Characterization of fuel crud deposited in simulated PWR primary coolant with different zinc addition.

Kyeong-Su Kim[a,b], Hee-Sang Shim[a], Seung Heon Baek[a], Jong-Hyeon Lee[b], Do Haeng Hur[a,*]
[a]*Safety Materials Technology Development Division, Korea Atomic Energy Research Institute*
[b]*Department of Materials Science and Engineering, Chungnam National University*
[*]*Corresponding author:dhhur@kaeri.re.kr*

1. Introduction

Crud is a corrosion products deposited on fuel cladding surface in primary circuit of pressurized water reactors (PWRs), and it is formed precipitation or adhesion of metal ion and oxide particles released from the surface of the structural materials in primary coolant. The activated by a neutron flux in the core. The activated corrosion products are the major source of radiation build-up and occupational radiation exposure of worker during shutdown maintenance period [1,2].

The crud deposition on fuel assemblies can increase temperature of fuel cladding surface due to increased thermal resistance and it can be caused to accelerate fuel cladding corrosion. In addition, when the crud on fuel assemblies becomes locally thick, this leads the distortion of neutron flux along axial direction of fuel assemblies, which is called by the crud induced power shift (CIPS) or axial offset anomaly (AOA). This phenomenon often causes reducing core shutdown margin [3-6].

According to previous studies, the crud deposition rate is influenced by several factors as follows: particle concentration in primary coolant, dissolved oxygen, dissolved hydrogen, pH and temperature of coolant, and sub-cooled nucleate boiling (SNB) on the heated cladding surface. In some literatures, it was reported that the corrosion products were mainly composed of nickel ferrite and those solubility was minimal at pH = 7.4 [7]. Based on such a background, pH of PWR primary water has been increased from 6.9 to 7.4 in order to minimize the crud deposition on fuel claddings [8,9].

Zinc addition into the primary coolant has been also proposed as a potential method to minimize radiation field. In PWR, cobalt nuclides such as Co-58 and Co-60, which are formed by activation of Ni-58 and Co-59, respectively, are known as the major sources of the radiation field. Zinc has been known to interact strongly with oxide films in primary circuit. It is reported that zinc is incorporated with corroded oxide films and substituted with nickel atom, resulting its releasing into into the coolant. Thus, the Co-58 concentration in primary coolant becomes higher than that of Co-60, when zinc is added into the coolant. To reduce the radiation field of reactor coolant system as well as to mitigate PWSCC of Ni-based alloy, Zinc is added in a concentration range of 5 to 40 ppb in many PWRs following recommendation of the EPRI guideline [10]. However, the effect of zinc on the crud deposition behavior has not been clearly elucidated, up to now [11, 12].

Therefore, this study aimed to investigate the zinc effect on the crud deposition behavior with increasing its concentration. Crud deposition test was conducted at sub-cooled nucleate boiling (SNB) condition in simulated primary water with zinc of 0, 20 and 100 ppb, respectively. In addition, the morphologies and chemical composition of the crud was analyzed using scanning electron microscope equipped with energy dispersed spectroscopy. The boiling event during crud deposition test was investigated using acoustic emission (AE) analyzer.

2. Experimental Methods

2.1. Specimen and solution preparation

ZIRLO^{TM} tubes, which are generally used as a fuel cladding material, were chosen as a heat transfer tube. The dimensions of the heat transfer tube were outer diameter (OD) of 9.5 mm, inner diameter (ID) of 8.3 mm and length of 550 mm, respectively. The cladding tube was degreased in acetone and washed by distilled water before the test. Cladding tube was heated by internal heater to produce SNB condition on tube surface during the crud deposition tests. The heated zone was 250 mm length from the end of welded side. The gap between inside of the tube and internal heater (OD = 8.2 mm) was stuffed with MgO paste.

The simulated PWR primary water is prepared by dissolving LiOH of 2 ppm and H_3BO_3 of 1000 ppm into the high purity demineralized water with the resistivity above 18 MΩ-cm. In addition, Zn was added as a depleted zinc acetate (DZA) of 20 ppb and 100 ppb, respectively, to the primary coolant. The dissolved oxygen was controlled to be less than 5 ppb and dissolved hydrogen was maintained 35 cc/kg by controlling the hydrogen overpressure of the solution tank.

The sources for crud deposition were prepared using Ni- and Fe- ethylene diamine tetraacetic acid (EDTA), respectively. The mixed chemical solutions containing in depleted zinc acetate, Fe of 120 ppm and Ni of 70 ppm in weight were stored in 30 L injection tank and injected by 1.1 cc/min into the test section.

2.2. Deposition loop system

Loop system for crud deposition was constructed in such a way that primary water circulate, as shown in Fig. 1. The loop system consisted of the following main components ; solution tank of primary water, high pressure (HP) pump, pre-heater for test section inlet temperature control, crud source tank, injection pump for mixed Ni and Fe sources, test section equipped with a fuel cladding and AE acquisition system, heat exchanger, back pressure regulator (BPR) for system pressure control.

