Corrosion Properties of K-claddings in PWR-simulating Loop

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1. Introduction

A development of more corrosion resistant Zr alloys than Zircaloy-4 has been required because the corrosion resistance of fuel claddings is one of the main limitations to the extension of fuel burn-up in PWR [1]. A number of recent works concentrated on the development of the advanced Zr alloys such as ZIRLO [2] and M5 [3] have shown that Nb would be the most beneficial alloying element to improve the corrosion resistance of Zr alloys. The optimum Nb content for the superior corrosion performance was changed depending on the other alloy compositions and manufacturing processes. K-cladding, which was manufactured of the advanced Zr alloy with a high Nb content, showed an excellent corrosion resistance in autoclave corrosion test when alloying addition and heat treatment were properly controlled. However, the mechanistic understanding is not enough to predict the in-pile corrosion performance of K-cladding. The objective of this study is to investigate the corrosion properties of K-claddings in PWR-simulating loop. Microstructure and oxide characteristics of K-cladding were also investigated to develop a further mechanistic understanding on the corrosion behavior.

2. Experimental procedure

Zr fuel cladding used in this study are K3 (Zr-1.5Nb-0.4Sn-Fe-Cu), K6 (Zr-1.1Nb-Cu) and Zircaloy-4 (Zr-1.3Sn-0.2Fe-0.1Cr) claddings. Specimens for the corrosion test, 50 mm in length, were pickled in a solution of 10 vol.% HF, 30 vol.% HNO_3, 30vol.% H_2SO_4 and 30 vol.% H_2O. The corrosion tests were conducted at 360°C in PWR-simulating loop system containing 2.2 ppm Li and 650 ppm B under the pressure of 18.5 MPa in a manner consistent with the ASTM G2-88. The corrosion behavior of the specimens was evaluated by measuring the weight gain with the exposure time.

The microstructures of the alloys were examined using a transmission electron microscope (TEM) equipped with an energy dispersive X-ray spectroscope (EDS). Specimens for TEM observation were prepared by a twin-jet polishing with a solution of 10 vol.% $HClO_3$ and 90 vol.% C_2H_5OH. The selected area diffraction patterns (SADP) were obtained and analyzed to determine the crystal structure of the precipitates, and the micro-chemical analyses on the precipitates were conducted using EDS.

The oxide was observed using optical microscopy and scanning electron microscope. The oxide characterization was also carried out by synchrotron radiation microdiffraction method at the 1B2 bending magnet beamline of the Pohang Light Source method.

3. Results and discussion

3.1. Corrosion behavior

The corrosion behavior of K3, K6 and Zircaloy-4 was investigated in PWR-simulating loop condition. K-claddings showed a better corrosion resistance than Zircaloy-4. Corrosion rate of Zircaloy-4 was changed periodically while K-claddings did not show any transition behavior in the corrosion rate and maintained a lower corrosion rate up to 600 days. It was also found that corrosion rate of K6 is lower than that of K3

Figure 1 shows the corrosion behavior of K6 cladding annealed at 470°C, 510°C and 570°C. Corrosion rate of K6 cladding increase with increase of a final annealing temperature.

3.2. Microstructure

Microstructure characterization with an emphasis on the SPP characteristics was performed for K3 and K6. The β-Nb with bcc structure and $Zr(Nb,Fe)_2$ with hcp structure were observed in K3 while β-Nb with bcc structure and $(Zr,Nb)_2Fe$ with fcc structure in K6. For the β phase, due to the low diffusion rate of Nb atoms,

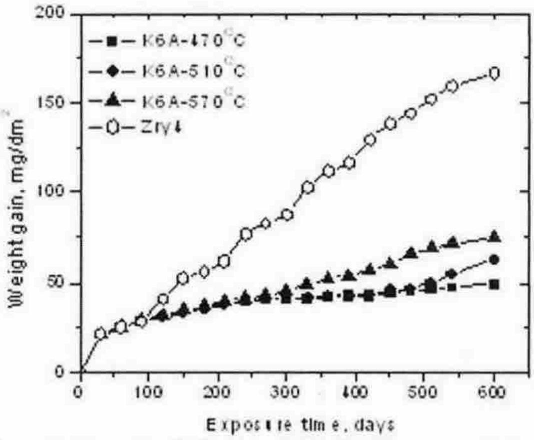

Figure 1. Corrosion behavior of K6 claddings annealed at 470℃, 510℃ and 570℃ in PWR-simulating loop containing 2.2 ppm Li and 650ppm B.

the precipitation kinetics of β phase are very slow. Thus, metastable phase such as β–enriched can precipitate [5] although the equilibrium phase was β–Nb containing more than 80% Nb.

