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〈Technical Note〉

Analysis of Corrosion Behavior of KOFA Zircaloy-4 Cladding

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Abstract

The corrosion behavior of KOFA cladding which is a standard Zircaloy-4 manufactured by Westinghouse Specialty Metal Plant according to the Siemens/KWU's HCW (Highly Cold Worked) standard Zircaloy-4 specification was analyzed using the oxide measurement data of KOFA fuel irradiated in Kori-2 nuclear power plant. Analysis of the measured KOFA cladding oxidation showed that oxidation of KOFA cladding was lower than the design prediction based upon Siemens/KWU's HCW standard Zircaloy-4 cladding. Although the measured fuel rods have relatively low burnup and oxidation and the amount of the measured data are small, analysis of manufacturing and in-reactor operation conditions of KOFA cladding indicates that the differences in the manufacturing processes and chemical composition of the Siemens/KWU's HCW (Highly Cold Worked) standard Zircaloy-4 and KOFA cladding may have somewhat contributed to lower corrosion of KOFA cladding than the expected.

1. Introduction

The cladding of KOFA(Korea Fuel Assembly) fuel is the standard Zircaloy-4 manufactured by the Westinghouse Specialty Metal Plant according to the specification of Siemens/KWU's standard Zircaloy-4. The properties of KOFA cladding satisfied the requirements of Siemens/KWU's HCW (Highly Cold Worked) standard Zircaloy-4 specification upon which KOFA fuel design is based. However, there still exists the differences in such manufacturing processes as cold pilgering and heat treatment between the KOFA and Siemens/KWU's HCW standard Zircaloy-4. Those differences in the manufacturing processes can result in the deviation in the microstructure which can subsequently make a difference in the in-pile performance such as corrosion, creep and irradiation growth. The oxidation of KOFA fuel irradiated up to the fuel rod burnup of 35,000 MWD/MTU for two cycles in Kori-2 nuclear power plant was measured by both the hot cell

Table 1. Power Histories of the KOFA Fuel Assemblies

Fuel	Cycle 7		Cycle 8		Cycle 9	
Assembly	Fxy*	Burnup** (MWD/KgU)	Fxy	Burnup (MWD/KgU)	Fxy	Burnup (MWD/KgU)
J38	1.30	19.1	1.12	35.0	-	-
J44	1.30	19.1	1.12	35.0	-	-
K40	-	-	1.25	18.0	0.46	25.4

(*) Cycle-averaged fuel assembly radial power factor

(**) Fuel assembly average burnup at the end of cycle

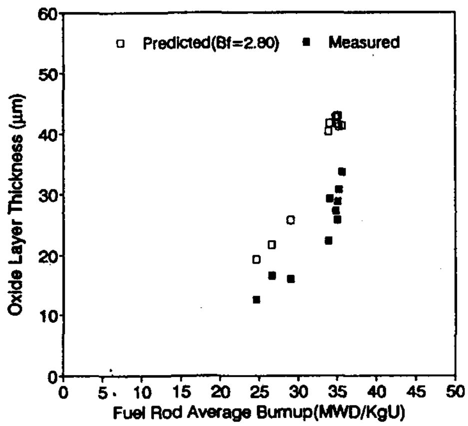

Fig. 1. Measured Oxide Layer Thickness of KOFA Fuel Rods Compared with the Design Prediction

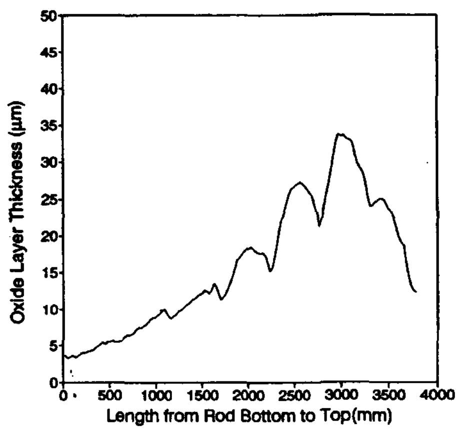

Fig. 2. Axial Variation of the Fuel Rod Oxidation

examination in the post-irradiation examination facility at KAERI(Korea Atomic Energy Research Institute) [1] and the poolside examination at Kori-2 site [2]. In this study, the oxidation of KOFA cladding will be analyzed and compared with the design analysis which employed the performance of Siemens/KWU's HCW standard Zircaloy-4, and a new corrosion model constant for the KOFA cladding will be derived. And the reasons for the lower corrosion of the KOFA cladding than the expected will be sought.

