Characterization of Oxide Layer with Precipitates of HANA-6 Exposed in Simulated PWR Primary Water Environment

Hun Jang*, Jea Young Lim, Sung Yong Lee, Yoon Ho Kim, Yong Kyoon Mok
Department of Nuclear Fuel Technology, KEPCO NF, 242, Daedeok-daero, 989beon-gil, Yuseong-gu, Daejeon
Corresponding author: janghoon@knfc.co.kr

1. Introduction

Corrosion resistance of fuel cladding material is one of most important parameters to sustain the fuel integrity and safety. A domestic Zr-base alloy named as HANA-6 has been developed to improve the corrosion properties. It is reported that the superior corrosion resistance of HANA-6 is related to small size of β-Nb precipitates (ppts) [1].

Among various affecting factors on corrosion property, role of ppts in Zr-base alloys is known as one of critical parameters governing corrosion properties. The delayed oxidation behaviors of β-Nb ppts and their amorphization behaviors in HANA-6 and other Zr-base alloys have been frequently reported [1-3]. On the other hand, although $Zr(Nb,Fe)_2$ ppts could be formed in the HANA-6 alloy due to Fe impurities contained in Zr-sponge [4,5], the oxidation behavior of $Zr(Nb,Fe)_2$ ppts contained in HANA-6 alloy has not been fully understood.

In this study, oxide characteristics of HANA-6 corroded in simulated PWR environment for 165 and 315 days were investigated. And, oxidation behaviors of $Zr(Nb,Fe)_2$ ppts contained in HANA-6 alloy were investigated by TEM with EDS techniques.

2. Experimental Details

HANA-6 and reference alloys were fabricated through their typical manufacturing processes in laboratory. The plate type specimens having a dimension of 20 x 20 x 1 mm were used for test. The measured chemical compositions of HANA-6 were 1.2 wt.% of Nb, 0.07 wt.% of Cu, 600 ppm of Fe.

Table I shows test environment. The water temperature was maintained at 360 ℃. The water chemistries were controlled in special water loop system to simulate PWR primary environment.

Table I: Corrosion test environment

Test environment	360 ℃ water (19 MPa)
Dissolved oxygen	< 5 ppb
Dissolved hydrogen	~ 2.7 ppm (~ 31 cc/kg)
Conductivity	~ 22 μS/cm (1200 ppm H_3BO_3 + 2.2 ppm LiOH)
pH	6.3 ~ 6.5 at room temperature

The corrosion tests were performed for 387 days. During the test, HANA-6 specimens tested for 165 and 315 days were taken to investigate the oxidation behaviors of ppts incorporated in oxide layer by TEM/EDS technique.

3. Results and Discussion

3.1 Corrosion Test Results

Figure 1 shows the corrosion weight gain of HANA-6 and reference alloys tested in simulated PWR environment for 387 days. The corrosion weight gain of HANA-6 was much lower than those of Ref. A and B alloys. For HANA-6, the transition of corrosion rate was not observed on specimens tested up to 387 days.
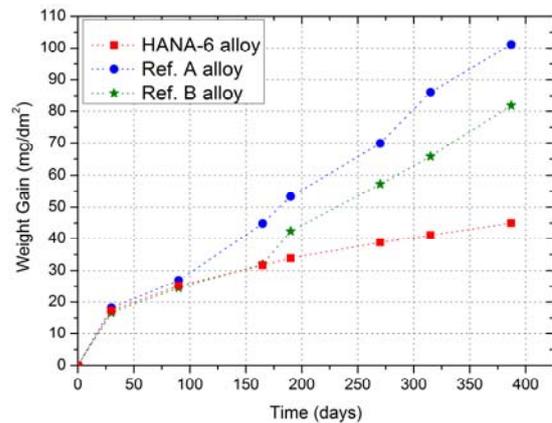
Fig. 1. Corrosion test results of HANA-6 and reference alloys in simulated PWR water.

