High-temperature steam-oxidation behavior of Zr-1Nb-1Sn-0.1Fe cladding tube at temperatures of 800-1000℃

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1. Introduction

Cladding is one of the most important components for the safety of nuclear power plant. The major role of cladding is to prevent the release of the harmful radioactive isotopes which are generated from fissions. Since 1960s, Zirconium alloys have been used as the material for cladding owing to their superior properties, such as high mechanical strength, high corrosion resistance, and low neutron absorption cross section. However, Zirconium alloys have a critical disadvantage that they lose their mechanical stability during the accident situation such as loss of coolant accident (LOCA). During the accident, the temperature of the cladding can increase up to 1000℃, the oxidation rate of the cladding increases, which make the cladding brittle. To prevent cladding failure, NRC issued a regulation Title 10 § 50.46 [1], which specifies cladding temperature of 1204℃ and 17% ECR should not be exceeded.

The fundamental reason of the mechanical degradation of cladding is the formation of the oxide which is brittle. Theoretically, the oxide layer is formed following parabolic rate. However, from many experiments, sub-parabolic rates are often observed. There have been many suggestions so far; chemical and stress gradient across the oxide layer could initiate the sub-parabolic rate [2], the phase transformation of Zirconium dioxide from tetragonal to monoclinic could be the reason [3], change of the grain size of Zirconium dioxide could cause the cubic oxidation rate [4], and there is a suggestion that if electron migration is the major mechanism of the oxide growth, then the sub-parabolic rate can show up [5]. However, the reason why the sub-parabolic rate appears is still not certain.

Another important degradation mechanism is breakaway oxidation. The breakaway oxidation refers to the phenomenon in which weight gain rate deviates from normal kinetics [1]. This change usually accompanies hydrogen absorption, which deteriorates ductility of the cladding. A clear explanation that why the breakaway oxidation appears is still not clear. Most of the people believe the phase transformation of Zirconium dioxide cause instability within the oxide, which causes breakaway oxidation to appear. However,

how much effect is caused from the phase transformation is not so sure.

In this study, detailed analysis about the oxidation kinetics and the breakaway oxidation of Zr-1Nb-1Sn-0.1Fe were carried out at temperatures between 800 - 1000℃. By measuring the weight gain of the specimens, the oxidation kinetics were analyzed, sub-parabolic rates were observed on every temperature. The breakaway oxidation was only observed at 1012℃, surface color change was observed on the specimens which go through the breakaway oxidation.

2. Methods and Results

2.1 Experimental Setting

The experimental setting has already been described in the previous work [6]. As received Zr-1Nb-1Sn-0.1Fe cladding tubes were used, each specimen was cut into 40mm. Before performing the experiment, the specimens are cleaned at the solution of 50% ethanol and 50% acetone. And the specimens were heated using a radiant heating furnace, which is composed of six heating lamps. The radiant heating furnace enables us to heat the specimens at the heating rate higher than 50℃/s. When the specimens are heated, steam was supplied at the rate of 3.5mg/square centimeter per second from the bottom of the equipment.

2.2 Thermal Benchamrk

Through the thermal benchmark, we make sure that the criteria specified in the draft guideline can be satisfied [7]. The method and result of the thermal benchmark has already been described in the previous work [6]. Axial and circumferential temperature distribution were within the criteria described in the guideline.

2.3 Oxidation Kinetics

Weight gain data is shown in Fig. 1. Breakaway oxidation was observed at 1012℃. On every temperature, weight gain data are fitted to Eq. 1, where Kn is the oxidation rate constant, n is the rate exponent, and t is the time. On every temperature, rate exponents
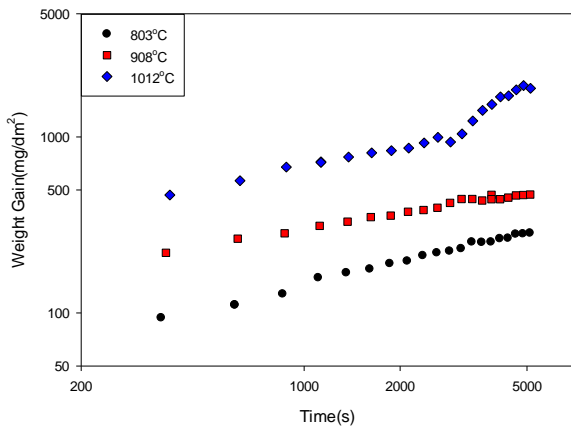
Fig. 1. Log time versus log weight gain graph obtained from the experiments using Zr-1Nb-1Sn-0.1Fe cladding tube.
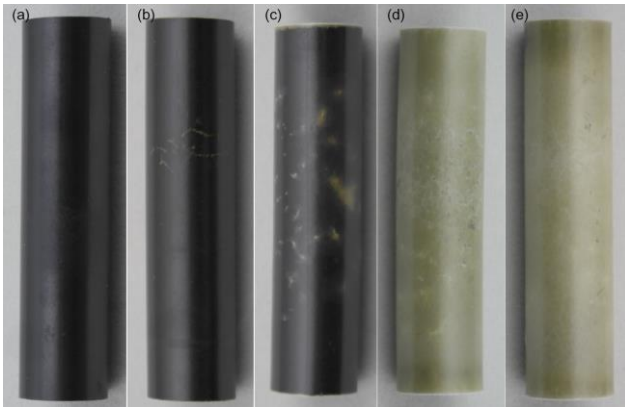

Fig. 2. Surface appearance of the Zr-1Nb-1Sn-0.1Fe cladding tubes, which are oxidized at 1012℃ for (a)1129s, (b)2129s, (c)3129s, (d)4129s, (e)5129s

were higher the 2, sub-parabolic rate was observed on every temperature.

$$W^n_{oxygen\,absorbed} = K_n \cdot t \quad (1)$$

2.4 Breakaway Oxidation

The meaning of breakaway oxidation is the deviation of weight gain rate from normal kinetics. In this regard, our specimens undergo breakaway oxidation at about 3129s. However, the draft guideline recommends to use surface color change of Zirconium alloys as the indication of the breakaway oxidation [7]. The picture of the color changed specimens are shown in Fig. 2. The interesting finding was that the transition to linear oxidation rate took place after the color change of the specimen is initiated. We guess this is because the color change of the specimen occurred in little area at the oxidation time between 2129s and 3129s, so that they have little effect on the total weight gain of the specimen, which is averaged value for all the area of the specimen.

3. Conclusions

Zr-1Nb-1Sn-01Fe cladding tubes were oxidized at 800 - 1000℃ to analyze oxidation kinetic and breakaway oxidation behavior. Sub-parabolic behaviors were observed on every temperature, breakaway oxidations was observed at 1012℃. On every specimen, which goes through the breakaway oxidation, surface color change was accompanied. In addition, it was confirmed that transition to linear oxidation rate took place after the color change of the specimen is initiated.

ACKNOWLEDGMENTS

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