

## Corrosion and Oxide Properties of HANA-6 Alloy in Simulated PWR Primary Water

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### 1. Introduction

Zr base alloys have been used as material of nuclear fuel. It is known that corrosion property of fuel cladding is one of most important parameter to sustain the fuel integrity and safety. In this regard, domestic Zr-base alloy, HANA-6 (Zr-1.1Nb-0.07Cu), has been developed to improve the corrosion properties.

It is known that the corrosion resistance of HANA-6 alloy is increased by precipitates (ppts) of small size  $\beta$ -Nb phase with copper addition [1]. The delayed oxidation behaviors of  $\beta$ -Nb ppts and their amorphization behaviors with oxidation have been frequently reported [1-3]. On the other hand, although the ppts of  $Zr(Nb,Fe)_2$  phase could be formed in the Zr-Nb-Cu alloys 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 investigated.

In this study, corrosion test of HANA-6 alloy were performed in simulated PWR primary water. And, the oxidation behaviors of ppts contained in HANA-6 alloy were investigated by TEM/EDS technique.

### 2. Experimental Details

HANA-6 and reference alloys were fabricated by typical manufacturing processes in laboratory. The corrosion specimens with a dimension of 20 x 20 x 1 mm were cut from the fabricated samples. The measured chemical compositions of HANA-6 were 1.2 wt.% of Nb, 0.07 wt.% of Cu, 600 ppm of Fe. Also, the measured chemical compositions of other reference alloys were satisfied by their specification.

Table I shows corrosion test environment. The test temperature was 360°C to accelerate the corrosion kinetics. Other environmental parameters were controlled by recirculated water loop system to simulate PWR primary water chemistries.

Table I: Corrosion test environment

Test environment	360°C water (19 MPa)
Dissolved oxygen	< 5 ppb
Dissolved hydrogen	~ 2.6 ppm (~ 30 cc/kg)
Conductivity	~ 22 $\mu$ S/cm (1200 ppm $H_3BO_3$ + 2.2 ppm LiOH)
pH	6.3 ~ 6.5 at room temperature

Five specimens in each tested alloy were prepared by polishing and pickling. The corrosion tests were performed for 315 days. During the test, one HANA-6

specimen tested for 165 days was taken to investigate the oxidation behavior of ppts by TEM/EDS technique.

### 2. Results and Discussion

#### 2.1 Corrosion behavior

Figure 1 shows the weight gain by corrosion of HANA-6 and reference alloys. The corrosion weight gain of HANA-6 was much lower than those of ref. A and B alloys.

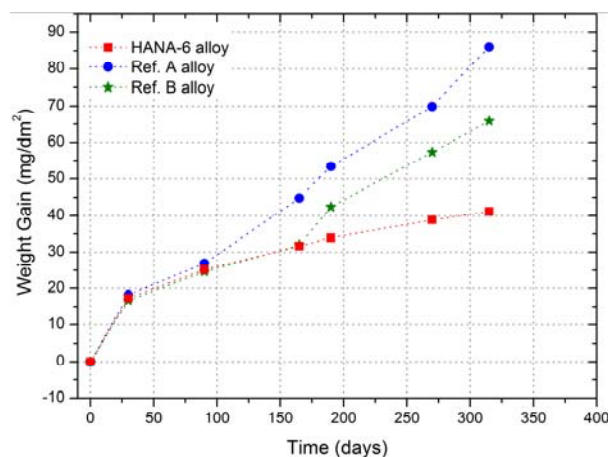


Fig. 1. Corrosion test results of HANA-6 and reference alloys in simulated PWR water.

#### 2.2 Characterization of Oxide Layer with Precipitates

The overall oxide characteristics with ppts formed on HANA-6 alloy exposed to simulated PWR water for 165 days was investigated by TEM and EDS analyses in detail. And, the results were summarized as shown in Fig. 2. The oxide thickness was 1.97  $\mu$ m which is well corresponded to corrosion weight gain as the following correlation, 1  $\mu$ m ~ 15 mg/dm<sup>2</sup> [2]. Equiaxed grains with large number of lateral cracks were observed in outer oxide layer. And, columnar grain with large lateral cracks were observed in inner oxide layer which are similar oxide morphologies of Zr-base alloys [1-3,5].