The precipitates are known to play a critical role in influencing the corrosion resistance. The precipitates are incorporated into the unoxidized state in the oxide film because the oxidation of the intermetallic precipitates is delayed compared to the Zr matrix. The late oxidation of the incorporated precipitates is accompanied by the change of the oxide properties. The oxidation of β-Nb was found to be delayed more than the $Zr(Fe,Cr)_2$-type precipitates when they were incorporated into the oxide [6]. On the other hand, the number of precipitates per unit volume was considered to be the predominant metallurgical factor controlling the corrosion kinetics [7].

In this study, the particle size increased with increase of a final annealing temperature, which could be responsible for the degradation of the corrosion resistance. However, the effect of the precipitate size on the corrosion resistance of Nb-containing Zr alloys was contrary to that of Zircaloy-4. The corrosion resistance of Zircaloy-4 is improved when the size of SPP is greater than about 100nm [4], In contrast, small SPP size is needed for maximum corrosion resistance of Nb-containing Zr alloys in PWR [2,3].

3.2. Oxide

In the oxide formed on the Zr alloy with a high corrosion rate, a lot of cracks are observed preferentially above the delayed parts of the oxidation front [8]. Figure 2 showed the oxides of K3 and K6 claddings annealed at 470°C, 510°C and 570°C. For the K-claddings corroded for 300 days in PWR-simulating loop, the crack was not observed in the oxide.

The stability of the tetragonal phase is thought to be closely related to the improvement of corrosion resistance. The mechanism of the stabilization of the tetragonal phase in the oxide is still under discussion and can be explained in several ways such as the high compressive stress in the oxide [9], the small grain size [10] or the presence of the point defect [11]. Recently, it was reported that the destabilization of tetragonal phase can induce the initiation of cracks [8]. Although the tetragonal phase was lower in Zr-1Nb-O as compared to Zircaloy-4, the corrosion resistance of Zr-1Nb-O was better than Zircaloy-4 [8].

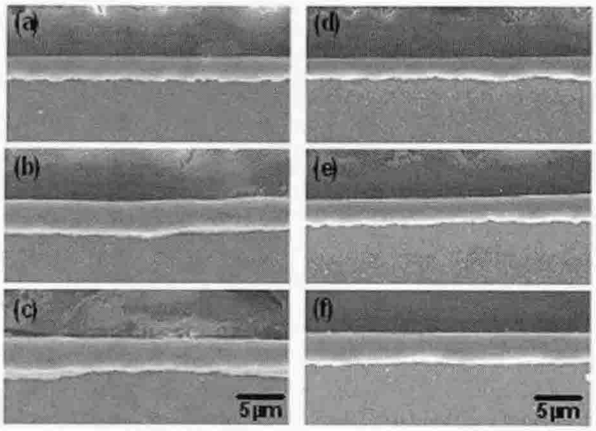

Figure 2. Scanning electron micrographs of the oxides of (a, b, c) K3 and (d, e, f) K6 cladding annealed at (a, d) 470°C, (b, e) 510 °C and (c, f) 570 °C.

4. Conclusions

The corrosion resistance of K-claddings was superior to Zircaloy-4 and decreased with increasing the final annealing temperature. K6 showed the better corrosion resistance than K3. Microstructure characterization, which was focused on the SPP characteristics, showed that the β-Nb with bcc structure and $Zr(Nb,Fe)_2$ with hcp structure were observed in K3 while β-Nb with bcc structure and $(Zr,Nb)_2Fe$ with fcc structure in K6. The observation on cross section of the oxide was performed by OM and SEM to investigate the interface roughness and crack pattern in the oxide and the crystal structure of oxide was examined by XRD. However, there is no big difference between K3 and K6 in the results on the thin oxide.

Acknowledgements

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