

Corrosion properties of HANA-4 in 360°C pure water and LiOH solution

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1. Introduction

The advanced Zr alloys have been developed continuously with a focus on an improvement of the corrosion resistance. Recently, a series of Nb-containing Zr alloys named HANA has been developed to improve the corrosion resistance of the fuel claddings by optimizing the alloy composition and the heat treatment condition [1]. Nb-containing Zr alloys behave differently in LiOH solution where Zircaloy-4 shows an acceleration corrosion behavior. LiOH has been added into a coolant to control the pH and thereby preventing the formation of CRUD which might cause an activity problem during a reactor operation. Therefore, it is crucial to investigate the corrosion behavior of the newly-developed Zr alloys in LiOH solution such as HANA. This investigation aims at contributing to the understanding on the corrosion mechanism of Nb-containing Zr alloys. In this study, the corrosion behavior of HANA-4 alloys was investigated and compared with Zircaloy-4 in 360°C water and in 360°C water containing 70ppm LiOH. Since a lack of an understanding on the corrosion mechanism is thought to be partly due to an insufficient oxide characterization, the oxides formed during the corrosion tests were characterized to clarify the reason why HANA-4 alloys exhibited an improved corrosion resistance.

2. Experimental procedure

HANA-4 (Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr) and Zircaloy-4 (Zr-1.3Sn-0.2Fe-0.1Cr) were used in this study. The two main differences in the chemical compositions between two alloys are the addition of Nb and the smaller Sn content in HANA-4 when compared to Zircaloy-4 while the contents of Fe and Cr are identical in the two alloys. HANA-4 was manufactured as tubes with an outer diameter of 9.5mm and a wall thickness of 0.57mm. The final annealing for HANA-4 tubes was performed at 470°C to make a tube with a stress-relieved microstructure. On the other hand, the commercial Zircaloy-4 tubes were used in an as-received state as a reference.

Corrosion tests were performed by using autoclaves for 830 days in 360°C pure water and in 360°C water containing 70ppm LiOH. The corrosion test specimens were cut into the segment tubes with a length of 40mm for HANA-4 and 30mm for Zircaloy-4 and then pickled in a solution of 10vol% HF, 30vol% H₂SO₄, 30vol%

HNO₃ and 30vol% H₂O. The corrosion behavior was evaluated by measuring the weight gain of the corrosion test specimens which were periodically taken out of the autoclaves.

The oxides formed on the corrosion test specimens were characterized by a optical microscopy to examine the oxide growth on the Zr alloys. The samples for the optical microscopy were prepared by cutting the corroded tube and polishing the cross-section on the SiC paper with grit number 4000.

3. Results and discussion

Fig. 1 shows the corrosion behavior of HANA-4 and Zircaloy-4 in 360°C pure water and in 360°C water containing 70ppm LiOH. HANA-4 showed a much better corrosion resistance than Zircaloy-4 in both corrosion conditions. The corrosion rate of Zircaloy-4 was two times higher in pure water and seven times higher in LiOH solution when compared to that of HANA-4. Even though the corrosion condition was changed from pure water to LiOH solution, the corrosion rate of HANA-4 was only slightly increased. However, Zircaloy-4 showed an accelerated corrosion behavior after 330 days in LiOH solution with the corrosion rate being increased by approximately 5 times after the transition point.

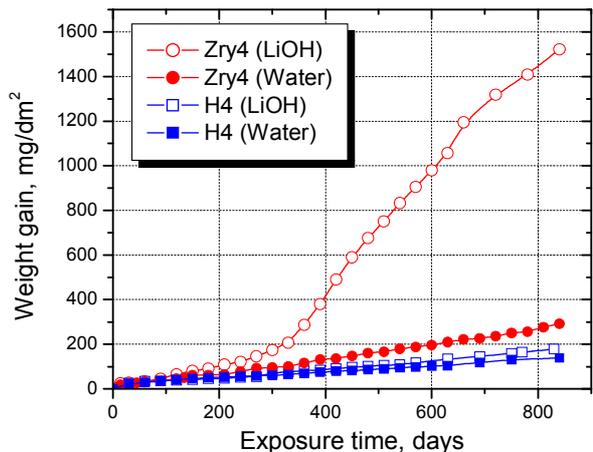


Figure 1. Corrosion behavior of HANA-4 and Zircaloy-4 in 360°C pure water and 360°C water containing 70ppm LiOH.