2. Analysis of KOFA Zircaloy-4 Cladding Corrosion

The oxide layer thickness of KOFA fuel cladding irradiated in Kori-2 was measured by both the eddy current poolside examination at site and the destructive hot cell PIE (Post-Irradiation Examination) at KAERI. The maximum measurement error of the eddy current oxide measurement is considered less than 5μm[2]. The measurements of the cladding oxidation were performed in total for ten fuel rods in three fuel assemblies. The power histories of those fuel assemblies are given in Table 1. The circumferentially-averaged axial maximum oxide layer thickness of the fuel rods are shown in Figure 1. Figure 2 shows the axial variation of the oxidation for a highly oxidized fuel rod, and all other fuel rods showed the similar axial oxidation profiles. The lower corrosion regions in the axial distribution resulted from such effects of the spacer grids in the fuel assembly as the enhanced heat transfer between the cladding and coolant and the slight power depression due to neutron absorption by Inconnel spacer grid. The axial peak of the cladding corrosion occurs at the position of around 80 % from the bottom where the axially peak temperature of the cladding occurs.

In the design analysis of KOFA fuel corrosion, COMO-C code [3] is used, which is based upon the following corrosion model.

$$S(t) = c_1 \exp(-b_1/T_0)\, t^{1/3}$$

for pre-transition range (1)

$$dS/dt = B_f\, c_2 \exp(-b_2/(T_0 + q''S/\lambda_{ox}))$$

for post-transition range (2)

where,

S = oxide layer thickness

t = time

b_1, b_2, c_1 and c_2 = constants

T_0 = absolute cladding-tube surface temperature at outside of oxide layer

B_f = fitting factor (irradiation factor)

q'' = surface heat flux

λ_{ox} = thermal conductivity of oxide layer

The fitting factor, B_f is to be empirically determined from the in-pile corrosion data bases and the transition of the Zircaloy-4 oxidation is assumed to occur at the thickness of 2.1μm.

Based upon the fact that the KOFA cladding was manufactured according to the Siemens/KWU's HCW (Highly Cold Worked) standard Zircaloy-4 cladding specification, the fitting factor of the KOFA cladding in the design analysis employed the value of the Siemens/KWU's HCW standard Zircaloy-4, 2.8 which was determined on a best-estimate basis from the in-pile corrosion data base

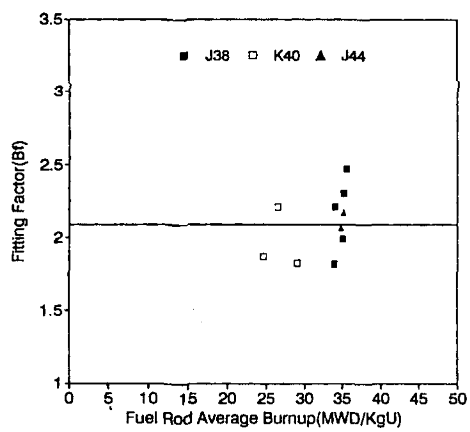

Fig. 3. Derivation of the Fitting Factors for KOFA Cladding

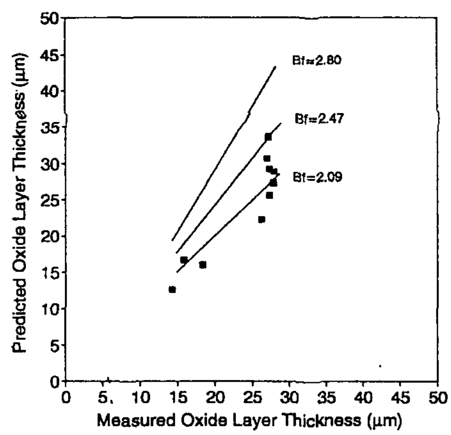

Fig. 4. Comparison of the Measured Oxide Layer Thickness with the Predicted one of KOFA Cladding

with the standard deviation of 0.11. However, as shown in Figure 1, design analysis of KOFA cladding corrosion over-estimates at least 23 % compared with the measured data. It was attempted to derive a new fitting factor for KOFA cladding from the oxide measurement data. Results are shown in Figures 3 and 4. The average of the KOFA cladding fitting factors is 2.09 and the standard deviation is 0.217. Therefore, the best-estimated, 2.09 and the upper limit, 2.47 of the KOFA cladding fitting factors are about 25 % and 12 %, respectively lower than those of Siemens/KWU's HCW standard Zircaloy-4.

