The air oxidation kinetics of Zr-alloys claddings immersed in seawater

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1. Introduction

Due to hydrogen explosion in the Fukushima nuclear power plant, Analysis of fuel cladding became one of important issues. And we need the research related seawater because seawater was flowing in the reactor. Oxidation reaction between Zr cladding and steam cause hydrogen explosion. Thus we have to know the detail information related with oxidation kinetics of fuel claddings under the mixture of air and steam at high temperature and oxidation rate of Zr cladding immersed in seawater. There are not available data related with the oxidation of Zr alloys under the mixture of air, steam and seawater. The goal of the study is to obtain the fundamental data and help safety analysis.

2. Methods and Results

2.1 Specimen and apparatus

In the study, Zircaloy-4 and Zirlo were used as Zr alloys because they are used for a cladding material in Korea nuclear power plants. Specimens were cut to the height of 10~12mm and drilled to make 2 holes at the top of side. The hole size is about 2mm. Before oxidation experiment, specimens were cleaned by etching.

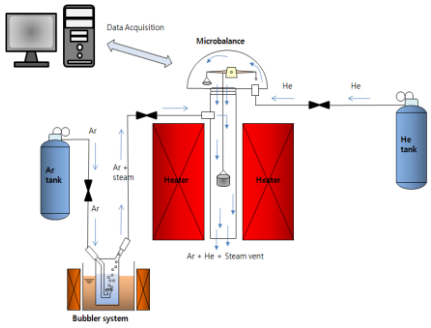
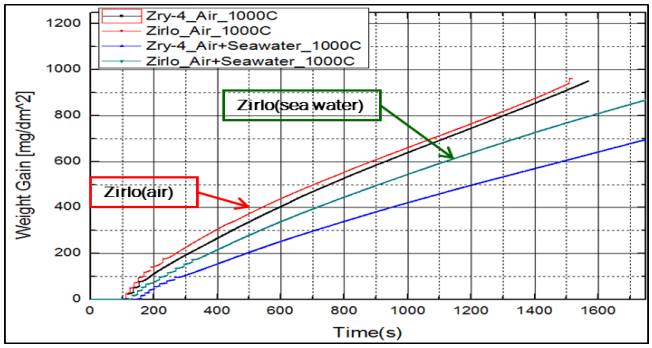


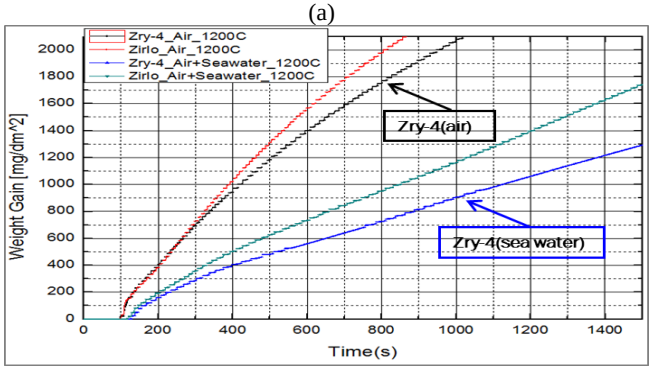
Fig. 1 Apparatus for Thermo-Gravimetric Analysis (TGA) of oxidation experiment.

2.2 Experimental Results

Figure 2 shows the result of Zr alloys oxidation immersed at (a) 1000℃ and (b) 1200 ℃. The oxidation rate of specimen immersed in seawater was turned out to be slower than usual Zr alloys. There was a bigger difference between the immersed specimen and usual Zr alloys as an experimental temperature increases. And we could find that sea water has influence on the oxidation rate of Zry-4 than that of Zirlo.



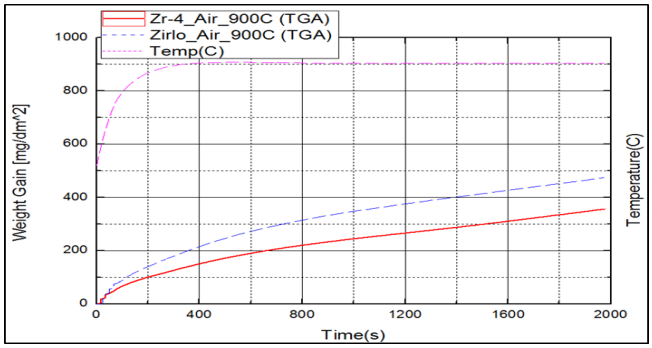
(a)



(b)

Fig. 2 Experimental results of the oxidation of Zr alloys immersed in sea water at (a) 1000℃ and (b) 1200 ℃.

Figure 3 shows the experimental result of Zr alloys oxidation in 900℃ air and 1000℃ steam. In the oxidation experiment in air, the oxidation rate of Zirlo was higher than that of Zry-4. On the other hand, in the oxidation experiment in steam, the oxidation rate of Zirlo also was higher than that of Zry-4 in the early, but the oxidation rate of Zry-4 was higher than that of Zirlo as time goes by.