3.2 Characterization of Oxide Layer with Precipitates after 165 Days Corrosion Test

The oxide characteristics with ppts formed on HANA-6 specimens exposed to simulated PWR water for 165 and 315 days was investigated by TEM/EDS analyses. Fig. 2 shows summary of oxide characteristics formed on HANA-6 specimen tested for 165 days [6]. Equiaxed grains with large number of pores or cracks were observed in outer oxide region (up to 0.52 μm from oxide/water interface). And, columnar grains which is known as barrier oxide layer were observed in inner oxide layer (below equiaxed grain) which is similar oxide morphologies of Zr-base alloys [1-3,5].

β-Nb (or β-enriched) and ZrNbFe (possibly $Zr(Nb,Fe)_2$) ppts were frequently observed in columnar oxide layer. The characteristics of ppts in columnar oxide layer could be divided by 3 regions.
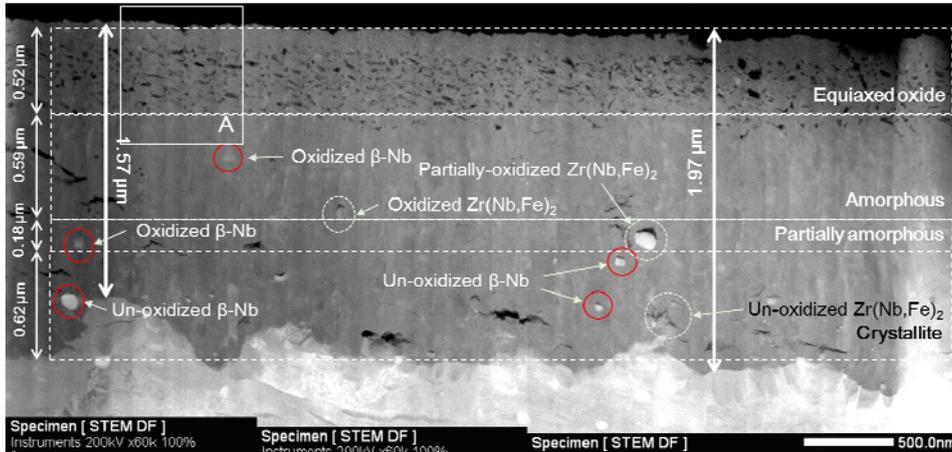
Fig. 2. Summary of characteristics of the oxide layer formed on HANA-6 after 165 days corrosion test [6].
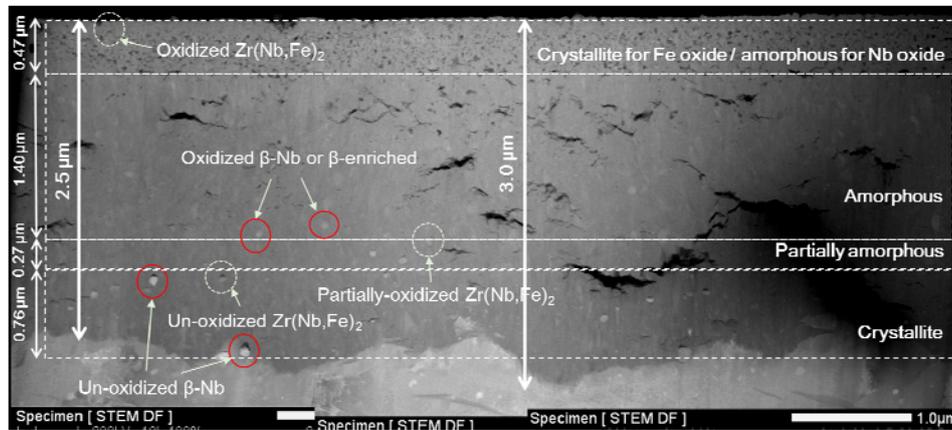
Fig. 3. Summary of characteristics of the oxide layer formed on HANA-6 after 315 days corrosion test.

