Corrosion and oxide characteristics of HANA alloys

Jeong-Yong Park[1], Byung-Kwon Choi[1], Kyu-Tae Kim[2] and Yong Hwan Jeong[1]
[1]*Zirconium Fuel Cladding Team, Korea Atomic Energy Research Institute, Daejeon 305-353, Korea*
[2]*Korea Nuclear Fuel Co., Ltd., 493 Deokjin-dong, Yuseong-gu, Daejeon 305-353, Korea*
parkjy@kaeri.re.kr

1. Introduction

The advanced Zr cladding with a superior corrosion resistance has been required because the corrosion resistance of fuel cladding is one of the main limitations to the extension of fuel burn-up in PWR. The Zr alloy with a high Nb content have shown an excellent corrosion resistance when properly heat-treated to obtain the metallurgical structure in which the fine precipitates were homogeneously distributed. Based on the previous reseaches [1-4], HANA claddings, which are the advanced Zr alloy with a high Nb content, were manufactured by controlling the alloying element addition and the heat treatment. The objective of this study is to investigate the corrosion properties of HANA claddings in out-of-pile conditions. Oxide characteristics of HANA cladding were also investigated to develop a further mechanistic understanding on the corrosion behavior.

2. Experimental procedure

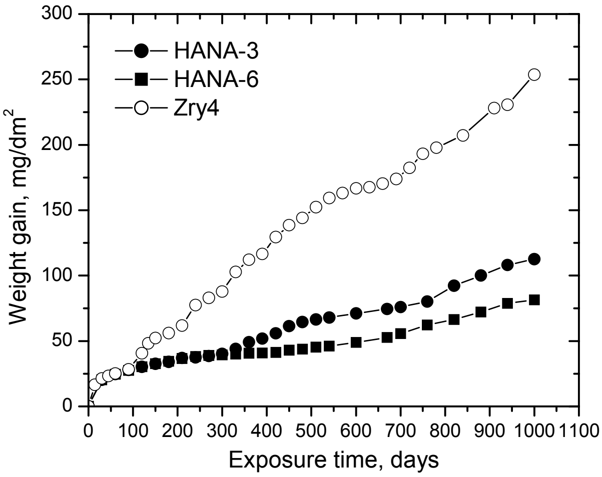
The advanced Zr alloys used in this study were HANA-3 (Zr-1.5Nb-0.4Sn-0.1Fe-0.1Cu), HANA-6 (Zr-1.1Nb-0.05Cu), and Zircaloy-4 (Zr-1.3Sn-0.2Fe-0.1Cr) was used as a reference cladding for comparison of corrosion properties. Specimens for the corrosion test, 50 mm in length, were cut from the manufactured tubes, and pickled in a solution of 10 vol.% HF, 30 vol.% H_2SO_4, 30 vol.% HNO_3 and 30 vol.% H_2O. The corrosion tests were conducted in 360^{o}C PWR-simulating loop system containing 2.2ppm Li and 650ppm B in a manner consistent with ASTM G2-88.

The oxide characterization was also carried out by the X-ray diffraction method using a synchrotron radiation. The specimens for the diffraction experiment were prepared by cross-sectioning the corroded samples followed by a mechanical polishing of the cross-section with up to 2000 grit SiC paper. The diffraction experiment was performed at the 1B2 bending magnet beamline of the Pohang Light Source (PLS) in Korea. The beam energy of 12 keV, which corresponds to a wavelength of 0.1033167 nm, was used to obtain the diffraction pattern of interest in the diffraction geometry.

3. Results and discussion

The corrosion behavior of HANA claddings in PWR-simulating loop was shown in Figure 1. In PWR-simulating loop, HANA claddings showed much lower corrosion rate than Zircaloy-4. HANA-6 showed a better corrosion resistance than HANA-3. The weight gains of HANA-3 and HANA-6 were about 40% and 30% as compared to Zircaloy-4 at 1000 days in 360^{o}C PWR-simulating loop condition. The corrosion rates of the claddings were shown to be lower in PWR-simulating loop than in 360^{o}C static autoclave. This is caused by that the dissolved oxygen concentration was controlled at around 4 ppb which was much lower as compared to the corrosion condition of static autoclave such as 360^{o}C water.

Figure 1. Corrosion behavior of HANA alloys and Zircaloy-4 in PWR-simulating loop containing 2.2 ppm Li and 650ppm B.