The primary water was transported using the HP pump from solution tank to test autoclave via pre-heater. Then, the primary coolant returned to solution tank after passing through test autoclave. Then, two solution tanks containing same concentration of zinc were used alternately to maintain zinc concentration during crud deposition test. The zinc concentration was controlled to 0, 20, and 100 ppb, respectively. The solution temperature at inlet of test autoclave was adjusted to 320ºC before increasing the temperature of internal heater installed into fuel cladding. During the deposition test, the heat flux of internal heater was kept 65 W/cm^2 to provide SNB condition on the cladding surface. The pressure in the test autoclave was regulated at 120 bar, which was saturated temperature at 325ºC. After these conditions were stabilized, curd source solution was injected into downstream of the test autoclave with a flow rate of 1.1 cc/min using a metering injection pump. Crud deposition test was conducted for 25 days. During the test, the SNB from the heated fuel cladding surface was monitored using acoustic emission technique (AE) for 300 s and sampled 20 ml of primary coolant every day, to monitor zinc concentration in the loop system [13]. Detail experimental conditions of the tests were summarized in Table 1.

Table 1. Experimental conditions for crud deposition test.

Zinc (ppb)	Temp./ Pressure	Solution	Deposition Time	AE data
0	320 ºC/ 120 bar	1000 ppm B & 2 ppm Li, and 120 ppm Fe & 70 ppm Ni	25 days	300 s/ day
20				
100				

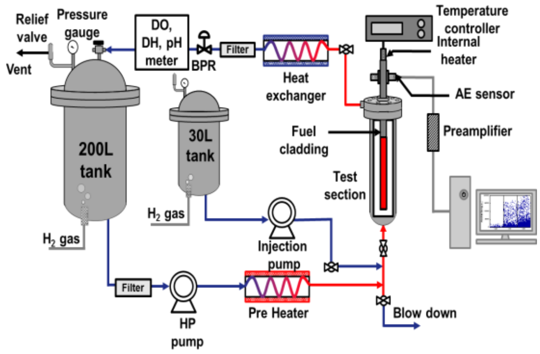

Fig. 1. Schematic diagram of fuel crud deposition system.

2.3. Boiling signal monitoring

AE sensor was directly coupled with the sensor holder and directly installed to the cladding tube at position 65 mm away from the upper end of the fuel cladding tube, as shown in Fig. 1. The connected the AE sensor and pre-amplifier was monitored AE signal. A low frequency AE sensor (type R3a) was chosen to collect the boiling signals. The resonant frequency range of low frequency sensor is from 30 to 75 kHz. In this work, the AE signals from the sensor were pre-amplifier by gain of 40 dB. The threshold value was set at 46 dB to eliminate background noise. During the test, an air circulator was installed to prevent the temperature rising of the sensor.

2.4. Measurement of deposits

After deposition tests, the cladding specimens were cut to measurement of deposit mass and microscopic analysis of the deposit. The deposits on the surface of the tubular specimens were dissolved in an inverse aqua regia solution. Thereafter, the concentrations of Ni, Fe and Zn were analyzed using an inductively coupled plasma-atomic emission spectroscope (ICP-AES). The morphologies of the deposits were examined using a scanning electron microscope (SEM).

3. Results and discussion

Fig. 2 shows the SEM micrographs of crud deposited on fuel cladding surface after deposition test under three different zinc concentrations. Fuel cruds were mainly polyhedral-shaped oxide particles. However, some string-like structure with length of tens micrometer were observed in fuel crud deposited under zinc addition of 100 ppb. The amount of oxide particles was almost similar for zinc concentrations of 0 and 20 ppb, but it seemed to be decreased at 100 ppb zinc concentration. This is well corresponded with the ICP-AES data as shown in Fig. 3 [14].

Fig. 3 shows the metal deposit quantity of the cruds obtained using ICP-AES. The amount of metal deposit was similar value for the cruds formed under zinc concentrations of 0 and 20 ppb. However, the amount of metal deposit in the crud grown under 100 ppb zinc was remarkably decreased by 44% comparing to that of cruds for 0 and 20 ppb zinc conditions. This indicates that the zinc concentration affects to crud morphology as well as its quantity.