Regarding the effect of the alloying element on the corrosion properties of Zr alloys, the addition of Nb has already been confirmed to be beneficial in many

previous studies [1-4]. It has also been reported that the corrosion resistance of Zr alloys was increased with a decrease of Sn content. In this study, the synergistic effect of the addition of Nb and the reduction of Sn might be achieved in HANA-4 when compared to Zircaloy-4, although it was hard to determine which effect was more significant in the improvement of the corrosion resistance. Moreover, such a beneficial effect was even more remarkable in LiOH solution where a corrosion acceleration of Zircaloy-4 was generally observed.

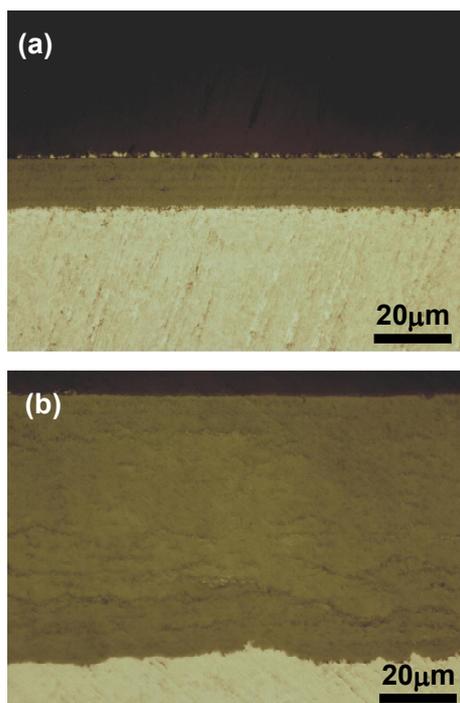


Figure 2. Optical micrographs of the cross section of the oxide formed on HANA-4 and Zircaloy-4 after 830 days in 360°C water containing 70 ppm LiOH.

After the corrosion tests, the cross-sections of the oxides were observed by a reflected light optical microscopy to examine the interface morphology. Fig. 2 shows the cross-sections of the oxide formed on HANA-4 and Zircaloy-4 which were corroded for 830 days in pure water and in LiOH solution. The oxide/metal interface was shown to be flat in HANA-4. However, Zircaloy-4 was shown to have a relatively irregular and wavy interface.

Moreover, a number of lateral cracks were also observed especially in the oxide on Zircaloy-4 in LiOH solution. It was revealed that the interface was more irregular in the alloy exhibiting a higher corrosion rate. However, it is not clear whether the irregular interface is one of the root causes for the higher corrosion rate of Zircaloy-4 even though an irregular interface is thought to be closely related to the inhomogeneous stress build-up during an oxide growth [5].

A layered structure was shown in the oxide formed in LiOH solution especially for HANA-4. However, the

layered structure was not able to be defined in the oxide of Zircaloy-4 which showed a breakaway corrosion behavior in LiOH solution. It was revealed that the oxide on HANA-4 maintained its protective nature even in LiOH solution. It is noted here that a layered structure was not developed in the oxide whose growth rate was very high. This seems to be due to the fact that equiaxed grains are predominant in a fast growing oxide rather than a periodic change of the grain morphology.

4. Conclusion

HANA-4 (Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr) showed a much better corrosion resistance than Zircaloy-4 in 360°C pure water and maintained a lower corrosion rate even in 360°C water containing 70ppm LiOH where Zircaloy-4 showed an accelerated corrosion behavior. The oxide grown on HANA-4 was observed to have a smaller total oxide thickness for the same corrosion period and a well-developed layer structure when compared to Zircaloy-4. The oxide protectiveness of HANA-4 was effective in maintaining a lower corrosion rate even in LiOH solution where a layered structure was not developed in the oxide of Zircaloy-4. The oxide of HANA-4 was protective enough to prevent it from becoming porous by an ingress of Li⁺ or LiOH.

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