A comparative study of Zry-4 oxidation in oxygen and air at 1000℃

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1. Introduction

In this study, we investigated the oxidation behaviors of Zry-4 cladding in oxygen and air at high temperature. The main difference in oxygen and air is an inclusion of nitrogen. The nitrogen seems to be inactive and there would be no interaction with the Zry-4 cladding. However, in reality, the nitrogen plays a significant role on the cladding degradation when the oxygen is sufficiently consumed [1]. In order to understand the effect of nitrogen, we performed the oxidation tests in each oxygen and air atmosphere at 1000ºC for an hour by varying the flow rate from 20 to 100 ml/min with an increment of 20 ml/min. In this paper, we provide the comparative results of oxidation behaviors of Zry-4 cladding at each oxygen and air atmosphere.

2. Experimental details

The oxidation tests were performed in the thermal balance system of Setsys which is a product of Setaram. The sample was Zry-4 cladding tube of 1 cm of height. The Zry-4 tube was suspended in the furnace of thermal balance. The experimental procedure is provided in the following.

1) The argon (Ar) was injected to remove impurities in the furnace and balance containment with a high flow rate for an hour.
2) The furnace temperature was heated until the target temperature, 1000ºC in Ar atmosphere.
3) After reaching the target temperature, an additional 10 min was added to make sure the thermal stability of the furnace at the target temperature.
4) After the 10 min of thermal stabilization period, the reactive gas (oxygen or air) is injected with a carrier gas of Ar for an hour. The ratio of flow rates of reactive gas and carrier gas is 2:1.
5) After an hour of the isothermal reaction period, the furnace is cooled down in Ar atmosphere with the highest cooling rate of the thermal balance system.

The tests were performed at different flow rate of reactive gas from 20 to 100 ml/min with the increase of 20 ml/min to see an effect of flow rate in the oxidation behaviors.

3. Experimental results

The mass gain curves of oxidation tests at each oxygen and air at each flow rate are given in the following.

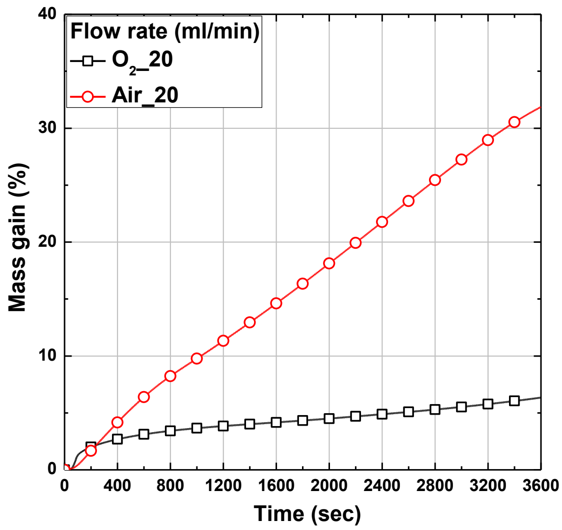

Fig 1. Mass gain curves (20 ml/min)

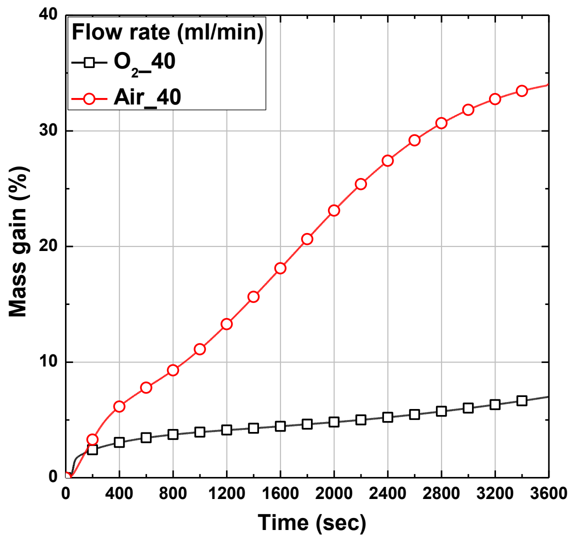

Fig 2. Mass gain curves (40 ml/min)

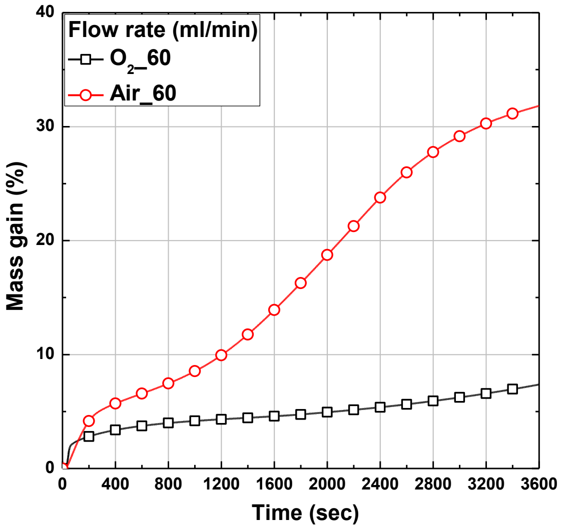

Fig 3. Mass gain curves (60 ml/min)