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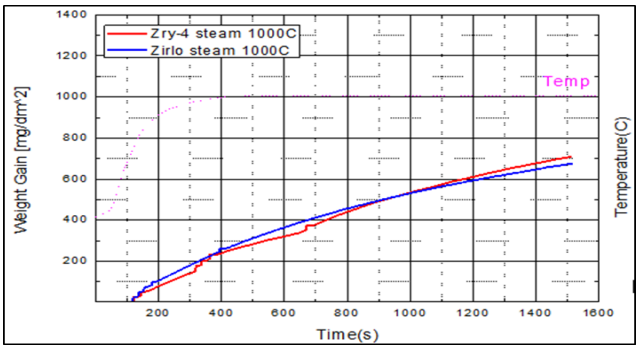
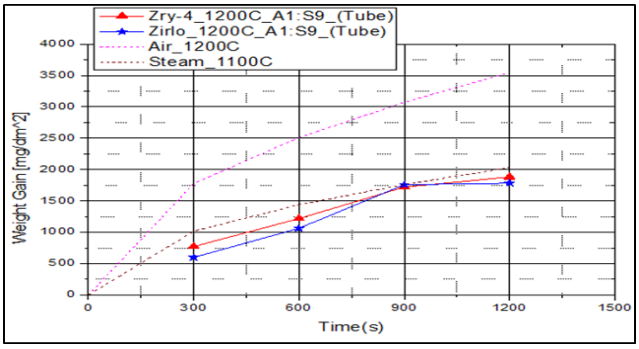


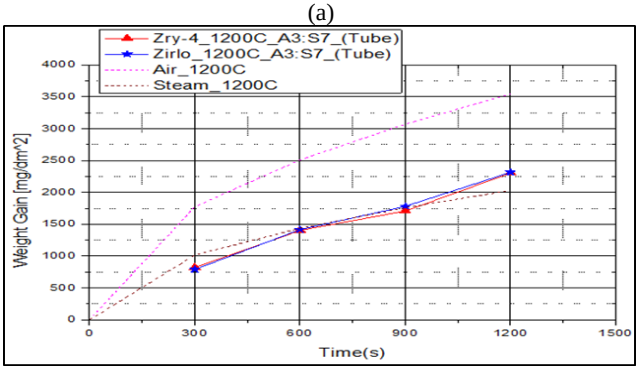
(b)

Fig. 3 Experimental result of Zr alloys oxidation in (a) air and (b) steam.

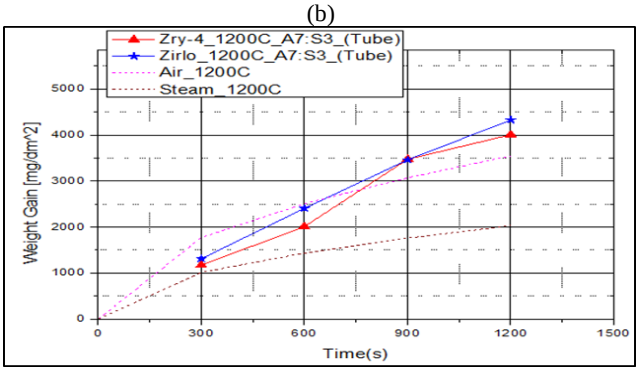
Figure 4 shows the experimental result of Zr alloys oxidation rate as air-steam mixture ratio changes. As the fraction of air in the mixture increased, the oxidation rate of Zr alloys also was high.



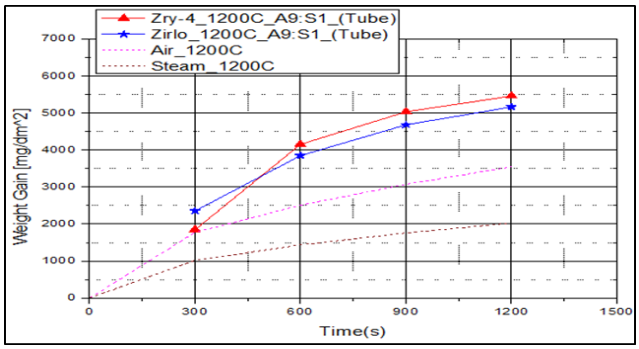
(a)



(b)



(c)



(d)

Fig. 4 Experimental result of Zr alloys oxidation rate under air-steam mixture with (a) 1:9, (b) 3:7, (c) 7:3, and (d) 9:1.

3. Discussion and Conclusions

First, the oxidation rate of the specimen was low when Zr alloy was immersed in sea water. Because protect layer was formed in the surface of Zr alloy and the layer was to slow down the rate of oxidation. Also the layer has a big effect on Zry-4 than Zirlo and higher temperature than low temperature.

Second, the oxidation rate in air was turned out to be higher than that under the steam. Figure 5 shows the protective oxide layer of Zry-4 specimen oxidized in air and steam.

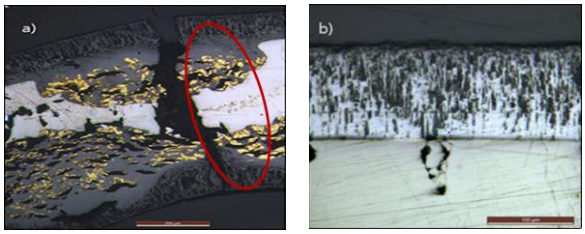


Fig. 5 Zry-4 specimen oxidized in (a) air and (b) steam at 1200℃

The main reason was the development of nitride phases in the metal layer below the oxide. These nitrides destroy the protective oxide layers locally, and enhance the oxidation rate in total.

Third, under air-steam mixture, the oxidation rate of Zr alloys also was high as the fraction of air in the mixture increased.

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