

Effect of nitriding on the air oxidation of Zry-4 at high temperature

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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. It is well known that the nitrogen affects the reaction kinetics in two ways. One is the nitriding which is the zirconium nitride (ZrN) formation. By forming the ZrN in the oxide scale, it leads to the incoherent oxide/nitride scale which includes a micro porosity due to a volume mismatch of ZrO₂ and ZrN. The other is the re-oxidation which is a phase transformation from the ZrN to ZrO₂ when the ZrN is re-oxidized by an incoming oxygen in air [1]. In the air oxidation, both nitriding and re-oxidation phenomena occur simultaneously and hence it is quite difficult to analyze the effect of nitrogen very precisely and quantitatively.

In addition, the nitrogen becomes active where the oxygen gas partial pressure is sufficiently lower than the nitrogen gas partial pressure. Firstly the oxygen is dissolved in the zirconium metal and forms the oxygen-stabilized alpha zirconium phase. At this point and location, the nitrogen incorporates into the oxygen-stabilized alpha zirconium where the oxygen gas pressure is locally very low. For this reason, it would be critical to know the active condition for the nitrogen reaction in the nitriding and re-oxidation. When it comes to the nitriding, the low oxygen content would be preferable for the ZrN formation. However, for the re-oxidation, a certain degree of oxygen content should be available for the efficient re-oxidation of previously formed ZrN. Therefore, there could be a competition between total contents of oxygen and nitrogen in air. Although the ratio between oxygen and nitrogen is constant as a 2:8, the absolute amount of oxygen and nitrogen content can be different by a various total flow rate.

In order to identify the active condition for the effect of nitrogen, we planned a series of oxidation tests with only oxygen atmosphere and only air atmosphere at 1000°C by varying the flow rate from 20 to 100 ml/min with an increment of 20 ml/min. By performing this test plan, we observed the global trend of reaction kinetics of air oxidation and oxygen oxidation.

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, and this sample loading configuration is helpful to eliminate an effect of buoyancy by a gas flow to the sample. 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, 1000°C 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 identify the effective flow rate condition for the nitriding and re-oxidation.

3. Experimental results

The final mass gains of each atmosphere tests according to the flow rate is summarized in Fig 1.

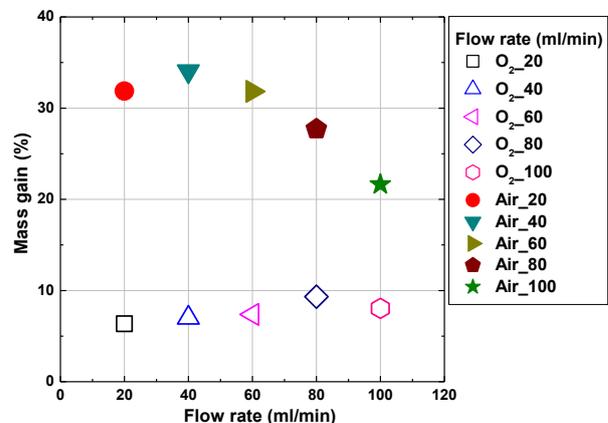


Fig 1. Final mass gain as a function of flow rate

As shown in Fig 1, the final mass gains of air in all flow rate range are 2-5 times higher than those of oxygen.

Table 1. Final mass gain (%)

Flow rate (ml/min)	20	40	60	80	100
Δm (air)	31.86	34.05	31.82	27.70	21.64
Δm (O ₂)	6.34	7.00	7.37	9.32	8.03
Difference	25.52	27.05	24.45	18.38	13.61
Ratio $\Delta m(\text{air}/\text{O}_2)$	5.03	4.86	4.31	2.97	2.69
Ratio Diff/ $\Delta m(\text{O}_2)$	4.03	3.86	3.31	1.97	1.69

From this observation, it is confirmed that the reaction rate of air oxidation is much higher than that of oxygen oxidation. As shown in Table 1, the difference in the final mass gain is significantly high. From two different atmosphere tests, the only difference is an inclusion of nitrogen, and hence the final mass gain difference may indicate the effect of nitrogen during the air oxidation. The effect of nitrogen on the cladding degradation seems quantitatively 1-4 times higher than the effect of oxygen according to the flow rate. These final mass gain differences between air and oxygen is over-plotted in Fig 2.

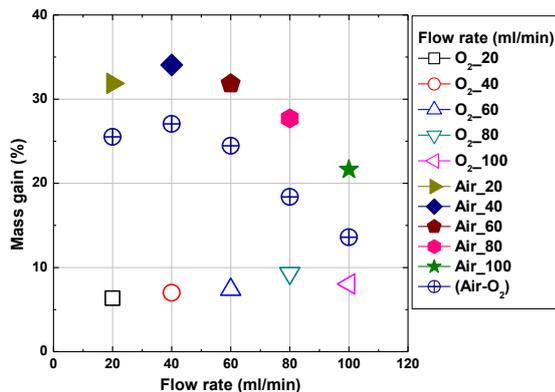


Fig 2. Final mass gain summary

As shown in Fig 2, the effect of nitrogen (i.e. mass gain difference between air and oxygen) is quite enhanced in the low flow rate and it decrease as the increase of flow rate. The highest mass gain difference was observed at the flow rate of 40 ml/min.

As previously explained, the effect of nitrogen is in two ways. One is the nitride formation when the oxygen gas pressure is locally sufficiently low. For this reason, the low flow rate tests might easily have a chance of locally oxygen starvation and it would lead to the active reaction of nitrogen for the nitride formation. The other is the re-oxidation of the nitride which is formed previously. In order to re-oxidize the nitride efficiently, a certain degree of oxygen must be available. For this reason, the high flow rate would be preferable. Thus,

there could be competition in the optimal range of flow rate where the effect of nitrogen is mostly active.

From the series of air oxidation tests and oxygen oxidation tests, we assumed that the difference of mass gains between air and oxygen oxidation tests indicate the effect of nitrogen. It is found that the effect of nitrogen is significantly enhanced in the low flow rate condition where the oxygen could be locally starved. However, a certain amount of oxygen needs to effectively re-oxidize the nitride. For this reason, there was a flow rate condition competition to achieve the most effective nitrogen reaction for both nitriding and re-oxidation.

3. Conclusions

In this paper, we performed the series of air and oxygen oxidation tests to identify the effect of nitrogen during air oxidation in a more quantitatively manner. We varied the flow rate for each test and we found that the effect of nitrogen is significantly dependent on the flow rate. For the nitride formation the low flow rate is preferred, but the high flow rate is preferred for the re-oxidation of the nitride. The metallographical analysis is ongoing to understand better the effect of nitrogen and its most active condition. This study is preliminary analysis to quantify the role of nitrogen during the air oxidation. Further experimental and analytical study is planned for the better understanding and the air modeling for the active role of nitrogen.

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REFERENCES

- [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.