Several ppts incorporated in the oxide layer frequently observed in mostly inner part of oxide layer. The most of ppts were identified as  $\beta$ -Nb (or  $\beta$ -enriched) phase. The remaining ppts were identified as  $Zr(Nb,Fe)_2$  phase. From the phase diagram of Zr-Nb-Fe [4], it could be formed by 600 ppm of Fe contained in Zr-sponge.

In inner part of oxide layer, the ppts remained unoxidized. And, the ppts have their crystal structures. But, the ppts were partially oxidized at a region above 0.6  $\mu\text{m}$  away from metal/oxide interface. As the results of oxidation of ppts, the crystal structures were partially transformed to amorphous form. Above 0.9  $\mu\text{m}$  away from metal/oxide interface, the crystal structures of ppts were fully transformed to amorphous form, and those were fully oxidized. As the results of oxidation, the amorphization of  $\beta\text{-Nb}$  and  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppts has been observed from several authors [1,2,6]. It was reported that these amorphization of crystalline  $\beta\text{-Nb}$  is due to the sudden ingress of oxygen into the phase with limited diffusion of Nb [2,3].

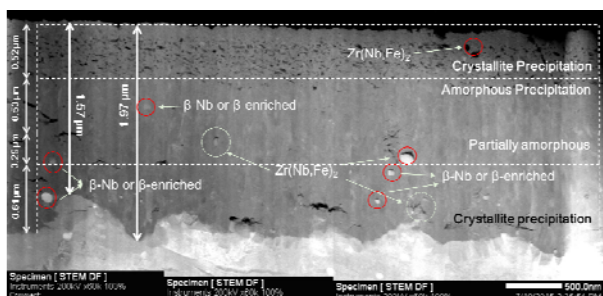


Fig. 2. Summary of characteristics of the oxide layer formed on HANA-6 exposed to PWR simulated water for 165 days.

### 2.3 Characterization of $\text{Zr}(\text{Nb},\text{Fe})_2$ ppts in Oxide Layer

The relative oxidation kinetics between  $\beta\text{-Nb}$  and  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppts were investigated as summarized in Fig. 2. The  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppt was fully oxidized at a distance of about 0.2  $\mu\text{m}$  away from the region at which  $\beta\text{-Nb}$  ppt was fully oxidized. C. Proff reported the Gibbs free energy for oxide formation of  $\beta\text{-Nb}$  was  $-728 \text{ kJ/mol O}_2$ . While, that of  $\text{Zr}(\text{Nb},\text{Fe})_2$  was  $-702 \text{ kJ/mol O}_2$  [7]. This slight difference of free energy could be one of the reasons of slight slower oxidation kinetic of  $\text{Zr}(\text{Nb},\text{Fe})_2$  phase.

It was reported that  $\beta\text{-Nb}$  was difficult to find in outer oxide region because the boundaries of amorphous  $\beta\text{-Nb}$  ppts were fully dissolved to near crystal Zr oxide after end of the oxidation process [2,3]. However, the difference of chemical composition of Nb in  $\beta\text{-Nb}$  ppt remained due to the limited diffusion of Nb [3]. Likewise, in this study, although the oxidized  $\beta\text{-Nb}$  ppts could be found in the outer region by EDS mapping, it was difficult to distinguish the  $\beta\text{-Nb}$  ppts from TEM images. On the other hand, the oxidized  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppt in outer oxide region was found by TEM and EDS mapping. The amorphous  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppt after the end of oxidation process was finally transformed to highly defective crystal structure.

### 3. Conclusions

The corrosion resistance of HANA-6 alloy has been confirmed from corrosion test in simulated PWR water for 315 days. By using TEM/EDS technique, the oxide layer with presence of  $\beta\text{-Nb}$  (or  $\beta\text{-enriched}$ ), and  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppts have been characterized as follows.

1.  $\beta\text{-Nb}$  and  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppts incorporated in oxide layer were not oxidized up to 0.6  $\mu\text{m}$  from metal/oxide interface.
2. Amorphization of both  $\beta\text{-Nb}$  and  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppts during their oxidation process were observed.
3.  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppt showed slightly slower oxidation kinetics compared with  $\beta\text{-Nb}$  ppt. However, the difference was not significant.
4. The amorphous  $\text{Zr}(\text{Nb},\text{Fe})_2$  ppt in outer oxide layer was finally changed to highly defective crystal structure.

### Acknowledgements

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