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Effect of surface oxidation of ZIRLO fuel cladding tube on crud deposition

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1. Introduction

As pressurized water reactors (PWRs) are driven to power uprates, lifetime extension and higher burnup for enhancing economics of power generation, some reactors have experienced increased deposits on fuel cladding tubes. These deposits are originated from the corrosion products released from the primary coolant system surfaces, and defined as 'crud' [1]. Crud has often led a lot of problems in the primary coolant system such as fuel cladding corrosion, power distortion and reduction, and radio-activity build-up of out-of-core [2-3]. Although a crud-induced localized corrosion (CILC) is a severe accident, in which fuel is leaked into the coolant, it is rarely happened but a crud-induced power shift (CIPS) has frequently occurred in worldwide PWR plants. CIPS, or power axial offset anomaly (AOA) has long been realized in the nuclear industry since early 1970s. In late 1980s, severe AOA phenomena were found in Callaway plants in U. S. and later in many power plants around the world [4,5].

The axial offset (AO) is defined by the power distortion between the top half of the core and the bottom half of the core. When the plant exceeds acceptable limit of 3% in AO value, it is judged as AOA occurrence and this is forced to reduce power or shutdown. AOA is caused by a hideout for large accumulation of boron into porous crud and its formation is accelerated by increased sub-cooled nucleate boiling (SNB) with sufficient corrosion product supply. Therefore, to prevent or mitigate crud deposition on fuel claddings, the release of corrosion products in coolant should be minimized or crud deposition on fuel rods should be made unfavorable [6]. However, the latter is more reasonable to attempt than the former because the corrosion product release is remarkably reduced since the steam generator tube materials have been replaced from Alloy 600 to Alloy 690, which has superior resistance in corrosion problems [7.8]. Therefore, minimizing the crud deposition in core can be regarded in terms of either electrokinetic interaction between fuel clad surface and corrosion product particles or boiling dynamics for heat transfer from heated surface to coolant. The fuel clad surface is easily oxidized to ZrO_2 in PWR operational conditions. Therefore, the effect of oxidation of the fuel cladding tube on crud deposition was studied. The surface zeta potential were evaluated from the relationship between the zeta potential and velocity of tracer particle on the specimen [9]. The ZrO_2 and corrosion products, which are mainly Fe_3O_4 or $NiFe_2O_4$, have opposite charge, as believed to be the case for ZrO_2 with a negative charge [5] and Fe_3O_4 with a positive charge at neutral pH [10]. Thereby, Paramonova and Short have suggested the ZrC and ZrN as a coating material of Zr-alloy fuel clad, which has low adsorption energy for positive particles, to mitigate crud deposition [6,11]. The boiling dynamics would be expected to be strongly affected by surface oxidation. Because heat transfer is deteriorated as the oxide thickness increases. Thereby, the oxide thickness is limited to less than 100 μm for at least three EFPY.

In this work, we investigate the effect of surface oxidation of Zr-alloy fuel cladding tube in terms of electrokinetic interaction between fuel clad surface and corrosion products, and boiling properties under the SNB condition on crud deposition. Surface properties of as-received and oxidized ZIRLO^{TM} tubes were compared in water contact angle and surface zeta potential. Their boiling properties at the primary coolant condition were also measured using acoustic emission method. The quantitative amount and morphology of the cruds deposited on as-received and oxidized fuel clads were analyzed by ICP-AES and scanning electron spectroscope (SEM), respectively.

2. Experimental

Commercial ZIRLO^{TM} tubes with 9.5 mm out diameter and 0.6 mm thickness are used in this work. The surface oxidation specimen was prepared by heat treatment at 400^{o}C in air for 33 days. The oxide was a monoclinic zirconia (ZrO_2) and its thickness was about 4.6 μm. All samples were cleaned with ultrasonicating in aceton, ethanol and deionized water for each 10 minutes. The surface characteristics of the specimens were observed by contact angle and surface zeta potential measurements. Magnetite particles were used as a tracer dispersing into deionized water for measuring surface zeta potential and their hydrodynamic diameter was about 74 nm. All specimens were cut to 4.0 mm width, the spacing of plate electrodes of the dip cell was larger than 5 mm.

