Effect of Nb and Fe Content on Corrosion and Oxide Characteristics of Zr-Nb-Fe alloys

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1. Introduction

The corrosion resistance of fuel claddings has been considered to be one of the key properties to control the performance and the safety of nuclear fuel. Zr-based alloys have been used as fuel cladding materials and a great number of researches have been done to improve the corrosion resistance of the Zr-based alloys. Among the various alloying elements, Nb and Fe are considered to be very effective for improving the corrosion resistance of the Zr-based alloys [1,2]. The aim of this study is to investigate the effect of the Nb/Fe ratio on the corrosion of the Zr alloys. Microstructure observation, corrosion test and oxide characterization were performed for the Zr-Nb-Fe ternary alloys with various addition of Nb and Fe.

2. Experimental procedure

The Nb content ranged from 0.3 to 0.7 wt.% and the Fe content ranged from 0.1 to 0.7 wt.% in the Zr-xNb-yFe ternary alloys. The Nb/Fe ratio was controlled by decreasing the Nb content with increasing Fe content so that the total amount of Nb + Fe content was the same in all of the alloys. The lowest Nb content (0.3 wt.%) selected in this study was the critical Nb content to form the Nb-containing precipitates which was observed in our previous study [3]. The addition ratio of Nb/Fe in the experimental alloys was controlled to be 0.6, 1.0, 1.7, 3.0 and 7.0. The experimental alloys were manufactured by the sequence of vacuum arc melting, β-quenching, hot rolling and cold rolling (3 times). The Nb/Fe ratio in the precipitates was analyzed using a transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscopy (EDS). The corrosion test was performed in a static autoclave of 360℃ water under a saturation pressure of 18.9MPa. The corrosion resistance was evaluated by measuring the corrosion weight gain of the corroded samples after suspending the corrosion test at a periodic term. The oxide characteristics were analyzed using small angle XRD and synchrotron X-ray in Pohang Accelerator Lab.

3. Results and discussion

Each alloy was shown to have the recrystallized structure with equiaxed grains and the measured grain size ranged from 4.2 to 4.7 μm depending on the alloy composition. However, the difference of the grain size in the alloys was not significant although the alloys had a variety of Nb/Fe ratios. Fig. 1 shows the TEM microstructure of the second phase particles in the alloys. The precipitates with various sizes were uniformly distributed in the grain as well as the grain boundaries.

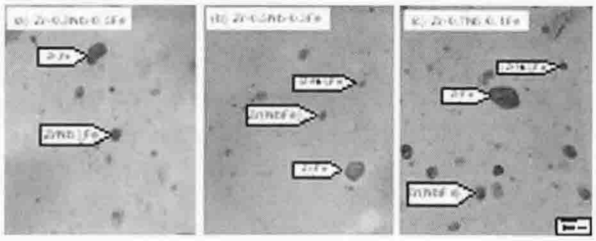

Fig. 1 TEM micrographs for the precipitates of the Zr-xNb-yFe alloys after a final annealing.

From the precipitates analysis, $Zr(NbFe)_2$ precipitate of the HCP structure having a composition of about 38at.%Zr - 32at.% Nb - 30at.%Fe was mainly observed in the alloy with a higher Nb/Fe ratio. $(ZrNb)_2Fe$ precipitate of a cubic structure having a composition of about 60at.%Zr - 13at.%Nb - 27at.%Fe was mainly observed at a lower Nb/Fe ratio than 1.0. The crystal structure of the precipitate was critically changed between 1.0 and 1.7 for the Nb/Fe ratio. Similar results to this observation were reported in previous studies [4, 5]. The main precipitates in the investigated alloys were Zr_3Fe, $(ZrNb)_2Fe$ and $Zr(NbFe)_2$. In the alloys with a high Nb content, the hcp $Zr(NbFe)_2$ precipitate was mainly observed while the fcc $(ZrNb)_2Fe$ precipitate was frequently observed in the alloys with a high Fe content. The Zr_3Fe precipitate was observed in all of the alloys even though its fraction was very low. The β-Nb phase was not observed in this alloy system although the Nb content increased to 0.7 wt%. It could be thought that the formation of the ZrNbFe-type precipitate was more promoted than the β-Nb phase in the alloy with the high Fe content.

