Influence of Dissolved Hydrogen Concentration on Crud Deposition Formed on Zirlo Fuel Cladding in Nuclear Primary Water

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1. Introduction

Corrosion products are released from the materials exposed to a primary coolant system in nuclear power plants and transported into the core. In addition, they are activated, rereleased back into the coolant and redeposited on the surface of the primary coolant system. They thereby have led to various problems such as a radioactivity increase in the coolant system, a crud-induced power shift (CIPS), and material degradation. In particular, the CIPS is a crucial issue because it can be a reason for a power reduction or a fracture of the fuel cladding [1,2].

Some cases for CIPS have been reported throughout the world, especially in plants that employ longer operation cycles [1-3]. The corrosion products, i.e., crud, formed on fuel claddings in plants that have experienced CIPS are analyzed as various forms of nickel ferrite, nickel oxide, bonaccordite and zirconium oxide [4,5]. Thus, the corrosion products deposited on fuel cladding have been widely studied under various water chemistry conditions [6]. However, it has not been discussed clearly whether the dissolved hydrogen (DH) influences the corrosion products formed on the fuel cladding surface, which is one of the important water chemistry factors in the primary system.

In this work, we report the effect of the DH concentration on the amount of corrosion products formed on the Zirlo fuel claddings in a DH range of 5-70cc/kg, and those physicochemical characteristics. The amount of deposits on the fuel cladding was quantized through an ICP-AES analysis, and their microstructure with their chemical compositions was investigated using SEM and TEM equipped with EDS.

2. Methods and Results

2.1 CRUD deposition test

A test loop simulating a crud to lead CIPS was designed as shown in Fig. 1. In particular, the test section for the crud deposition consisted of an autoclave with an ID of 20mm and a Ziro cladding tube of 9.5mm inserted by an internal heater. The primary water was prepared by dissolving 3.5 ppm of LiOH and 1500 ppm of H_3BO_3 into deionized (DI) water. Then, 39 ppm and 1 ppm of the Ni- and Fe-ethylene diamine tetraacetic acids (EDTA) were used, respectively, as a source of corrosion products. Dissolved oxygen is controlled to less than 5 ppb and dissolved hydrogen is varied at 5 to 70cc/kg H_2O to investigate the effect of dissolved hydrogen concentration on the crud deposition. The system pressure in the high temperature region was maintained at 122.9 kg/cm^2, which is the equilibrium pressure at 325°C and the coolant flow rate was 60cc/min. The specimen is heated to 327°C at a thermocouple sensor point using the internal heater to provide the condition of the sub-nucleated boiling (SNB) on the fuel cladding surface, and the loop test was conducted for 14 days. To minimize the dissolution of chemicals including boron on the specimen surface during a slow cooling, the coolant in the test section was discharged through a rapid cooling system after the loop test was completed.
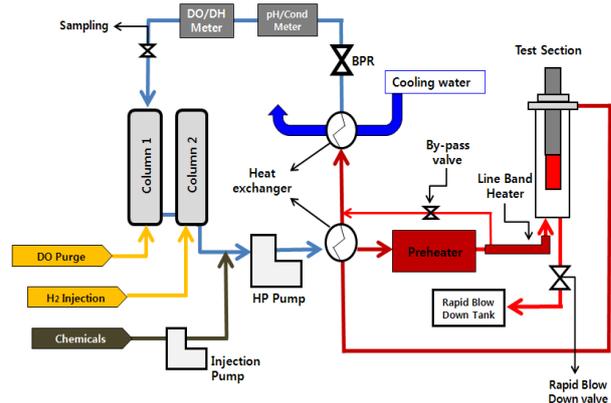

Fig. 1 Schematic drawing of the recirculating primary system used for deposition tests.

2.2 Surface analysis for the deposits

The tubular specimens were cut into a number of pieces using decane ($C_{10}H_{22}$) as a cutting coolant to analyze their chemical and structural properties after the tests. The deposits on the surface of the specimens are separated in 10 ml of DI water using a high-power ultrasonicator and concentrations of chemical components including in crud are analyzed by ICP-AES and atomic absorption spectroscope (ASS). The morphology and composition of crud deposits were investigated by an SEM equipped with an EDS, and the microstructure of needle-like deposits was examined by a TEM.

