EFFECTS OF FUEL CLADDING SURFACE STATES ON THE CRUD DEPOSITION IN SIMULATED PRIMARY WATER OF PWR

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ABSTRACT

The objective of this work is to elucidate the effects of fuel cladding states on crud deposition in simulated primary water at 328°C and 130 bars. The test tubes were prepared with two different surface states: the as-received cladding and the chemically etched cladding. Water boiling phenomena occurring on the two cladding surfaces were simultaneously monitored using the acoustic emission technique during the crud deposition tests. The amount of crud deposition decreased on the chemically etched cladding by about 51% compared to that on the as-received cladding tube. The effects of the surface states on the crud deposition are extensively discussed in the view point of the water boiling behavior, surface roughness and wettability.

INTRODUCTION

Crud (an acronym for chalk river unidentified deposits) is a corrosion product deposited on the fuel cladding surface in the PWR primary coolant system [Byers and Deshon. (2004), Deshon et al. (2011)]. These crud can increase fuel cladding surface temperature due to an increased thermal resistance, resulting in accelerated fuel cladding corrosion. Above all, the thick crud may shift the core neutron flux from the top of the core to the lower half of the core along the axis of the fuel assemblies, called crud induced power shift (CIPS) or axial offset anomaly (AOA). This phenomenon leads to a loss of shutdown margin, resulting in the power reduction of the nuclear power plants (NPPs) [Deshon. (2004), Uchida et al. (2011)].

Based on large scale laboratory experiments and fuel inspection results, it has been well known that crud is driven by sub-cooled nucleate boiling (SNB) on the fuel cladding surface and the crud mass is proportional to the degree of SNB [Deshon. (2004), Ferrer et al. (2012)]. This is because sufficient corrosion products are supplied around the steam-liquid interface of a boiling bubble when the SNB occurs. In addition, porous crud through these SNB process is well formed on the fuel cladding. Because boron, which is added into the primary coolant for a neutron absorber, can be accumulated easily into the pores of the deposits, the porous crud deposition is a direct cause of the AOA phenomenon.

The water boiling behavior depends on surface properties, such as wettability (hydrophobic or hydrophilic) and microstructure (porosity) or roughness (cavities, scratches, and grinding marks). Several studies regarding these surface properties have reported that water boiling increases or decreases with the change of roughness and wettability [Jones et al. (2009), Jo et al. (2011)]. These water boiling behaviors have been experimentally investigated through visualized methods using a high-speed video camera, laser interferometry, and infrared thermometry. However, because the visualized methods are very hard to observe the water boiling in conditions involving high temperature and highly pressurized water, such as the primary coolant system, these methods are applicable only under low temperature and pressure.
Meanwhile, an acoustic emission (AE) method is an on-line non-destructive evaluation method used to sense transient elastic wave resulting from a rapid release of energy within a dynamic process. This method is widely used in metal corrosion, plastic deformation, crack growth, and various chemical engineering processes including bubble dynamics. Recently this technique have been utilized to evaluate boiling behavior on heated surfaces under high temperatures and pressures as well as under low temperatures and pressures [Park et al. (2017), Baek et al. (2017)].

The objective of this work is to elucidate the effects of fuel cladding surface properties on crud deposition in simulated primary water at 328°C and 130 bars. To identify water boiling behavior with surface properties, a series of visualization tests was performed first in a transparent glass cell at atmospheric pressure. Based on the visualized tests at 1 bar, crud deposition tests were performed at 328°C and 130 bars. In all tests, water boiling behavior on the fuel cladding surface was monitored using the AE technique.

**EXPERIMENTAL PROCEDURES**

**Specimen and solution preparation**

A ZIRLO™ cladding, which is commonly used as a fuel cladding material, was chosen as the test tube. The dimensions of the test cladding tubes were 9.5 mm outer diameter (OD), 8.3 mm inner diameter (ID) and 550 mm length. We prepared tube specimens with two different surface states: One was an as-received cladding tube, the other was a chemically etched cladding tube. The chemically etched cladding tube was prepared through immersion of an as-received tube in an acid solution composed of 45 vol % of nitric acid (70%-HNO₃), 5 vol % of hydrofluoric acid (60%-HF) and 50 vol % of distilled water for 3 min at room temperature. To prevent the chemical-etching on the inner surface, one end of the cladding tube was welded with a zirconium disc to give a leak tight joint. At this time, only a length of 300 mm from the welded end was etched, which fully covered a heated zone of the rod-type internal heater (heated zone = 250 mm). After the chemical etching, the cladding tube was rinsed immediately in distilled water for 10 min using an ultrasonic processor to avoid staining of the surface with residual etching chemicals.