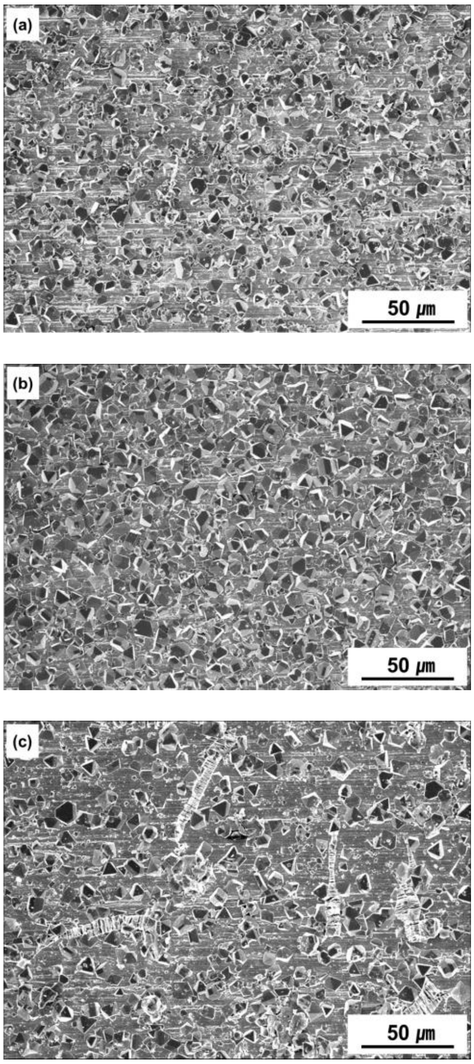

Fig. 2. SEM micrographs for crud on fuel cladding surface after deposition tests for 25 days under the three different zinc concentrations: (a) 0 ppb, (b) 20 ppb, and (c) 100 ppb.

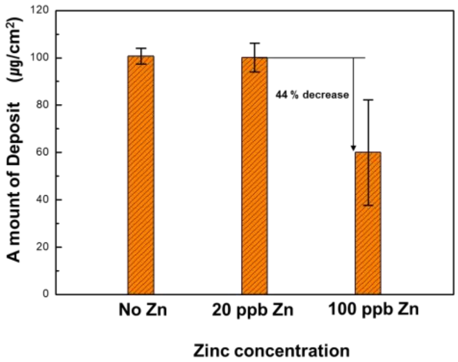

Fig. 3. Quantity of fuel crud deposited for 25 days in a simulated PWR primary water including different zinc concentrations.

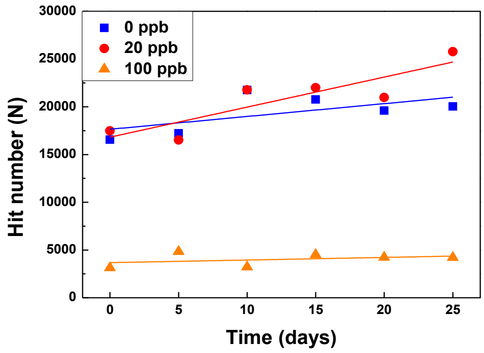

Fig. 4. Hit numbers for the boiling events during crud deposition tests under different zinc concentrations.

Fig. 4 presents the hit numbers with increasing deposition time for each test. All deposition tests were conducted under equivalent SNB condition, which is monitored using acoustic emission analysis. Acoustic sound is emitted when vapor bubbles leave from cladding surface into the coolant. Thus, hit number for the boiling events means the degree of SNB in each test set. Hit numbers at zinc condition of 0 ppb and 20 ppb are similar in starting stage with about 17,000 times. However, hit number at 20 ppb zinc condition increases up to about 25,000 times, while that at no zinc addition shows relatively lower change from 17,000 to 19,000 times as the deposition time increase to 25 days. In addition, hit number at 100 ppb zinc condition shows very low value with about 3,500 times compared to that at 0 ppb and 20 ppb zinc condition. Furthermore, hit number at 100 ppb zinc condition rarely changed with increasing test time to 25 days [15,16].

Variation of zinc concentration in simulated PWR primary water significantly affects to crud morphologies and its amount as shown in Figs. 2 and Fig 3. These characteristics are negligible difference in crud deposited under zinc addition of 20 ppb compared to those at no zinc addition. However, the oxide structure having long string shape was newly formed and quantity of crud decreased by 44% from that in cruds for 0 ppb and 20 ppb zinc condition as shown Fig. 4. Furthermore, the number of boiling events remarkably decreased by zinc addition of 100 ppb over 75% compared to those for 0 ppb and 20 ppb. Although the chemical composition and microstructure of the curds was not analyzed enough in this work, it is clearly seen that the amount of crud can be controlled by variation of zinc concentration as well as its morphology. Currently, worldwide PWR reactors permit the zinc addition in concentration range of 5-20 ppb. In view point of crud quantity and its morphology, it is needed that the zinc concentration is considered under various conditions.

4. Conclusions

This work has investigated the effect of zinc addition on fuel curd deposition, SNB, and amount of deposit. The main results can be derived:

(1) The deposited amount of zinc addition on fuel crud deposition in primary water decreased with zinc concentration increased. Therefore, zinc injection is expected to be preferred for the crud deposition in fuel assemblies of PWRs operating at long fuel cycles.

(2) The hit number of the boiling AE signals showed lower values on the fuel cladding with 100 ppb zinc concentration. This means that the higher zinc concentration, the degree of SNB decreases on the cladding surface.

(3) Zinc can be substituted for the Ni of Ni ferrite to form zinc ferrite. This means that the lower Ni in crud, a source of increased radiation fields, which is effective in long cycles PWRs safety.

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