The Effect of Zn Addition on CRUD formation.

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1. Introduction

CRUD is the depositing of corrosion products on fuel rods from the coolant circulated in a nuclear power plant. With the high temperatures reached in the reactor core, there is a high probability of the reactor reaching a sub-cooled nucleate boiling state. As CRUD formation is the function of reactor power and coolant temperature, it is predominantly formed around micro-bubbles that occur alongside the sub-cooled nucleate boiling. The basic composition of CRUD is known as Ni-ferrite($Ni_xFe_{3-x}O_4$), with x being 0.4<x<0.8.

CRUD causes several reactor integrity problems. The first is B accumulation in CRUD, which creates an axial offset anomaly in the reactor core by absorbing neutrons. Another problem is radioactivity increasing on the inner surfaces of primary systems. After Co and Ni, which are dissolved in primary systems are deposited on fuel cladding, they are irradiated by neutrons and become radioactive isotopes, such as Co-60 and Co-58. These isotopes escape from fuel cladding and replace CRUD in the primary system's inner face.

To better understand these two problems, we performed several experiments. We first traced each material's concentration in simulated coolant, depending on time, during CRUD formation. we also performed XPS and SEM analysis of CRUD samples to see Zn effects and B accumulation.

2. Methods and Results

In this study, we set up an experimental device that can copy the real phenomenon on the upper position of nuclear fuel cladding and thus make artificial CRUD.

This device was designed to simulate coolant encounters with SUS-304 foil and Zry-4 tubes at 300℃ and 150bar.

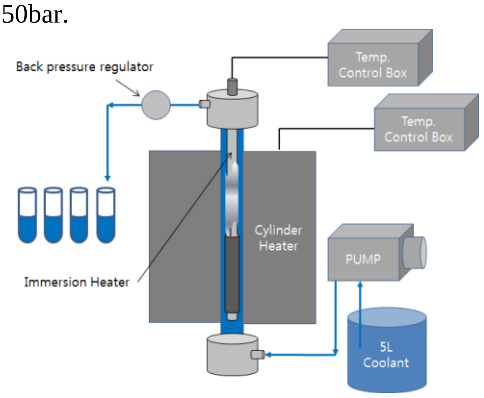


Figure 1. CRUD experiment device conceptual design.

After the experiment started, the system kept the flow rate at 3~5mL/min, so as to maintain the concentration of boron and corrosion products.

There are two kinds of simulated coolant that were injected into system. Composition and concentration data are shown in Table1. To get an obvious ion concentration change and rapidly make CRUD, we made three-times-higher ion (Fe, Cr, Ni, Co, and Zn) concentrations, except for B and Li.

Elements	B	Li	Fe*3	Cr*3	Ni*3	Co*3
ppm	1000	3	25.68	2.37	1.35	0.24
mg	5720	18.14	25.68	2.37	1.35	0.24

Elements	B	Li	Fe*3	Zn*3	Cr*3	Ni*3	Co*3
ppm	1000	3	25.68	3	2.37	1.35	0.24
mg	5720	18.14	25.68	3	2.37	1.35	0.24

Table 1. Ion composition and concentration of simulated coolant (top: no Zn addition, bottom: Zn addition)

To confirm the fact that accumulated B on fuel cladding causes AOA, we performed ICP analysis on simulated coolant based on time.

All four experiments showed a decreasing trend in B concentration. (Figure 2.)

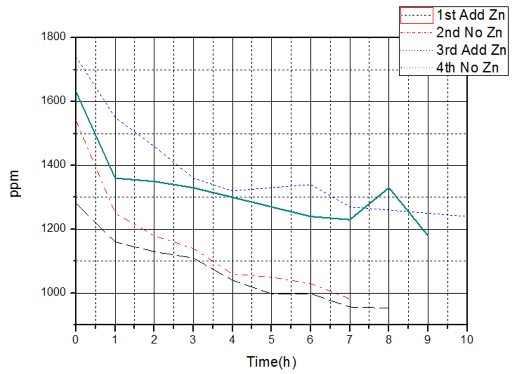


Figure 2. Decreasing trend of B concentration from ICP analysis

To confirm whether or not B definitely accumulated in CRUD, we performed a CRUD sample analysis using XPS and SEM-EDX. To get CRUD sample, SUS-Foil and Zry-4 were attached to an immersion heater.

After each experiment ended, part of each SUS-304 foil underwent XPS analysis; CRUD powder samples from Zry-4 tubes were subjected to SEM-EDX analysis. We found the XPS and SEM-EDX analysis results to be the same for B.