The test solution used in all experiments was 3.5 ppm Li as LiOH and 1500 ppm B as H₃BO₃ in deionized water. This solution was used to simulate a typical primary water environment in PWRs.

**Analysis of Specimen**

To characterize the wettability of the two cladding tube surfaces, the static contact angle was measured at room temperature (RT) under air condition. A water droplet (3 μl of deionized water) was first placed downward vertically onto the specimen surface using a syringe. A side-view image of the droplet was then captured by a high resolution camera, and the static contact angle was finally determined by using image analysis software. Measurements were made at three different points on a specimen surface and were repeated two times at each point. In this paper, the mean value was reported together with the standard deviation.

The values of surface roughness were measured in an area of 800 μm x 800 μm using a non-contacting surface profiler. In this paper, the arithmetical mean roughness (Ra) is used. During this measurement, the surface images were also observed using a topographical 3-dimension scanning method.

After the deposition test was done, the tube specimens were cut into some of pieces using decane as a cutting fluid. The deposits on the surface of the specimens were dissolved in aqua regia solution and the concentrations of Ni and Fe were analyzed using an inductively coupled plasma-atomic emission spectroscope (ICP-AES). The morphology and composition of deposits formed on the surface were
analyzed using a scanning electron microscope (SEM) and an energy dispersive spectroscopy (EDS).

**Water boiling test at atmospheric pressure**

The experimental apparatus used for the visualized boiling test and the AE data acquisition at atmospheric pressure is schematically shown in Figure 1. The boiling tests were conducted in a transparent glass cell filled with the simulated primary water, whereby the water boiling behavior could be observed visibly. The water boiling was realized by a stepwise heating of the cladding tube using the rod-type internal heater. Detailed control of the water boiling process is as follows: First, the bulk water was heated to 95°C using a hot plate, i.e., 5°C lower than the saturation temperature at atmospheric pressure. When the temperature of the bulk water was stabilized at 95°C, the power of the hot plate was switched off. Afterwards, the internal heater was quickly powered on and the cladding tube was heated until the temperature of the internal heater was stabilized at 120°C. At this stage, the water boiling behavior on the cladding surface was observed using a digital camera. After these measurements were done, the cladding tube was heated through a stepwise increase of the internal heater temperature from 120°C to 160°C with an increment of 20°C per step. At each step of temperature, observation of the water boiling behavior and acquisition of the corresponding AE data were made for 500 s.

![Figure 1. Schematic of experimental apparatus used for water boiling observation and AE data acquisition at atmospheric pressure.](image)

**Crud deposition test**

Crud deposition tests were performed in a circulation loop, as shown in Figure 2. The simulated primary coolant water was stored in the solution tank of 200 liters and recirculated through the test loop system. The inlet solution into the test section was preheated and the temperature of the flowing water adjacent to the cladding tube was maintained at 328°C. The temperature of the internal heater was maintained at 380°C to provide the condition of SNB on the surface of the cladding tube during the crud deposition test. 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 cm³/kg·H₂O. The flow rate adjacent to the cladding tube in the test section was controlled at 5 m/s. After all these conditions were stabilized, we started to inject the mixed Fe and Ni ions into the test section through the metering injection pump. The mixed precursor ions of Fe and Ni 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 was diluted in the simulated primary water stream and then its final chemistry was calculated to be 4.0 ppm Fe and 0.16 ppm Ni in the test
section. Each deposition test was conducted for 5 days. During the crud deposition tests, the acoustic sounds emitted from the water boiling on the heated cladding surface were monitored using the AE technique for 500 s every 24 hrs during the deposition tests.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{crud_deposition_system}
\caption{Schematic of the crud deposition system.}
\end{figure}

**AE measurements for water boiling**

An AE sensor was coupled to the upper end of the cladding tube, as shown in Figures 1 and 2. To minimize the variation of the AE signal attenuation, we used the cladding tube with the same dimension and geometry equipped to an autoclave lid in all test conditions at both 1 bar and 130 bar. The same internal heater was also used. The cladding tube with a length of 550 mm was equipped to the autoclave lid via a tube fitting, and the AE sensor was coupled with the tube at a distance of 65 mm away from the upper end of the tube. The distance between the AE sensor and the autoclave lid surface was 35 mm. The AE sensor was connected to a preamplifier, then the preamplifier was connected to the AE signal acquisition system. The AE signals were amplified with a gain of 40 dB, and the threshold value set at 48 dB to eliminate the background noise. The obtained AE signals can be analyzed by various AE parameters in AE-win software. In this test, a low frequency AE sensor (type R3a, 30-75 kHz resonant frequency) was chosen to collect the AE-boiling signals. This AE sensor is available to use in the temperature range of -65°C to 175°C. The heat shield of a disk-type was installed between the sensor and autoclave lid to protect a radiant heat from the heat sources. During the measurements, the sensor temperature was maintained below 60°C in all experiments.

