Effect of nitrogen on the breakaway in the zirconium alloy cladding

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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 ZrO_2 and ZrN. The other is the re-oxidation which is a phase transformation from the ZrN to ZrO_2 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 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. In this study we investigate the breakaway kinetic transition for both air and oxygen oxidation tests. This is an extension of analysis based on the data presented in the previous meeting [2].

2. Experimental results and discussion

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. Further experimental details are provided in [2], and in this chapter the experimental results are given. The mass gain curves of air and oxygen oxidation are shown in Fig. 1.

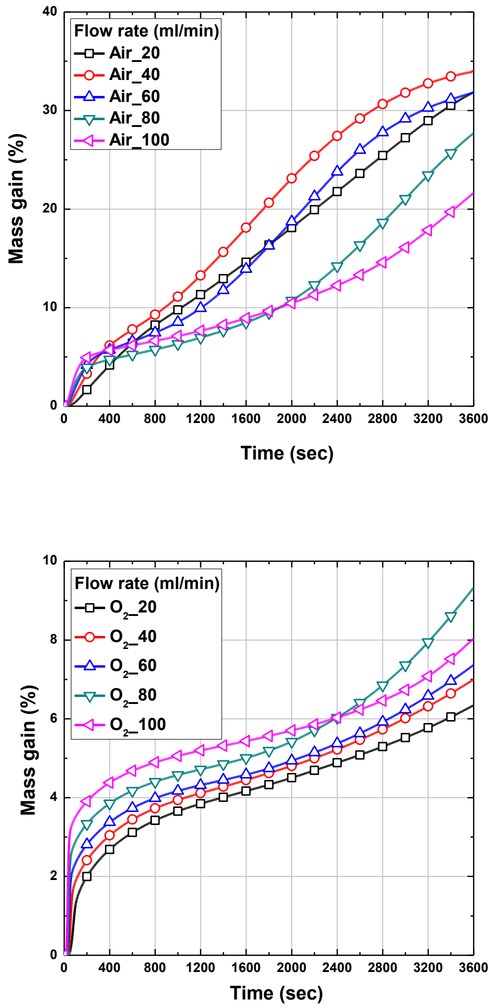

Fig. 1 Mass gain curves; air (up) and oxygen (bottom)

As shown in Fig. 1, the mass gain curves of air oxidation tests with different flow rate showed quite higher final mass gain than those of oxygen oxidation tests. This tendency of final mass gain difference was already reported in [2]. In the current analysis, we focus on the kinetic transition during the oxidation tests for one hour.

The kinetic transition can be easily seen in the log-linear scale graph of first derivatives of mass gain curves as shown in Fig. 2.

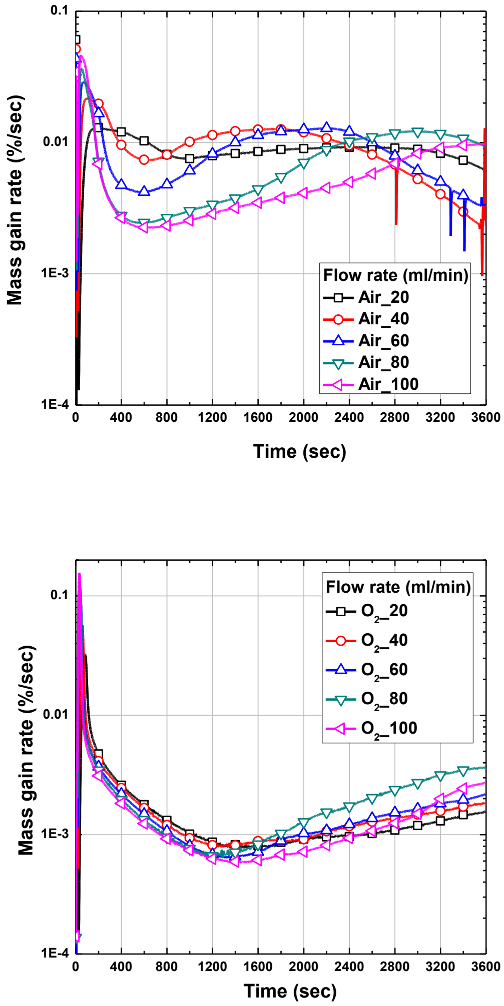

Fig. 1 First derivatives of mass gain curves; air (up) and oxygen (bottom)

In the air oxidation tests, the kinetic transition occurred earlier in higher flow rate tests. However, the final mass gain was higher in lower flow rate tests. It seems that the kinetic transition condition would be achieved earlier in higher flow rate tests for its higher uptake of air in the very beginning of the tests. In the air oxidation tests, no clear trend was seen in the first derivative curves which are reaction rate curves. The kinetic transition was occurred in the range of 400-1000 sec from the initiation of oxidation tests.

In contrast to the air oxidation, the oxygen oxidation tests showed a very similar trend for all flow rate tests, and the kinetic transition occurred also at 1000 sec from the initiation of oxidation tests.

The effect of nitrogen on the breakaway kinetic transition seems that it would give an earlier kinetic transition than the only oxygen is present. In addition, the effect of nitrogen seems to be affected significantly by the flow rate. As we discussed earlier in [2], the nitrogen can be reactive when the oxygen partial pressure is sufficiently low.

3. Conclusions

In summary, the effect of nitrogen on the breakaway kinetics was discussed by the comparison of tests data of air and oxygen with different flow rates. In this preliminary analysis, we found that the nitrogen would contribute the early kinetic transition and its behavior would be affected significantly by the flow rate. Further analysis is ongoing to fully capture the characteristics of nitrogen behavior on the kinetics.

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