Up to a region below 0.6 μm away from metal/oxide interface, the ppts remained as un-oxidized and crystallites. Between 0.6 ~ 0.8 μm away from metal/oxide interface, the ppts became partially oxidized. In the results of their oxidation, the crystal structures of the ppts were transformed to partially amorphous. Above 0.8 μm away from metal/oxide interface, the crystal structures of ppts were fully transformed to amorphous form, and those were fully oxidized. These amorphization phenomena of β-Nb and $Zr(Nb,Fe)_2$ ppts have been frequently reported by several researchers [1,2,7]. It was reported that these amorphization of crystalline β-Nb is due to the sudden ingress of oxygen into the phase with limited diffusion of Nb [2,3]. From our previous study, $Zr(Nb,Fe)_2$ ppt showed slightly slower oxidation kinetics when compared to oxidation kinetics of β-Nb ppt, but, the difference was not significant [6].

3.3 Characterization of Oxide Layer with Precipitates after 315 Days Corrosion Test

Figure 3 shows summary of oxide characteristics for the specimen tested for 315 days. Although the oxide thickness of specimen was increased when compared with specimen tested for 165 days, the oxide morphologies were similar, except large size of lateral cracks as shown in right side of Fig. 3. These large size of cracks could not be identified in this study. It can be expected that the cracks were formed during fabrication process of TEM specimen since the transition of corrosion rate of specimen did not observed after 315 days corrosion test.

The thickness of equiaxed oxide layer was 0.47 μm which is similar to the thickness of equiaxed oxide layer observed in specimen tested for 165 days. Also, columnar oxide layer observed in inner oxide layer could be divided by oxidation states of ppts to 3 regions. In comparison with oxide morphologies of specimen tested for 165 days, the oxide layers that un-oxidized crystalline ppts and partially oxidized ppts were observed, were slightly increased to 0.76 μm and 1.03 μm away from metal/oxide interface, respectively. On the other hand, remained columnar oxide layer that the oxidized and amorphous ppts were observed, was significantly increased to 1.4 μm from 0.6 μm. Therefore, the barrier oxide layer having oxidized and amorphous ppts was significantly increased during oxide growth before pre-transition region.

3.4 Characterization of Zr(Nb,Fe)₂ ppts in Outer Oxide Layer

To understand the oxidation behaviors of ppts in oxide layer, the oxidized ppts in outer oxide region were examined by TEM/EDS mapping technics. In case of β-Nb ppts, the oxidized β-Nb ppts were found in the outer region by TEM/EDS mapping. However, it was difficult to distinguish the β-Nb ppts from TEM images because the boundaries of amorphous β-Nb ppts were fully dissolved to near crystal Zr oxide after end of the oxidation process.

On the other hand, the oxidized Zr(Nb,Fe)₂ ppt in outer oxide region was found by TEM/EDS mapping as shown in Fig. 4. The amorphous Zr(Nb,Fe)₂ ppt after the end of oxidation process was decomposed to Fe- and Nb-rich oxide regions. The Nb-rich oxide was observed at the core of Zr(Nb,Fe)₂ ppt. Also, it still remained as amorphous. While, the Fe-rich oxide encircled the Nb-rich oxide, and it had their crystal structure. It is thought that the Fe atoms were diffused out during oxidation of Zr(Nb,Fe)₂ ppt due to the higher diffusion rate of Fe atoms. As a results of higher mobility of diffusing Fe atoms, Fe-rich oxide might be easily crystallized. On the other hand, the Nb atoms remained at their original site due to the lower diffusion rate.
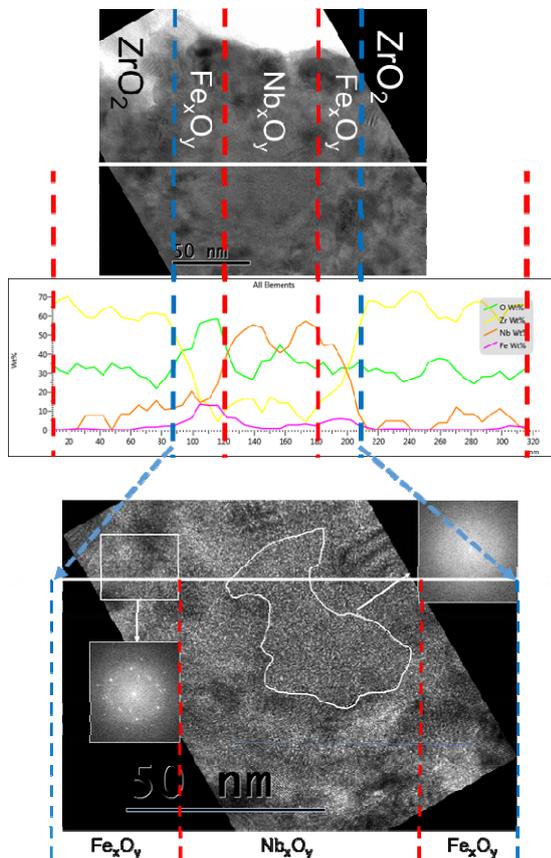
Fig. 4. Decomposed Zr(Nb,Fe)₂ ppts in the outer oxide layer after 315 days corrosion test.