**RESULTS AND DISCUSSION**

**Surface properties of the specimens**

Table 1 shows the roughness and contact angle values measured on the surfaces of as-received cladding and chemically etched cladding, respectively. The surface roughness was measured to be 0.15 μm for as-received and 0.04 μm for chemically etched tube. This indicates that the surface roughness of as-received cladding decreased by a factor of about four through the chemical etching. The contact angles were measured to be 77° for as-received cladding and 39° for chemically etched cladding. Here, a high contact angle corresponds to a low surface wettability. That is, the chemically etched cladding surface has a more hydrophilic property than the as-received cladding surface.
Table 1. Values of roughness and contact angle of the two cladding tube surface.

<table>
<thead>
<tr>
<th>Surfaces state</th>
<th>Surface roughness (Ra, μm)</th>
<th>Contact angle (°)</th>
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</thead>
<tbody>
<tr>
<td>As-received</td>
<td>0.15</td>
<td>77</td>
</tr>
<tr>
<td>Chemically etched</td>
<td>0.04</td>
<td>39</td>
</tr>
</tbody>
</table>

**Water boiling behavior at atmospheric pressure**

Figure 3 shows the visualized images of the water boiling behavior on as-received cladding and chemically etched cladding at atmospheric pressure. Water boiling increased on both cladding tubes with an increase in the internal heater temperature. However, vapor bubble density and size remarkably increased on the as-received cladding compared with those on the chemically etched cladding. Furthermore, the onset of nucleate boiling was first formed on the as-received cladding at 120°C of the internal heater temperature, whereas that appeared on the chemically etched cladding at 140°C of the internal heater temperature. These differences seem that because the imperfections, such as cavities, scratches and grinding marks, on the as-received cladding surface were acted as the boiling nucleation sites. It was reported that the vapor bubble was formed at these imperfections first, and actively occurs during water boiling [Basu et al. (2002)]. In addition, vapor bubble size is related with the surface wettability. According to the normalized bubble size as a function of the contact angle, the bubble size was observed to be increased with increasing contact angle [Nam et al. (2011)]. This means that water boiling is more favored on a rough and hydrophobic surface. Therefore, the bubble density and size can be increased more on the as-received surface than the chemically etched surface.

![Visualized water boiling images](image)

Figure 3. Visualized water boiling images with an increase in internal heater temperature ($T_{IH}$) at atmospheric pressure: (a) as-received cladding and (b) chemically etched cladding.

Combined with the above observation, the boiling-AE signals were simultaneously acquired for 500 s. Figure 4 shows the AE energy distribution and AE hit number of boiling-AE signals monitored at each heater temperature on the as-received cladding and the chemically etched cladding. As shown in Figure 4 (a) and (b), the AE energy distribution of boiling signals was expanded to a high level in both cladding tubes with an increase in the internal heater temperature. However, the boiling AE signal has a higher AE energy on the as-received cladding than the chemically etched cladding. Studies for correlation between the AE energy and bubble diameter show a trend that the AE energy is proportional to the bubble size [Husin et al. (2010) and Carmi et al. (2011)]. In our case, the bubble size also increased with increasing the internal heater temperature as shown in the visualized results. Thus, it is considered that a big bubble
may be attributed to a high AE energy. However, in the present work, because the AE signals detected from the fuel cladding surface include various boiling dynamics, such as bubble formation, growth, departure, travel, collision, collapse, and burst, it is difficult to distinguish exactly the bubble size from this data. However, this result clearly exhibited that the AE energy level is expanded with increasing water boiling dynamics. In addition, when these boiling AE signals were quantitatively converted to the AE hit number as shown in Figure 4 (c), the AE signals remarkably increased on the as-received cladding than the chemically etched cladding. This implies that water boiling occurs actively on the as-received surface than the chemically etched surface. Consequently, it is confirmed that a rough and hydrophobic surface lead to an increase of water boiling.