The corrosion behavior in the pre-transition regime was similar regardless of the alloy type. The calculated corrosion exponent was between 3 and 4, which means that the pre-transitions corrosion behavior was controlled by the cubic rate law rather than the parabolic rate law. Although the pre-transition behavior was similar between HANA claddings and Zircaloy-4, it was found that the time to transition and the post-transition corrosion rate is different depending on the alloy type. In Zircaloy-4, the kinetic transition occurred at the relatively earlier time (90 days) as compared with HANA-3 (300 days) and HANA-6 (420 days). Moreover, the post-transition rate of

Zircaloy-4 was 3-4 times higher than that of HANA claddings.

From the corrosion test results, Nb-containing Zr alloy cladding exhibited a lower corrosion rate as compared to Zircaloy-4, which suggests that Nb is beneficial to corrosion resistance of Zr alloys. In addition, the corrosion rate of Zr alloys cladding increased with decreasing Sn content. It is also confirmed that Cu addition was beneficial to the corrosion resistance of Zr alloys.

The crystal structure and the phase distribution in the oxide were examined quantitatively by synchrotron radiation microdiffraction. The microbeam X-ray is incident on the region of interest in the oxide and the diffracted intensity in the form of a ring pattern is detected by a CCD camera. Upon varying the position of the incident beam, it was possible to assess the crystal structure of the oxide as a function of the position from the metal/oxide interface to the outer oxide. After indexing each peak on the diffracted intensity plotted against the two-theta angle, the fraction of the tetragonal phase was calculated using the Garvie-Nicholson formula which was proposed to calculate the phase fraction of the ZrO_2 powder [5].

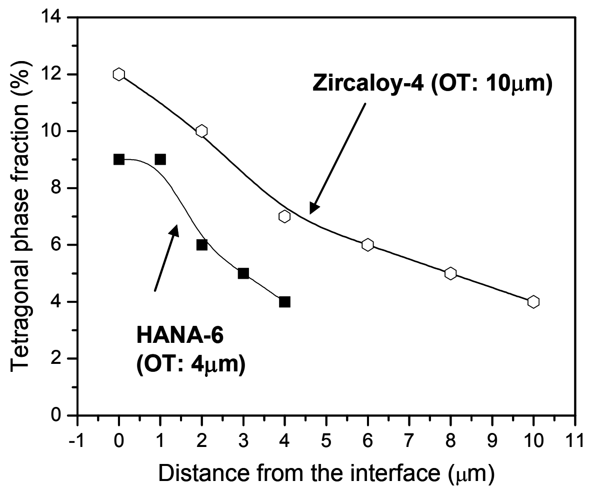


Figure 2. Tetragonal fraction in the oxide of the alloys corroded for 700 days in PWR-simulating loop containing 2.2 ppm Li and 650ppm B.

Figure 2 shows the calculated fraction of the tetragonal phase as a function of the distance from the metal/oxide interface in the oxide on HANA claddings and Zircaloy-4 corroded for 700 days in PWR simulating loop. The fraction of the tetragonal phase in the oxide ranged from 3 to 12% over the entire oxide with a decreasing tendency from the metal/oxide interface to the outer surface. The tetragonal fraction of Zircaloy-4 was higher than that of HANA claddings.

Because the oxide thickness as well as alloy compositions is considerably different between HANA claddings and Zircaloy-4, it was difficult to compare the tetragonal phase fraction of the alloy directly in order to investigate the stability of the tetragonal phase in the oxide. However, the relative stability of the tetragonal fraction in HANA-6 maintained its higher value to a further distance from the interface than those of Zircaloy-4. It was suggested the stability of tetragonal phase in the oxide promoted the protectiveness against oxidation.

4. Conclusions

Corrosion properties of HANA-3 (Zr-1.5Nb-0.4Sn-0.1Fe-0.1Cu), HANA-6 (Zr-1.1Nb-0.05Cu) were investigated in out-of-pile conditions. Oxide characteristics were also examined to develop a further mechanistic understanding on the corrosion behavior. The corrosion resistance of HANA claddings was superior to Zircaloy-4. HANA-6 showed a better corrosion resistance than HANA-3. Synchrotron radiation microdiffracion experiment was performed on the oxide. The tetragonal phase fraction of HANA-6 maintained its higher value to a further distance from the interface than that of Zircaloy-4. It was suggested the stability of tetragonal phase in the oxide promoted the protectiveness against oxidation.

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