Fig. 2 shows the corrosion weight gain as a function of the exposure time and the Nb/Fe ratio. The corrosion resistance was decreased by increasing the Nb/Fe ratio. It was noted that the corrosion resistance was critically changed with the Nb/Fe ratio between 1 and 1.7. The corrosion kinetics was divided into two groups according to the Nb/Fe ratio. When the Nb/Fe ratio is lower than 1.0, the alloys showed a lower corrosion rate than the alloys with a higher Nb/Fe ratio.

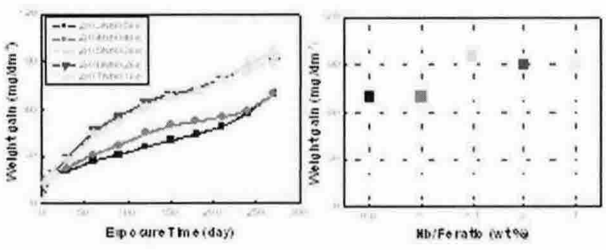

Fig. 2 Corrosion behavior of the Zr-xNb-yFe alloys corroded at 360℃, water for 270 days.

This resulted from the precipitate characteristics in the alloys changed with the Nb/Fe ratio. From the matrix properties, the effect of the matrix composition can be considered to be equivalent in all of the alloys because the contents of Nb and Fe are higher than their solubility in all of the alloys. And the grain size and the precipitate area fraction in the alloys were similar. It was reported from a recent study on the corrosion of the ternary Zr-Nb-Fe system that the corrosion behavior in steam significantly depended on the SPP volume fraction [5]. In this study, however, the corrosion behavior of the alloys was shown to be different from the previous results [5].

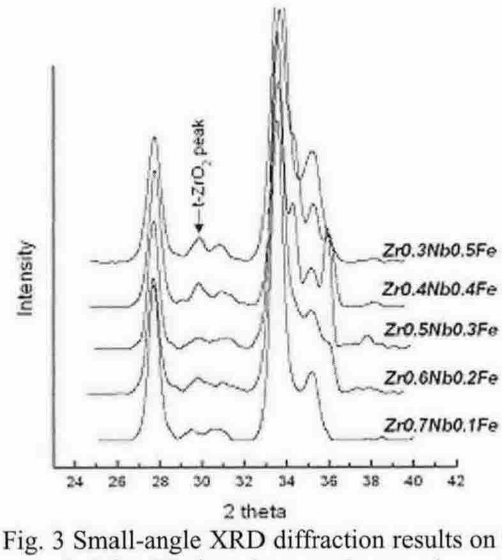

Fig. 3 Small-angle XRD diffraction results on the oxide corroded for 30 days in a static autoclave of the Zr-xNb-yFe alloys.

From the analysis on the crystal structure of the oxide using small angle XRD in Fig. 3 and synchrotron X-ray, the volume fraction of the tetragonal ZrO_2 phase was higher in the alloys having a low Nb/Fe ratio. Therefore, it is suggested that the tetragonal ZrO_2 phase would be more easily stabilized by the precipitation of $(ZrNb)_2Fe$ than $Zr(NbFe)_2$ in the Zr-Nb-Fe alloy.

4. Conclusion

The grain size and the area fraction of the precipitate in all the tested alloys were almost the same even though Nb/Fe ratio was greatly changed. But the mean diameter and the crystal structure of the precipitates were affected by the variation of the Nb/Fe ratio due to the different diffusion rates of Nb and Fe. The corrosion resistance of the Zr-xNb-yFe ternary alloys was improved by decreasing the Nb/Fe ratio. From the microstructure and corrosion studies, it seems that the corrosion resistance would be more closely related to the crystal structure of the precipitate rather than the other properties such as the size distribution of the precipitates.

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