![Graphs](image_url)

**Figure 4.** Variation of boiling-AE signals during the water boiling tests at atmospheric pressure: (a) distribution of AE energy on the as-received cladding and (b) distribution of AE energy on the chemically etched cladding, and (c) AE hit number on the two cladding tubes.

**Water boiling and crud deposition behavior at 130 bars**

Figure 5 shows AE energy distribution and the AE hit number of boiling-AE signals monitored for 500 s every 24 hrs on the as-received cladding and the chemically etched cladding during the crud deposition tests. The distribution of AE energy on the as-received cladding was expanded to the higher levels as time passed, whereas AE signals on the chemically etched cladding were consistently detected in the lower energy ranges regardless of the test time, as shown in Figure 5 (a) and (b). Furthermore, the AE hit number remarkably increased on the as-received cladding compared to that on the chemically etched cladding, as shown in Figure 5 (c). These results indicate that the water boiling was violently occurs on
the as-received cladding than the chemically etched cladding during the crud deposition tests. This means that the surface having a rough and hydrophobic property affect water boiling behavior in high temperature and highly pressurized water, such as the primary coolant system. Consequently, these factors on the as-received surface lead to an increase in the degree of SNB, resulting in an increase in the number of boiling signals.

Figure 5. Variation of boiling-AE signals during the crud deposition tests: (a) distribution of AE energy on the as-received cladding and (b) distribution of AE energy on the chemically etched cladding, and (c) AE hit number on the two cladding tubes.

Figure 6 shows the SEM micrographs and the chemical compositions of the cruds observed on the two cladding tubes after the deposition tests. Polyhedral particles were uniformly deposited on the two cladding tubes, but the amount and size of crud apparently increased on the as-received cladding compared to those on the chemically etched cladding. Furthermore, the boiling chimneys were clearly observed on the as-received cladding, whereas no chimneys were observed on the chemically etched cladding. These deposits were analyzed to be magnetite by EDS. It is well known that crud mass increased through the repetitive SNB process [Deshon. (2004), Ferrer et al. (2012)]. However, it should be noted that the porous crud leads to an increase of the degree of SNB, resulting in an increased crud deposition. According to the boiling model, the vapor bubble size is proportional to the porosity of boiling chimney and the density of vapor bubble also increased inside the chimney pore [Pan et al. (1987), Pan et al. (2015)]. This is because these pores can be filled with water, of which temperatures would exceed the boiling temperature there. As shown in Figure 5, the energy and density of boiling AE signal on the as-received cladding tube remarkably increased from 3 days to 5 days during the crud deposition.
This indicates that vapor bubble size is diversified and water boiling is actively enhanced by boiling chimneys formed as time passes as well as the effect on surface properties. Consequently, the crud mass can be increased more on the as-received cladding by increased bubble size and density during the crud deposition test.

Figure 7 shows the amount of cruds deposited on the as-received cladding and chemically etched cladding after the deposition tests. The deposit mass decreased by 51 % for the chemically etched tube compared to that for the as-received tube. This means that the amount of cruds was heavily dependent on the surface roughness and wettability of the cladding. Based on the results of the present work, it is concluded that a smooth and hydrophilic properties on the fuel cladding surface reduced water boiling, resulting in a decrease in the amount of crud deposits.

![Figure 6](image)

<table>
<thead>
<tr>
<th>Point</th>
<th>Chemical composition (Atomic %)</th>
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<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>A</td>
<td>56</td>
</tr>
<tr>
<td>B</td>
<td>58</td>
</tr>
</tbody>
</table>

Figure 6. SEM images and chemical compositions of cruds deposited on the two cladding tubes after the deposition tests: (a) as-received cladding and (b) chemically etched cladding.

![Figure 7](image)

Figure 7. Amount of crud after crud deposition tests at 328°C and 130 bars.
CONCLUSIONS

We investigated the effect of surface roughness and wettability on the crud deposition in a PWR primary condition. The chemically etched surface had properties of a relatively low roughness and a high wettability compared to the as-received surface. Water boiling phenomenon decreased more on the chemically etched cladding tube than the as-received cladding tube by the effects of surface roughness and wettability, and this was confirmed through the visualization method and the AE technique. Consequently, the amount of cruds decreased by about 51% on the chemically etched cladding tube compared that on the as-received cladding tube. Therefore, the cladding tube is reasonable to be controlled to more a smooth and hydrophilic surface to mitigate the crud deposition in PWR primary condition.

ACKNOWLEDGMENT

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REFERENCES

