Oxidation Resistance Enhancement of a Zirconium Alloy by High-Temperature Pre-Oxidation

Cheol Min Lee [a], Hee-Jae Lee[a], Tae Won Cho[a], Gwan Yoon Jeong[a], Mi Jin Kim[a], Ji-Hyeon Kim[a], Yong-kyoon Mok[b], Dong-Seong Sohn [a*]
[a]*Ulsan National Institute of Science and Technology, UNIST-gil 50, Eonyang-eup, Ulju-gun, Ulsan, 689-798, Korea*
[b]*KEPCO Nuclear Fuel, 989 beon-gil 242, Daedeok-daero, Yuseong-gu, Daejeon, 34057, Korea*
**Corresponding author: dssohn@unist.ac.kr*

1. Introduction

Zirconium alloys have been used as the material for cladding tube in light water reactors owing their good mechanical strength, acceptable corrosion resistance, and low thermal neutron absorption cross section. However, after the Fukushima accident, the accident resistance of a zirconium alloy has been arisen as a problem, since the zirconium alloys show relatively high oxidation rate above 1000 °C. Due to the high oxidation rate, the zirconium alloy claddings can rapidly become brittle during the accident as the absorbed oxygen embrittles the cladding. In addition, hydrogens which are generated due to the cladding oxidation can explode when they exceed a certain concentration, which can destroy the containment building and cause the radioactive materials to be release to the outside. To solve this problem, many researches have been conducted, and one of the solutions is to develop accident resistant tolerant fuels (ATF).

Recently, it was proposed that the high-temperature pre-oxidized zirconium alloy can also be applied as the future ATF [1]. It was reported that a zirconium alloy which was pre-oxidized at 1200 °C shows the significantly reduced oxidation rate during the subsequent oxidation at 1000 and 1100 °C than the predicted values which were calculated according to the parabolic rate [1]. However, how this kind of enhancement appears is still not clear, more pre-oxidation conditions need to be studied. Therefore, the pre-oxidation temperature other than 1200 °C was analyzed in this study, and the results will be presented.

2. Methods and Results

2.1 Specimen preparation

The zirconium alloy cladding tube used in this study is Zr-1Nb-1Sn-0.1Fe, and the composition ranges are shown in Table I. The length of each specimen was 40 mm, the outer diameter was 9.5 mm, and the thickness was 0.57 mm. Before performing the experiments, the specimens were cleaned using Alconox, acetone, and ethanol in an ultrasonic cleaner.

Table I: Chemical Composition of the Zirconium Alloy

Element	Zr	Nb	Sn	Fe
Composition (wt%)	Balance	0.8-1.2	0.8-1.1	0.09-0.13

2.2 Oxidation equipment

The oxidation equipment used in this study is a radiant heating furnace. The details of the equipment was explained in our previous study [2], which can be summarized as follows.

- The radiant heating furnace has a very high heating rate (40 °C/s), so that the rapid temperature increase of the cladding during the accident can be reproduced.
- The temperature of the specimen was measured painstakingly, and it was confirmed that the maximum temperature difference within the specimen is lower than 20 °C, which is assumed to be uniform [3].
- The oxidation experiment was performed in the 100% steam environment, and the steam flow rate was about 3.5 mg/(cm^2·s).

The pre-oxidations were performed at 1012 °C for 270 s. After the pre-oxidations, the specimens were cooled to the room temperature. Then the subsequent oxidations were performed at 1012 °C. After each oxidation test, the weight gains of the specimens were measured with a precision of 0.1 mg.

2.3 Weight gains

The weight gain results are shown in Fig. 1. The y-axis of the graph (W_{total}) represents the sum of the weight gains from the pre-oxidation and subsequent oxidation. It can be confirmed that the weight gains of the pre-oxidized specimens are lower than those of the non-pre-oxidized specimens, which clearly indicate that the pre-oxide formed at 1012 °C significantly enhances the oxidation resistance. In addition, it can also be confirmed that the oxidation rate transition, which is known as the breakaway oxidation, only appears on the non-pre-oxidized specimen. Therefore, it can also be said that the pre-oxide formed at 1012 °C enhances the breakaway oxidation resistance.

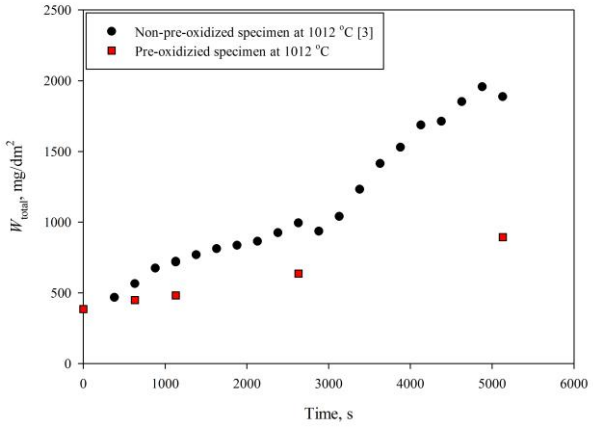

Fig. 1. Weight gains of the non-pre-oxidized specimens and the pre-oxidized specimens; The pre-oxidation was conducted at 1012 °C for 270 s, the subsequent oxidation was conducted at 1012 °C. W_{total} represents the sum of the weight gains from the pre-oxidation and subsequent oxidation.

3. Conclusions

Zr-1Nb-1Sn-0.1Fe cladding tube which was pre-oxidized at 1012 °C was subsequently oxidized at 1012 °C to test the effect of the pre-oxide. It was concluded that the specimen with the pre-oxide shows lower weight gains and better breakaway oxidation resistance compared to those of the non-pre-oxidized specimens.

REFERENCES

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