3. Discussion

The reasons why the corrosion of KOFA cladding is lower than the design calculation will be discussed in this section.

There exist the differences in the manufacturing processes between KOFA and Siemens/KWU's claddings. Table 2 compares the pilgering processes of KOFA and Siemens/KWU's HCW cladding. KOFA cladding had four pilgering steps while Siemens/KWU's HCW cladding had three pilgering steps. However, the final pilgering step of KOFA cladding still had slightly higher reduction of area than Siemens/KWU's cladding. Degree of recrystallization, texture, second phase particle size distribution and the accumulated annealing parameter of KOFA cladding were found comparable to those of Siemens/KWU's HCW standard Zircaloy-4 as shown in Table 3 [4]. The chemical composition of KOFA cladding are compared with the standard Zircaloy-4 requirement in Table 4 [5]. Tin content of KOFA cladding is about 1.51 % which can not be considered as a low tin Zircaloy-4. Silicon content of KOFA cladding, which is known to decrease the corrosion as its content increases [6] is relatively high as about 95 ppm. Nitrogen content which is known to increase the corrosion [7] is slightly low and all other elements lie in the middle of the bands required by the specification.

Kori-2 plant can be considered as a lower coolant temperature plant such that nominal core inlet temperature is 288℃ and nominal core outlet temperature is 325℃ . However, lower coolant temperature can not be the cause of lower corrosion of KOFA cladding than the expected since the temperature is explicitly considered in the COMO-C code corrosion model as shown in Equations (1) and (2). The radial power histories of the fuel rods were obtained by the core follow calculation of which the uncertainty is known less than 4 %. Since PWR cores are usually operated with all the control rods out of the core, the axial power distribution of the fuel rod does not vary much with time.

The corrosion of the cladding also depends upon the coolant chemistry in the primary system. The coolant chemistry scheme of Kori-2 changed from the constant pH scheme - pH 6.9 at 300℃ is maintained - in Cycle 7 to the coordinated boron-lithium scheme - maximum lithium concentration of 2.2 ± 0.15 ppm is maintained - in the subsequent cycles as shown in Figures 5, 6 and 7. Since both chemistry schemes including the concentrations of the oxygen, hydrogen and other impurities in Kori-2 are within the ranges suggested by the EPRI PWR primary coolant chemistry guidelines [8], coolant chemistry in Kori-2 can not be a cause for the lower corrosion of the KOFA cladding.

Therefore, it can be speculated that the differences in the manufacturing processes and chemical composition between KOFA cladding and Siemens/KWU HCW standard Zircaloy-4 such as cold work, heat treatment, silicon and nitrogen may have somewhat contributed to lower corrosion of KOFA cladding than the expected.

Table 2. Pilgering Processes of KOFA and Siemens/KWU's HCW Claddings

	Tube OD × Thickness (mm × mm) Reduction of Area/Q-factor*				
CladdingTrex	First Step	Second Step	Third Step	Fourth Step	
KOFA Cladding	63.5×10.92 –	44.45×7.62 51.1%/1.01	31.75×5.08 51.7%/1.256	17.78×1.80 78.7%/2.02	9.50×0.64 80.03%/1.75
Siemens/KWU's HCW Standard Zircaloy-4	63.5×10.92 -	30×4.5 80%/1.23	16.7×1.65 78.3%/1.9	9.5×0.65 76.8%/1.75	- -

(*) Q-factor = $\ln(W_f/W_i)/\ln(D_f/D_i)$
W_f, W_i=wall thickness after and before pilgering process
D_f, D_i = mean diameter after and before pilgering process

Table 3. Microstructural Characteristics of Siemens/KWU's Standard Zircaloy-4 and KOFA Zircaloy-4 Cladding[4]

Parameter	Siemens/KWU's Standard Zircaloy-4	KOFA Zircaloy-4
Texture (Kearns number)	Fr : 0.49 Ft : 0.41 Fz : 0.10	Fr : 0.521 Ft : 0.413 Fz : 0.060
Recrystallization(%)	10~40	13~24
Average second phase particle size(μm)	>0.15	>0.2
Accumulated annealing parameter(hr)	7.1×10^{-18}~40×10^{-18}	17.6×10^{-18}

