiment. In addition, the solution dissolving silica of 2 ppm, magnesium of 40 ppb, calcium of 40 ppb and aluminum of 80 ppb, respectively, into Li/B chemistry coolant was continuously injected into bottom of test section with the rate of 1.0 mL/min. Other chemistry conditions of primary coolant were the same with the crud deposition experiment. The heat flux from clad surface was maintained to 65 W/cm^2 and the immersion test was conducted for 500 h.

2.3. Crud analysis

After the immersion tests in primary coolant containing the zinc content of 10 ppb and 60 ppb with or without silica and zeolite-forming ions, the cladding tube specimens were cut into tubular segments using a tube cutter to analyze the crud.

The morphology of as-deposited crud and its immersed crud was observed using a scanning electron microscope (SEM). The thickness and porosity of crud layer were evaluated from the cross-sectional images the cross sections, which was machined by a focused ion beam (FIB) technique, by using Lince and ImageJ softwares. In addition, crud particles were detached with a 3M tape from the cladding surfaces for XRD examinations. X-ray diffraction patterns were recorded in the 2θ range from 25° to 75° with a scanning rate of 1°/min using a Rigaku SMARTLab high resolution diffractometer with Cu-Kα radiation at 40 kV and 300 mA.

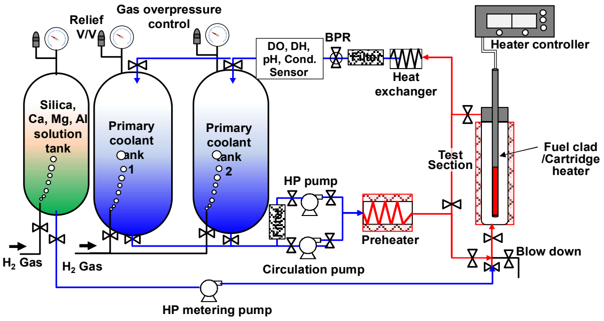

Fig. 2 Schematic of the immersion test loop for fuel crud under Zn injection with/without silica and zeolite-forming ions.

3. Results and discussion

Fig. 3 shows the SEM micrographs and XRD pattern of crud deposited on cladding tube for immersion test. Many protruding structures and various size pores were shown in Fig. 3(a). The crud layer was mainly composed of few micrometer and sub-micrometer polyhedral particles as shown in Fig. 3(b).

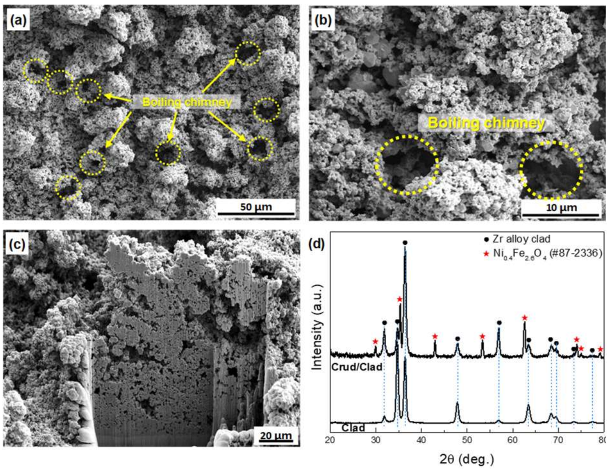

Fig. 3 (a-c) Surface and cross-sectional SEM micrographs of thick crud deposited fuel cladding tube, (d) XRD patterns of clad and crud deposited on clad.

In addition, the large pores as marked in yellow-dashed circles should be a boiling chimney, which is formed due to escape of boiling bubbles. It was observed that the deposited crud layer was very porous in cross-sectional image as shown in Fig. 3(c). The characteristic peaks of deposited crud were corresponded to those of spinel nickel ferrite ($Ni_{0.4}Fe_{2.6}O_4$, JCPDS No. 87-2336).