Figure 5 shows the results of EDS mapping on outer oxide layer of specimen tested for 165 days. The higher Fe concentration at outer oxide layer was observed. It is thought that the diffusing Fe atoms from Zr(Nb,Fe)₂ ppts could be responsible for the increasing Fe concentration in oxide layer. Therefore, Fe in Zr(Nb,Fe)₂ ppt could be depleted and dissolved to outer layer of ppts or bulk oxide layer.

wt.%	A	B
O	45.2	40.9
Fe	0.7	0.1
Zr	53.9	59.0
Nb	0.24	-
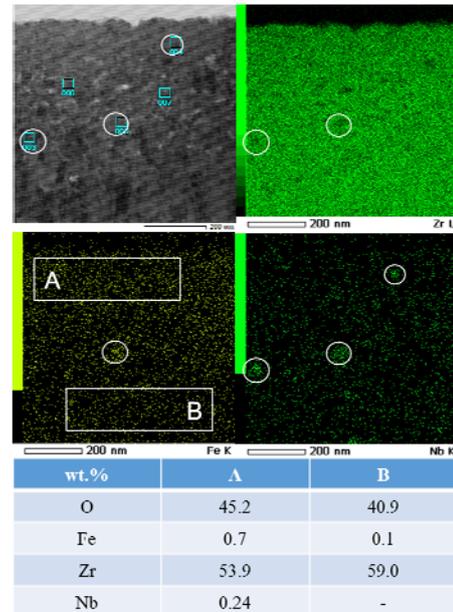
Fig. 5. Dissolution of Fe in Zr(Nb,Fe)₂ ppt to adjacent oxide layer after 165 days corrosion test.

3. Conclusions

The superior corrosion property of HANA-6 has been confirmed through corrosion test in simulated PWR water for 387 days. By using TEM/EDS technique, the oxide characteristics with presence of β-Nb (or β-enriched), and ZrNbFe (possibly Zr(Nb,Fe)₂) ppts have been characterized as follows.

1. Delayed oxidation behaviors of β-Nb and Zr(Nb,Fe)₂ ppts and their amorphization due to oxidation were observed from TEM/EDS analyses.
2. The oxide layers having crystallite and partially amorphous ppts were slightly increased with increasing corrosion test time from 165 days to 315 days. On the other hand, the columnar oxide layer having oxidized and amorphous ppts was significantly increased.
3. In outer oxide layer, Fe in Zr(Nb,Fe)₂ ppt was depleted and dissolved to outer layer of ppt and bulk oxide layer. With oxidation of Zr(Nb,Fe)₂ ppt, Fe-rich oxide in outer layer of ppt was changed to crystal structure. While Nb-rich oxide in inner layer of ppt still remained as amorphous.

Acknowledgements

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