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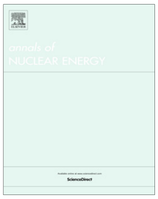

Effect of aluminum oxide coated on fuel cladding surface on crud deposition in simulated PWR primary water

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ABSTRACT

Deposits on fuel assemblies (crud) have been the main cause of local power shift, increased fuel cladding temperature, accelerated fuel cladding corrosion, and radiation buildup in nuclear power plants. We report the experimental results on aluminum oxide (Al_2O_3) as a fuel cladding coating for crud mitigation. Crud deposition tests were performed under a sub-cooled nucleate flow boiling condition in simulated primary water of pressurized water reactors at 328 °C. The amount of deposits on the Al_2O_3-coated cladding tube decreased by 23% compared with that on the uncoated cladding tube. The difference of zeta potentials between magnetite particle and cladding surface increased from 7.5 mV to 16.1 mV, when the cladding surface was coated with Al_2O_3. Therefore, the reduction of crud deposition can be attributed to the increased repulsive force between the magnetite particle and Al_2O_3-coated cladding surface. The effect of the Al_2O_3 layer is discussed from the view point of zeta potential, wettability, and thermodynamic stability.

1. Introduction

Corrosion products released from the surfaces of the structural materials in contact with the primary coolant of pressurized water reactors (PWRs) are deposited on the fuel assemblies. These corrosion products are referred to as crud, an acronym for chalk river unidentified deposits. Crud has been known to be composed of mainly Fe, Ni, and Zr oxides such as nickel ferrite, nickel oxide, iron oxide, zirconium oxide, and bonaccordite, etc (EPRI, 2004; Sawicki, 2008; Yeon et al., 2010; IAEA, 2011). Crud also has a porous structure because crud deposition is stimulated in a condition where sub-cooled nucleate boiling (SNB) occurs. In PWRs, pores within crud seem to be developed through the formation process of steam chimneys under SNB conditions.

Various chemical species dissolved in the primary coolant can be concentrated in these pores of the crud. Among them, concentrated boron-containing compounds can induce local power shift owing to neutron capture by boron, resulting in power output de-rating (Sawicki, 2008; Rák et al., 2015). Lithium can also be concentrated inside the pores, elevate pH there, and accelerate the corrosion rate of fuel claddings. In addition, the crud on fuel assemblies can increase fuel cladding temperature due to increased thermal resistance, resulting in accelerated fuel cladding corrosion (Cox, 2005; Edsinger et al., 2011).

The crud deposition has been a growing issue, as most utilities have moved to apply an extended fuel cycle and a high burn-up operation program (Park et al., 2017). Therefore, several methods have been implemented to plants to mitigate the above operational problems induced by crud. Elevated pH_T operation of the reactor coolant chemistry from 6.9 to 7.2–7.4 shows a reduction in crud deposition in PWRs (Stevens et al., 2006; EPRI, 2014). Ultrasonic fuel cleaning technology has been also used to remove crud from the reloaded fuel assemblies during overhaul (Yang et al., 2006; Deshon et al., 2006).

Crud source is basically originated from the corrosion products which are released from the corroded surface of steam generator tubes, stainless steel piping and reactor internals. These corrosion products are activated by a neutron flux in the core and thus become the main source of high radiation fields and occupational radiation exposure. Therefore, the mitigation methods of corrosion product release will be effective for crud reduction, as well as for radiation source term reduction in PWRs (Seo et al., 2014).

After the accident at Fukushima Daiichi in 2011, development of accident tolerance fuel (ATF) cladding materials have become an important research topic worldwide. One of the ATF options is to use a coated zirconium alloy cladding that can provide the necessary protection during an off-normal high temperature or

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LOCA (loss of coolant accident) conditions. The coating materials and their deposition technologies considered were extensively reviewed in the literature (Tang et al., 2017). Similarly, Dumnernchanvanit et al. have recently reported on the initial experimental evaluation results of crud-resistant materials as fuel cladding coatings to reduce crud deposition (Dumnernchanvanit et al., 2018).

In this work, we coated aluminum oxide (Al_2O_3) layer on a ZIRLO™ fuel cladding tube by using the atomic layer deposition (ALD) method. Crud deposition tests were performed to quantify the relative crud mass under a sub-cooled nucleate flow boiling condition occurring in a simulated primary water at 328 °C using a circulating loop system. The obtained results are discussed in the view point of electrostatic forces between magnetite particle and cladding surfaces, and wettability of the cladding surfaces.

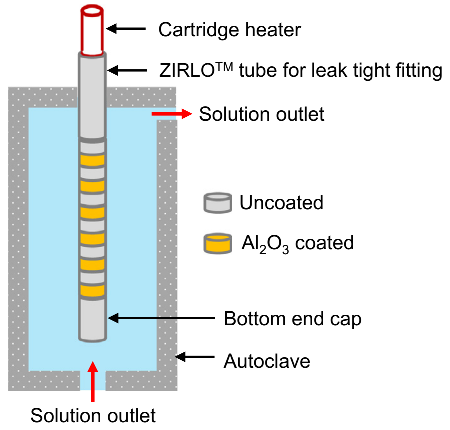

Fig. 1. Schematic of the specimens mounted on the rod heater in the test section.