The crud deposition test was performed in a primary simulation loop equipped with acoustic emission (AE) sensor, which is coupled with the fuel clad outside surface to monitor the SNB at 130 bars. A fuel cladding tube inserted with an internal electric heater was used as a heating source and was placed vertically in the test section as shown Fig. 1. The maximum heat flux of the internal heater is 80 W/cm^2 with the heating length of 250 mm and is closely mounted into fuel cladding tube using magnesium oxide paste. The annular gap between cladding tube to autoclave inner-diameter surface was 3.5 mm and the flow velocity on fuel clad surface was controlled at 5 m/s. The test solution was 3.5 ppm Li and 1,500 ppm B in weight, simulating a chemistry condition of PWR coolant. The dissolved oxygen in the coolant was controlled to be less than 5 ppb and dissolved hydrogen concentration was a 35 cm^3/kg·H_2O. The crud source solution was prepared by dissolving the Fe- and Ni-ethylene diamine tetraacetic acid (EDTA) of 1000 ppm and 40 ppm, respectively, in deionized water and provided with an injection rate of 1.0 ml/min. The system pressure and the inlet coolant temperature of test section were controlled at 130 bars and 325^{o}C, respectively. The internal heater temperature was maintained at 380^{o}C so that sub-cooled nucleated boiling occurs on the cladding surface. Each crud deposition test was performed for 5 days.

To investigate the boiling dynamics on as-received and oxidized ZIRLO tubes, The AE data were also acquired using the acoustic emission technique for 5 min every 24 hrs during the deposition tests. The AE sensor having the resonance frequency of 30-75 kHz was used to collect the AE boiling signals, which were filtered using a low pass of 100 kHz. Then, the AE signals were pre-amplified with a gain of 40 dB and a threshold value set at 47 dB to eliminate the background noises. The obtained AE signals were analyzed as various parameters in AE-win software.

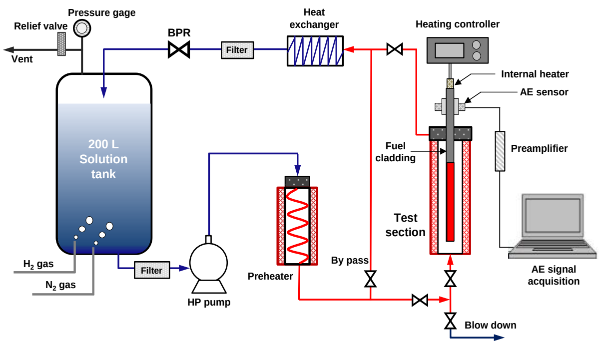

Fig. 1 Schematic drawing of the primary simulation loop

After the crud deposition tests, the tested tubes were cut into some of pieces using decane as a cutting fluid to minimize the loss of deposited cruds. The cruds deposited on some pieces dissolved in a 10 ml aqua regia solution under high-power ultrasonication for 120 minutes and the quantity of elements including Ni and Fe were analyzed using an inductively coupled plasma-atomic emission spectro scope (ICP-AES). In addition, the crud morphologies on some other pieces were observed using scanning electron microscope (SEM).

3. Results and discussion

3.1 Surface properties of the specimens

Fig. 2 shows the contact angle (CA) of a water droplet measured on the surfaces of as-received and oxidized fuel cladding tubes. A very small difference was observed in CA value, 72^o for as-received tube and 65^o for oxidized tube. This indicates that two specimens have similar hydrophobicity, which can affect not only corrosion product supply but also the boiling dynamics, under the same flow condition.

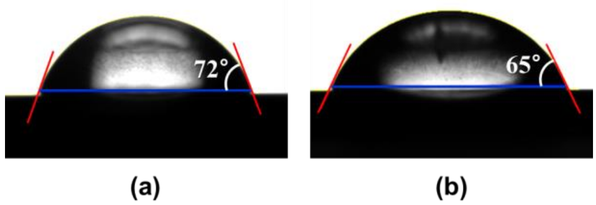

Fig. 2 Water contact angle of (a) as-received and (b) oxidized specimens

However, the surface zeta potential (SZP) between both specimens shows a meaningful difference as shown in Fig. 3. The zeta potential of tracer magnetite particles was about -36.0 mV in a pH 6.7 buffer solution at 25^{o}C. The SZP shows more positive value for the oxidized specimen with -37.0 mV, comparing to that of the as-received specimen with -43.5 mV. In other words, the oxidized specimen is expected to facilitate the crud deposition on the surface in PWR primary condition compared to as-received specimen because it has small difference in surface charge with the corrosion product particles in the same polarity.