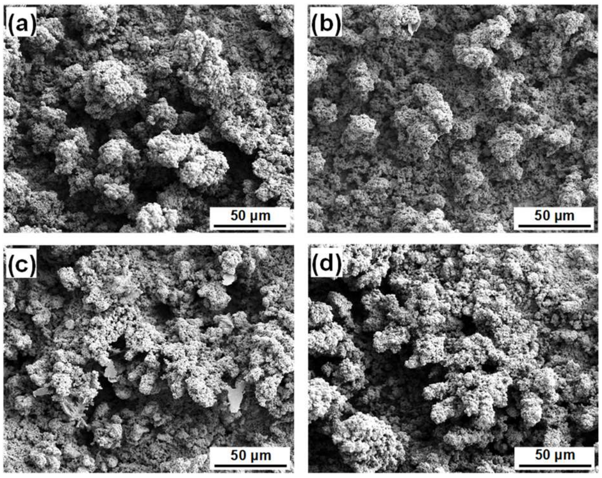

Fig. 4 SEM surface micrographs of the cruds in different Zn injection conditions: (a) 10 ppb Zn, (b) 60 ppb Zn, (c) 10 ppb Zn + impurities, and (d) 60 ppb Zn + impurities.

Fig. 4 shows the SEM surface micrographs of the cruds after immersion test in different Zn injection conditions. The surface morphologies of cruds immersed in simulated PWR primary coolant containing Zn content with or without impurities were similar with that of as-deposited crud. This means that the impact of zinc addition on the surface morphologies of crud deposited on fuel cladding is negligible.

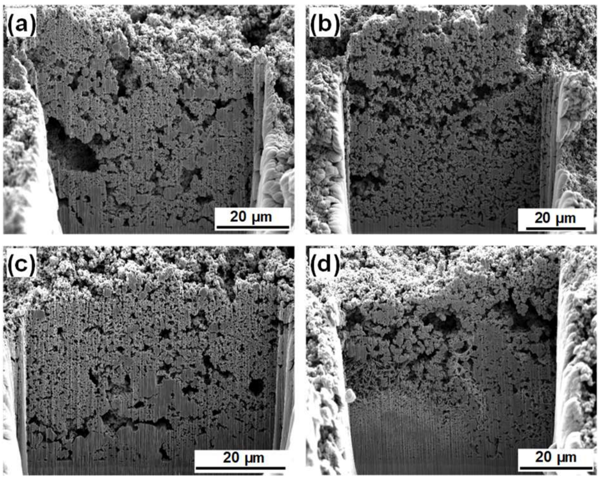

Fig. 5. Cross-sectional SEM micrographs of the cruds in different Zn injection conditions: (a) 10 ppb Zn, (b) 60 ppb Zn, (c) 10 ppb Zn + impurities, and (d) 60 ppb Zn + impurities.

Fig. 5 displays SEM cross-sectional micrographs for the cruds after immersion test in four different Zn injection conditions to evaluate thickness and porosity. The porosity of cruds immersed in simulated PWR primary coolant containing Zn content with or without impurities was similar with that of as-deposited crud in SEM figures. However, nanowire-shaped oxides were observed in some pore regions of crud immersed in the coolant containing 60 ppb Zn and impurities.

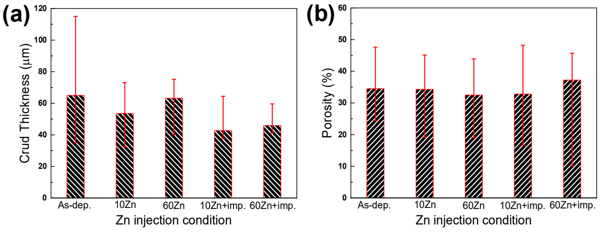

Fig. 6. Average thickness and porosity of cruds before and after immersion test in different Zn injection conditions.

The thickness and porosity of cruds were evaluated by using Lince and ImageJ software from the SEM cross-sectional images, which was machined by FIB technique. Fig. 6 shows the average thickness and porosity of the cruds. The average thickness of as-deposited crud was 65 μm and 34.5%, respectively. The average thicknesses of cruds were slightly decreased from 54-63 μm to 43-46 μm in the condition injecting zinc together with impurities comparing to that injecting zinc only. However, since the thickness of the crud layers consisting of protruding structures and boiling pores may vary depending on location, the comparative evaluation of the thickness of these cruds would be meaningless. Furthermore, the porosity is similar in the range of 32.5~37.5% for all cruds immersed in different Zn conditions.