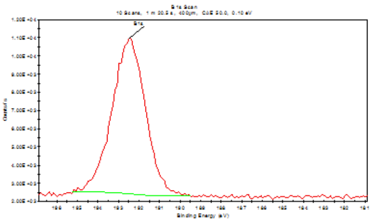
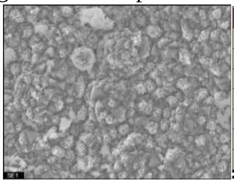


Figure 3. Boron peak on SUS-305 foil XPS analysis



Matrix Correction: ZAFElement	Wt%	At%
B K	04.33	13.78
O K	18.12	38.95
Zr L	01.49	00.56
Cr K	01.89	01.25
Fe K	67.23	41.40
Co K	02.49	01.45
Ni K	04.45	02.60

Figure 4. CRUD powder sample SEM-EDX analysis result

Zn is known for mitigating Alloy 600 PWSCC and decreasing primary system radioactivity. Zn has substitution reactions with divalent cations (Fe, Ni, Co, etc). It forms a strong protective film on the system's inner surface. Because of this protective film, we can control the depositing of corrosion and radioactive isotopes (Co-58, Co-60, etc.) on CRUD.

To confirm this Zn effect, we performed ICP and XPS analysis of simulated coolant and CRUD samples. We made comparison table with SUS-304 foil XPS analysis results. It is clear that there is an obvious difference in Ni peaks.

There is no Ni peak in the Zn-added experiment but there is a clear Ni peak in the no-Zn experiment's simulate coolant. This means that Zn has a decisive effect on CRUD formation, especially for Ni. In addition to the substitution reaction of Zn, we can make guesses as to the immediate Zn coating effect due to Zn's low solubility at high temperature.

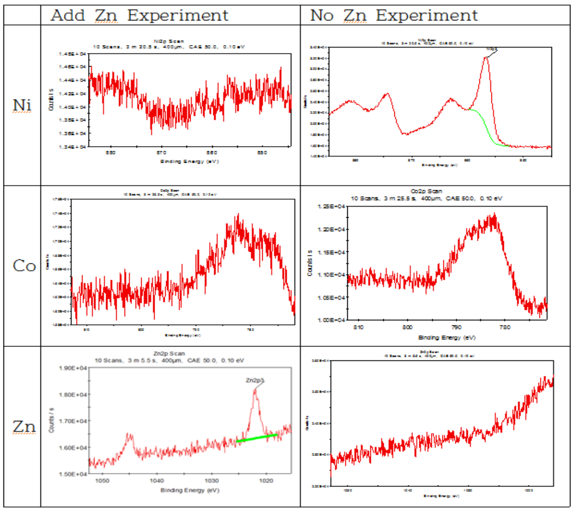


Table 2. Ni, Co, Zn peak on SUS-305 foil XPS analysis

Table 3. shows the ICP analysis results of output simulate coolant depending on time. In the no-Zn experiment, as time went on, the Co concentration decreased. On the other hand, the Zn-added experiment shows that Co concentration peaked early before returning to its initial state.

Co concentration decreasing in the no-Zn experiment means that Co ions were deposited on the inner surface of the experiment system. But from the Co peak in the Zn-added experiment, we can assume that added Zn in coolant starts a substitution reaction with Co the deposited on the inner surface in the previous experiment. Both of experiments showed that Ni concentrations peaked early. It seems because Co and Zn have stronger substitution reaction powers than Ni. So Ni deposited at previous experiment can be extracted to coolant in some degree.

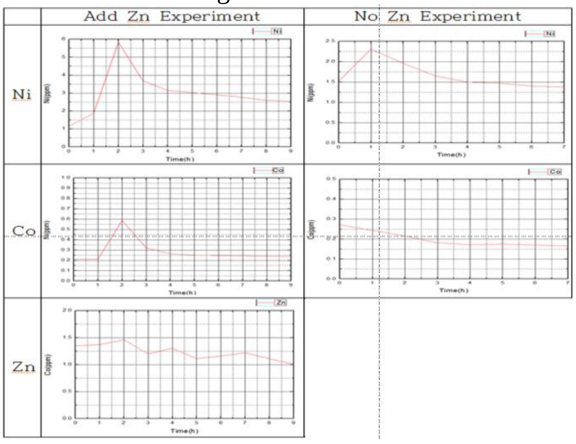


Table 3. Ni, Co and Zn concentration trends from ICP

3. Conclusions

In this study, by controlling the concentrations of simulated coolants, we made various CRUD samples. We also collected output coolant solution depending on time. With these samples, we performed XPS, SEM and ICP analysis and got meaningful results.

From the ICP analysis results that represent coolant ion concentration changes, we confirm that the B accumulation process and metal ion concentrations changed. With XPS and SEM-EDX analysis data from the CRUD samples, we got CRUD composition data and discovered the effects of Zn on Co and Ni.

From this study, we confirm B accumulation on CRUD and the effects of Zn on CRUD formation.

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