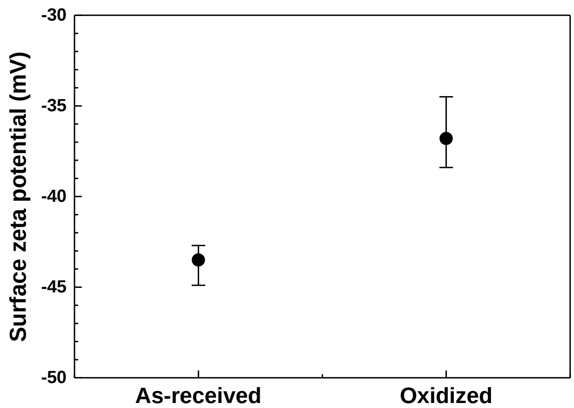

Fig. 3 Surface zeta potential values of as-received and oxidized specimens

3.2 Analysis of water boiling- AE signals

Fig. 4 presents the number of AE events measured for 5min per day on the as-received and the oxidized ZIRLO tubes during the crud deposition test. The AE events for as-received tube increased linearly until the third day and then, was maintained at about 3000 hits. However, although the AE events observed on oxidized tube show the difference by 3 times of those on the as-received tube in first day, those linearly increased until the fifth day and is eventually about 6 times of that on the as-received tube. This implies that the boiling processes such as bubble formation, growth, travel, departure and collapse vigorously occur on oxidized surface compared to as-received tube surface as the test time increases.

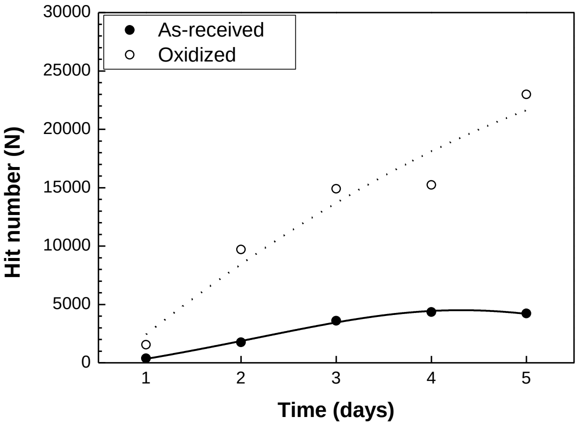

Fig. 4 The number of AE events on as-received and oxidized ZIRLO tubes during crud deposition test for 5 days.

3.3 Analysis of crud deposition quantity

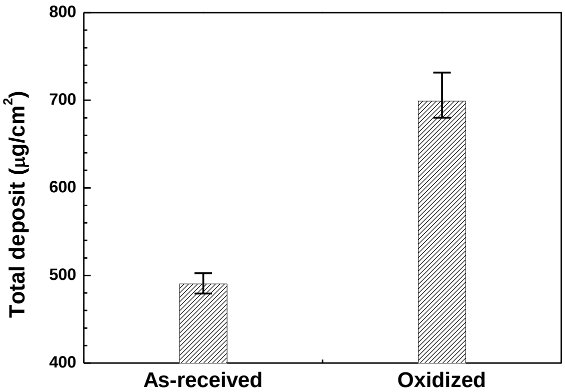

Fig. 5 The quantitative amount of cruds deposited on as-received and oxidized ZIRLO tubes

Fig. 5 shows the quantity of metallic Ni and Fe in cruds deposited on the as-received and oxidized Zirlo tubes. The total quantity of metallic Ni and Fe for the as-received and oxidized specimens were 490 $\mu g/cm^2$ and 711 $\mu g/cm^2$, respectively. In other words, the oxidized surface displays deposit amount increased by 45% compared with the as-received surface. This should be caused by the surface electrokinetic potential and the boiling dynamics of the specimens.

4. Conclusions

We investigated the effect of surface oxidation of ZIRLO fuel cladding tube on crud deposition in terms of surface electrokinetic potential and boiling dynamics in PWR primary coolant. The oxidized surface has a relatively low repulsion force with the corrosion products compared to the as-received surface and is more effective on the sub-cooled nucleate boiling. Thus, the oxidized surface is more favorable for crud deposition, compared to the as-received metallic surface. In addition, these results would be helpful to understand the crud deposition on oxidized surface in practical PWR environment.

Acknowledgments

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