Fig. 2 shows the surface morphologies and the compositional analyses of deposits on the specimens examined under a DH concentration of 25cc/kg and

35cc/kg H_2O, respectively. The morphologies and chemical compositions of corrosion products were very different. The Ni-rich needle-like structures were formed in few micrometer lengths between the buckled zirconium oxide layers under a DH condition of 25cc/kg, while polyhedral particles of $Ni_{1+x}Fe_{2-x}O_4$ spinel structure were only formed with irregular size on the specimen examined at a DH concentration of 35cc/kg.
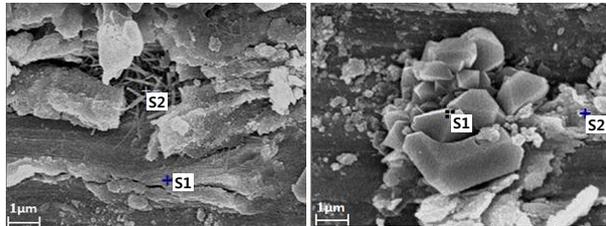

(a)   **(b)**

Dissolved hydrogen	Spectrum	Chemical composition (at%)			
		O	Fe	Ni	Zr
(a) 25 cc/kg H_2O	S1	66.8	0.7	0.7	31.8
	S2	14.7	3.4	5.8	76.1
(b) 35 cc/kg H_2O	S1	67.3	16.0	9.7	5.0
	S2	56.5	0.8	0	42.7

(c)

Fig. 2 SEM images and chemical compositions in atomic percent at different points. (a) 25 cc/kg, (b) 35 cc/kg and (c) their chemical compositions in at%.

Fig. 3 shows SEM and the cross-sectional STEM images along with the chemical composition of the needle-like structure formed in a DH condition of 25cc/kg. The needle-like structure displays a diameter of less than 100 nm and should be NiO including a small amount of iron. The NiO needle-like structure is a representative crud format that has been found in the CIPS-occurred nuclear power plants [3]. It indicates that the primary coolant condition of NPPs should be operated at the dissolved hydrogen at least higher than 35cc/kg to mitigate the needle-like NiO formation.
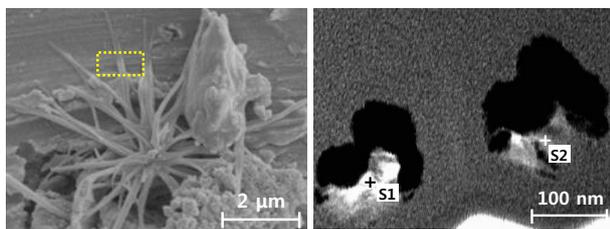
(a)   **(b)**

Spectrum	Chemical composition (at%)			
	O	Fe	Ni	Zr
S1	46.6	10.6	42.7	0.1
S2	44.1	9.9	45.9	0.1

(c)

Fig. 3 (a) SEM image of a needle-like structure formed on a specimen under 5cc/kg dissolved hydrogen concentration, (b) STEM image and (c) the EDS results of its cross-section prepared by FIB

2.3 Quantization of deposit weight

The effect of dissolved hydrogen concentration on the metal amount in deposits is shown in Fig. 4. The amount of deposits shows almost a similar value in the dissolved hydrogen range of 5 to 70cc/kg at 325℃. This indicates that the influence of dissolved hydrogen concentration on the crud deposition is negligible in the dissolved hydrogen range of 5 to 70cc/kg, which is the meaningful range for stress corrosion cracking (SCC). Therefore, operation strategies for the mitigation of primary water stress corrosion cracking can be chosen at lower or higher hydrogen contents without a concern of increase in the fuel crud deposition.
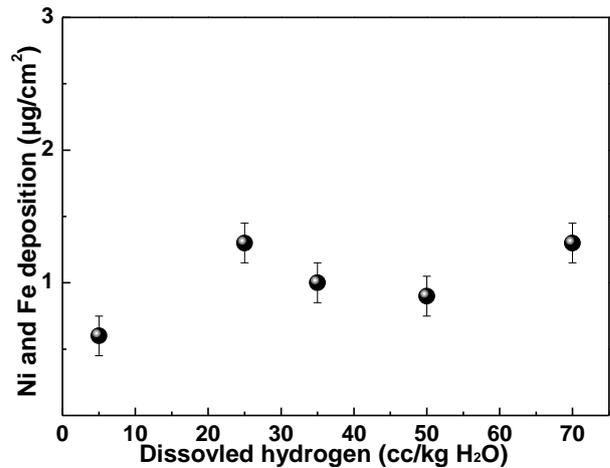

Fig. 4 The quantities of deposits for different dissolved hydrogen concentrations.

3. Conclusions

We investigated the effect of dissolved hydrogen concentration on crud deposition on the fuel cladding surface in the simulated primary environments of a pressurized water reactor. The needle-like NiO structures, which are well known to be a crud phase to lead CIPS, appeared in the corrosion products on the specimen examined at dissolved hydrogen concentrations of 5 and 25cc/kg, while polygonal nickel ferrite structures are only observed at hydrogen concentrations of 35, 50, and 70cc/kg. However, the deposit amount shows no remarkable change as a function of the dissolved hydrogen concentration. Therefore, this suggests that NPPs be operated at a hydrogen concentration of above 35cc/kg.

Acknowledgments

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