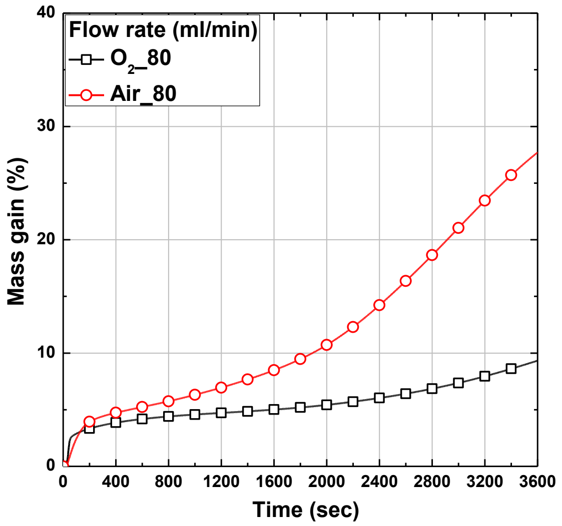

Fig 3. Mass gain curves (80 ml/min)

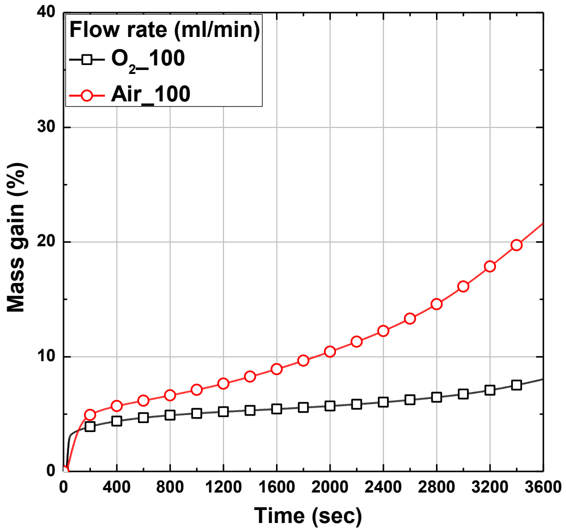

Fig 3. Mass gain curves (100 ml/min)

As shown in Fig. 1-5, the reaction rate is significantly higher in the air tests than in the oxygen tests. The final mass gains of air tests are 3-4 times higher than those of oxygen tests. To compare these differences in the final mass gains of different atmosphere tests, Fig. 6 shows the final mass gains at each flow rate.

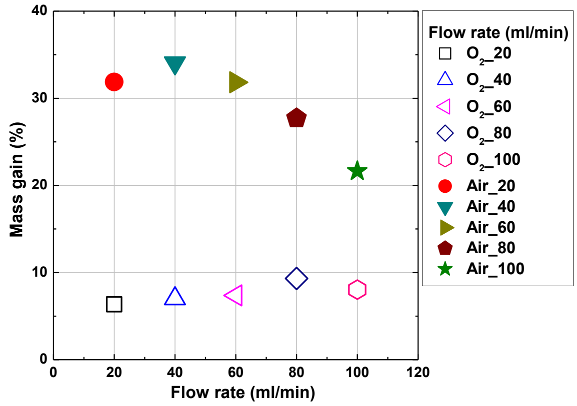

Fig 6. Comparison of final mass gain

As shown in Fig. 6, all of the final mass gains of air tests is far higher than those of oxygen tests. This indicates an effect of nitrogen during the air oxidation tests. It seems that the nitrogen significantly enhance the reaction rate more than 3-4 times than in the only oxygen tests.

In the oxygen tests, the zirconium metal reacted with only oxygen by developing the oxide scale after exceeding its oxygen solubility limit in the zirconium metal. However, in the air tests, the zirconium metal reacted with oxygen and nitrogen by forming the oxide and nitride. The nitrogen is incorporated in the zirconium metal at the very low oxygen partial pressure. Therefore the oxygen consumed firstly and nitrogen is reacted with zirconium. Due to the simultaneous reactions of both oxygen and nitrogen, the oxide and nitride mixture scale is formed. These oxide and nitride scales includes the porosities by the volume mismatch between oxide and nitride and results in the promotion of reaction rates. In addition, the nitride is easily re-oxidized by an incoming oxygen. By the re-oxidation of nitride, the oxide/nitride scale experiences the further mechanical degradation and it also increases the reaction rate.

The most interesting findings in this study is the decreasing trend of air oxidation mass gains with the increase of the flow rate. It indicates that the nitrogen is more actively reactive when the oxygen is sufficiently consumed. At the low flow rate, the oxygen seems to be more rapidly consumed than the high flow rate, and it gives the more active condition of nitrogen reaction with zirconium metal.

In contrast to the trend of mass gain as previously explained in the air tests, the trend of mass gains in the oxygen tests is overall increase with the increase with the flow rate. It reveals that the higher flow rate of oxygen includes a higher amount of oxygen to be reacted with the zirconium metal during the test period and results in the higher mass gain in the end.

3. Conclusions

In this paper, we preliminarily investigates the differences in the oxygen and air oxidation tests of Zry-4 cladding. The results showed that the reaction rates of air oxidation was significantly higher than the oxygen oxidation tests by the active reaction of nitrogen during the air oxidation tests. In addition, we experimentally confirmed that the nitrogen is more reactive at the lower flow rate which can easily achieves the almost oxygen starvation state when the nitrogen becomes incorporated into the zirconium metal. This is the preliminary experimental study to understand the role of nitrogen and the further study is ongoing to more quantitatively understand the effect of nitrogen.

ACKNOWLDGEMENT

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[1] Sanggil Park, Yunhwan Maeng and Jaeyoung Lee, Air oxidation kinetics of zircaloy-4, Transaction of the Korean Nuclear Society Spring Meeting, Jeju, Korea, May 18-19, 2017.