Table 4. Chemical Composition of KOFA Cladding Ingot Compared with the Requirements of Siemens/KWU's Standard Zircaloy-4 Specification[5]

Elements	Siemens/KWU's Standard Zircaloy-4	KOFA Zircaloy-4 Cladding Ingot
Alloying Elements(%)	Sn : 1.20~1.70 Fe : 0.18~0.24 Cr : 0.07~0.13 0 : 0.10~0.16 Fe+Cr : 0.28~0.37 Zr : balance	Sn : 1.42~1.60 Fe : 0.19~0.22 Cr : 0.10~0.12 0 : 0.11~0.12 Fe+Cr : 0.29~0.34 Zr : balance
Impurities(ppm)	C : 270 max. N : 80 max. Si : 120 max.	C : 135~147 N : 27~34 Si : 81~109

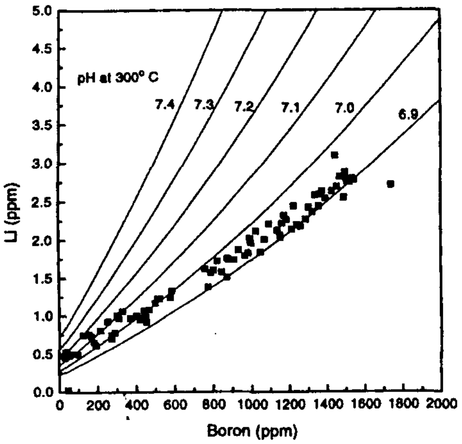

Fig. 5. Boron-Lithium-pH Variation in the Primary Coolant During Cycle 7 of Kori-2

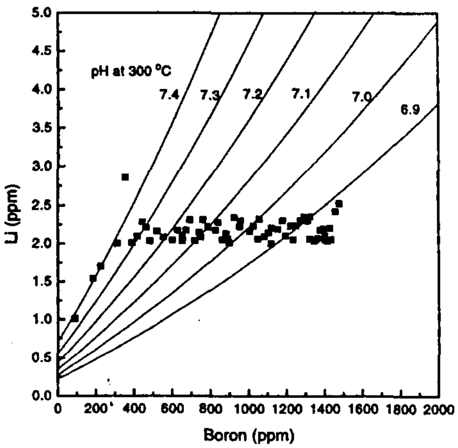

Fig. 6. Boron-Lithium-pH Variation in the Primary Coolant During Cycle 8 of Kori-2

In summary, although the burnup and oxide layer thickness of the measured KOFA fuel rods is relatively low and the amount of the corrosion data base are small, it can be said that corrosion of KOFA cladding is lower than the design prediction which was based upon the corrosion performance of Siemens/KWU's HCW standard Zircaloy-4, and the differences in the manufacturing processes and chemical composition of the cladding may have somewhat contributed to lower corrosion of KOFA cladding.

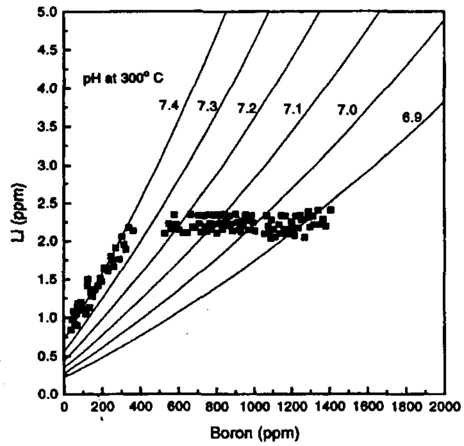

Fig. 7. Boron-Lithium-pH Variation in the Primary Coolant During Cycle 9 of Kori-2

4. Conclusions

The measured oxidation data of KOFA fuel cladding irradiated up to the fuel rod burnup of 35,000 MWD/MTU for two cycles in Kori-2 plant was analyzed and compared with the design calculation. Results showed that oxidation of KOFA cladding was lower than the design prediction which was based upon the performance of Siemens/KWU's HCW standard Zircaloy-4. Therefore, a new corrosion model constant for KOFA cladding was derived. Although the measured fuel rods have relatively low burnup and oxidation and the amount of the measured data are small, analysis of manufacturing and in-reactor operation conditions of KOFA cladding indicates that the differences in the manufacturing processes and chemical composition of the Siemens/KWU's HCW (Highly Cold Worked) standard Zircaloy-4 and KOFA cladding may have somewhat contributed to lower corrosion of KOFA cladding than the expected.

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