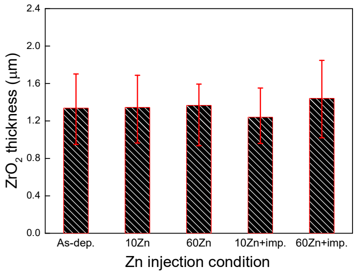

Fig. 7. Average thickness of zirconium oxide layer before and after immersion test in different Zn injection conditions.

Fig. 7 shows the average thickness of zirconium oxide layer on fuel cladding tubes before and after immersion test in different Zn conditions. The thickness of zirconium oxide layer beneath crud was measured in the range of 0.96-1.70 μm and the average thickness was 1.34 μm. The oxide thicknesses in crud specimens immersed in different Zn conditions were not changed with 0.25-1.44 μm from that in as-deposited crud specimen. Therefore, it is also considered that zinc and impurities contained into the coolant does not accelerate the oxidation of fuel cladding tube.

Fig. 8 shows the XRD results of the cruds before and after immersion tests. The characteristic peaks related with Zn compounds were not observed in cruds immersed in primary coolant including Zn content.

However, new characteristic peak was observed at 33.2°, which is consistent with (110) peak of SiO_2 (JCPDS No. 29-0085), for the cruds immersed in both 10 ppb and 60 ppb Zn conditions including impurities. An intensity of SiO_2 characteristic peak became larger with increase of Zn content from 10 ppb to 60 ppb. This means that the silica can be accumulated into porous crud structure in its high concentration. In addition, it is predicted that silica is easy to be accumulated into the crud through increasing the Zn concentration.

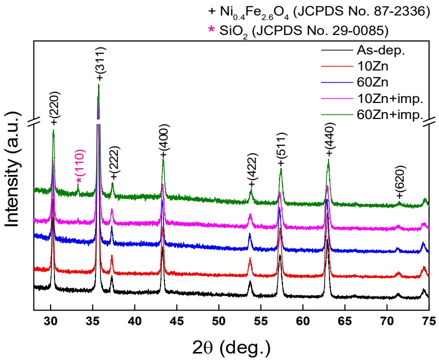

Fig. 8 XRD patterns of cruds before and after immersion test in different Zn injection conditions.

In our previous work [15], the Zn is incorporated with the crud structure when it is added during beginning operation stage, and its concentration increases with decreasing Ni content in the spinel nickel ferrite particles as the Zn concentration increases in the coolant. It might be because Zn cation is preferable to substitute better than Ni cation into spinel ferrite structure during crud deposition [12]. In contrast, both physical and chemical properties of already-deposited crud were not changed from that before immersion test in coolant regardless of Zn concentration. It would possibly be because the immersion time of 500 h is not enough Zn ion to substitute to Ni ion in nickel ferrite crud or the electrostatic force between corrosion product particles and crud surface is weaker than that between those and clad surface. However, the silica was measured in the cruds when the silica and zeolite-forming ions was together added during Zn injection and its intensity increased with increase of Zn content as shown in XRD results. This result indicates that the silica can accumulate into the porous crud structure at the concentration as high as 2 ppm and the zinc can affect to accumulation of silica to crud structure, although those chemistry conditions does not affect to the oxidation of fuel cladding tube. It means that the silica accumulation does not affect to the oxidation of fuel cladding tube due to reduction of thermal transport property at least in 500 h.

4. Conclusions

We have investigated the effect of Zn injection with or without silica and zeolite-forming ions on the characteristics of pre-deposited during immersion test in simulated primary coolant under four different Zn injection conditions. The change in surface morphology, porosity, and average thickness of crud layer is not found after immersion test in the primary coolant containing Zn with or without impurities for 500 h. In addition, such a chemistry change does not also affect the oxidation of Zr-alloy cladding. However, the silica was analyzed in the cruds after immersion test in the primary coolant containing silica and zeolite-forming ions regardless of Zn concentration. Therefore, the content including silica and zeolite-forming ions in the coolant should be strictly controlled during Zn injection.

Acknowledgments

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