2. Experimental methods

2.1. Specimen and solution preparation

In this work, Al_2O_3 was chosen as a coating material, based on its thermal compatibility with Zr-based cladding alloys and low neutron cross section. A comparison of these properties is given in Table 1 (Lide, 2005; Perry and Phillips, 1995; Fink and Leibowitz, 1995). A ZIRLO™ cladding tube, which is commonly used as a fuel cladding material, was used as the substrate for the coating. The cladding tube has a dimension of a 9.5-mm outer diameter (OD) and an 8.3-mm inner diameter. This tube was cut into tubular segments with a length of 6 mm and then the rings were ultrasonically cleaned in acetone and ethanol for 5 min. A part of the cladding tube was also segmented in small rectangle pieces and their OD sides were ground with silicon carbide (SiC) papers to have a flat surface to measure the wettability and surface zeta potential. At this time, the roughness of the flat surface was controlled to be the same as that of the as-received cladding tube.

Al_2O_3 layer was deposited using ALD technique on the surface of the prepared tubular and flat segments. ALD of Al_2O_3 layer was conducted at 250 °C with trimethylaluminum ($Al(CH_3)_3$, TMA) and de-ionized water (DIW) as reactants. One cycle of thermal ALD-Al_2O_3 growth consisted of a pulse of TMA, followed by a pulse of DIW. Each step was carried by a flow of nitrogen gas and separated by purge time. Two processes were performed alternately 200 times.

The ring specimens of as-received (uncoated) and Al_2O_3-coated segments were put on a cartridge heater. The diameter of the heater was designed to provide tight thermal contact with the ring specimens. As shown in Fig. 1, the six uncoated rings and six Al_2O_3-coated rings alternately were put on the heater rod. This is because alternate arrangement can reduce any error caused by the temperature gradient from the heater and coolant.

Test solution was prepared using high purity demineralized water with the resistivity near 18 MΩ•cm and nuclear grade chemicals of LiOH and H_3BO_3. The prepared solution chemistry was 3.5 ppm Li and 1500 ppm B in weight, which was used to simulate a primary water condition in the initial constant lithium regime of modified chemistry with maximum 3.5 ppm Li in PWRs. This solution of 200 L was stored in the solution tank.

The sources of Ni ions and Fe ions for crud deposition were prepared using Ni- and Fe-ethylenediaminetetraacetic acid, respectively. The mixed source solution of 1000 ppm Fe + 40 ppm Ni in weight was stored in the injection tank for injection to the test section.

2.2. Loop system for crud deposition

Crud deposition tests were performed in a 316 stainless steel autoclave connected to a primary water recirculating loop system, which was shown schematically in Fig. 2. The loop system consisted of the following main components: solution tank, high pressure pump (HP pump), pre-heater for solution inlet temperature control, crud source tank, metering pump for crud source injection, back pressure regulator (BPR) for system pressure control, heat exchanger, test section where the specimens are loaded.

The inlet solution into the test section was preheated and the temperature of the flowing water adjacent to the ring specimens was maintained at 328 °C. The temperature of the internal cartridge heater was maintained at 380 °C to provide the condition of SNB on the surface of the ring specimens during crud deposition tests. Our previous study confirmed the presence of active SNB in this condition through both acoustic emission method and boiling chimney observation (Baek et al., 2017; Park et al., 2017). The pressure of the test section was regulated at 130 bars. Dissolved oxygen was controlled to be less than 5 ppb and dissolved hydrogen was maintained at 35 $cm^3/kg{\cdot}H_2O$ (STP) by controlling the hydrogen overpressure of the solution tank. The flow rate adjacent to the specimens in the test section was controlled at 5 m/sec. After all these conditions are stabilized, injecting the crud source solution containing the mixed Fe and Ni ions into the test section was started via the metering injection pump. The mixed precursor ions were injected with a flow rate of 1.1 ml/min from the injection tank directly to the downstream of the preheater. This precursor solution is diluted in the simulated primary water stream and then its final chemistry is calculated to be 4.0 ppm Fe and 0.16 ppm Ni in the test section. The deposition test was conducted for 168 h without shutdown.

Table 1
Properties for the substrate materials and coating used in this work.

Material	Melting Temperature (°C)	Thermal Expansion Coefficient ($\times 10^{-6}$K)	Thermal Conductivity (W/mK)	Neutron Cross Section (barn)
Zr	1850	5.7	20	0.19 (Zr)
ZrO_2	2710	10.1	2	0.19 (Zr) 0.0002 (O)
Al_2O_3	2072	8.1	13	0.23 (Al) 0.0002 (O)