# Experimental study of Zry-4 air oxidation breakaway: various air flow rate condition at 900-1100 °C

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## 1. Introduction

Zirconium air oxidation has been investigated for last two decades as being risen the possibility of air ingress accident scenarios in the reactor and also spent fuel pool (SFP). There were several the air oxidation models applied in severe accident codes such as MELCOR, MAAP, ASTEC, ATHLET-CD and SOCRAT to simulate the air oxidation phenomenon under various severe accident (SA) conditions.

For the air oxidation model, there are two important parts: one is the determination of reaction rates for pre- and post-transition regime and the other is the estimation of onset of breakaway time. For the reaction rate, it has been widely used by adopting parabolic kinetic rate for pre-transition region and linear/accelerated kinetic rate for post-transition region. In addition, both model of critical oxide thickness and phase transformation, which are expressed by dependence of the temperature, have been used for prediction of the breakaway.

However, there have been many efforts to develop appropriate models to simulate zirconium air oxidation phenomenon, they still have limitations [3]. As considering the previous studies, which showed the air flow rate effects on the oxidation kinetics, it is needed to further separate effect tests (SETs) to reveal the air flow rate effects on the zirconium oxidation kinetics.

Therefore, to investigate the influence of the air flow rate on the oxidation kinetics, especially the breakaway, we conducted a series of oxidation tests with various air flow rate conditions at 900-1100℃. In this study, we observed that it showed different times to breakaway and critical oxide thicknesses when the air flow rate was varied under same temperature condition.

## 2. Experimental details

The air oxidation tests were conducted by commercial thermal balance system (SETARAM). The test segments were 1cm height of Zry-4 which is cut from original long tube. All the samples were cleaned by ultrasonicator in acetone and dried before the experiments. Further experimental details were provided in Ref [1].

## 3. Experimental results and discussion

Fig. 1 shows the results of mass gain rate under 200 mL/min air flow rate condition at 900℃, 1000℃ and 1100℃. At the early stage of all the tests, the mass gain rates were sharply increased because of the strong reaction between oxygen in air and pure Zr metal. After reached maximum points, it was decreased until it became minimum values. The mass gain rate increased again after lowest mass gain rate. In this transition point, it is called as a breakaway which can be identified in Fig. 1 (green arrows). For 1100℃, the breakaway could not be observed because it might be the absence of oxide phase transformation (t-$ZrO_2$ to m-$ZrO_2$) at this temperature condition, which was also observed by another researcher [5]. The overall trend of mass gain rate was increased as increased temperature under same air flow rate condition.

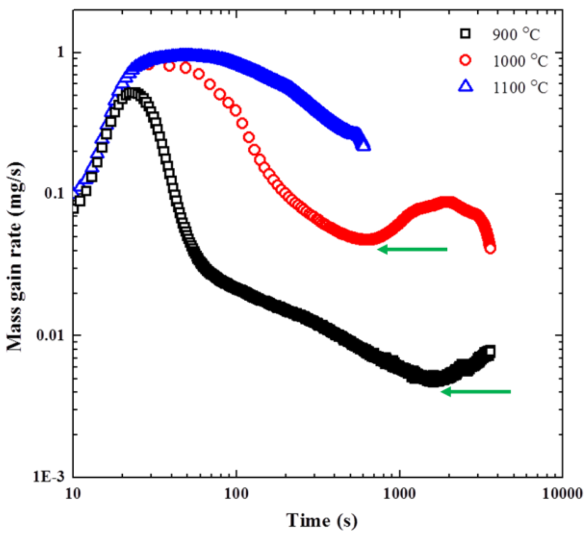


Fig. 1 Results of mass gain rate with 200 mL/min air flow rate condition: green arrows indicate the onset of breakaway and absence of the breakaway for 1100 ℃ (log-log scale)

To identify the air flow rate effects on the breakaway, the oxidation tests were conducted with four different the flow rate conditions (20, 40, 100 and 200 mL/min). As already mentioned above, there was no breakaway at 1100℃, so the breakaway data obtained from 900℃ and 1000℃ would be discussed in this study. Fig. 2 and Fig. 3 show the results of time to breakaway and critical oxide thickness, respectively. For 900℃, we could identify the trend of time to breakaway clearly. The time was delayed as increased the flow rate. This trend was also identified by M. Grosse et.al [4], which performed the oxidation tests at 850℃. Moreover, it could be identified that the critical oxide thickness was increased slightly as increased the flow rates as shown in Fig. 3. On the other hands, there were no evident trends at 1000℃ in terms of both the time to breakaway and critical oxide thickness. The times to breakaway were occurred in very similar points excepting for 20 mL/min case (Fig. 2). Moreover, it was observed that the critical oxide thickness was very scattered from approximately 70 to 125 μm. It is hard to understand these results clearly, but it might be associated with the oxygen starvation condition. The oxygen starvation condition has been considered as an important factor, which might determine the reactivity of nitrogen [2]. In addition, this condition could be preferably occurred at higher temperature under the same air flow rate condition. Therefore, it might not be experienced the global or local oxygen starvation condition at 900℃ and the oxygen might lead the reaction kinetics, which means the reaction relatively stable. On the contrast, it might be experienced the global or local oxygen starvation condition at 1000℃, especially for low flow rates, and the nitrogen might react actively with Zr metal, which signifies the reaction relatively complicated.

It is hard to interpret whole results of the breakaway phenomenon as respect of the air flow rate. However, there are some points should be noted:

- The tendency, the time to breakaway delayed as increased the air flow rate, might be expected to other temperature region, such as 600℃, 700℃ and 800℃, in light of the results from Ref [4] (850℃) and presented in this study (900℃).

- To identify the flow rate effect on the breakaway for higher temperature (1000℃), higher air flow rates might be needed to exclude the oxygen starvation condition, which leads to reaction kinetics relatively complex.

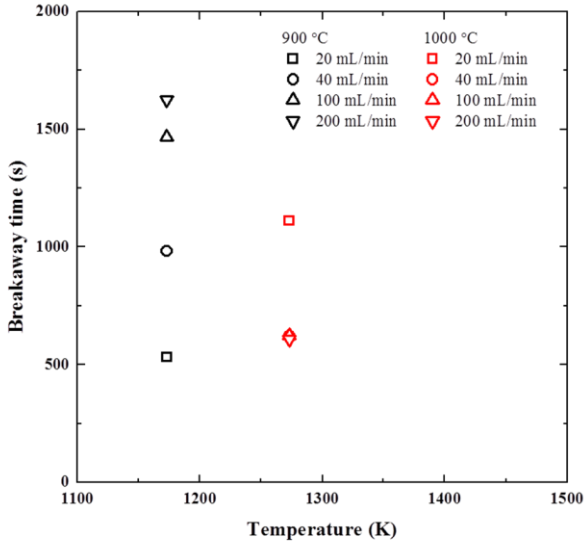


Fig. 2 Results of time to breakaway under various air flow rate conditions

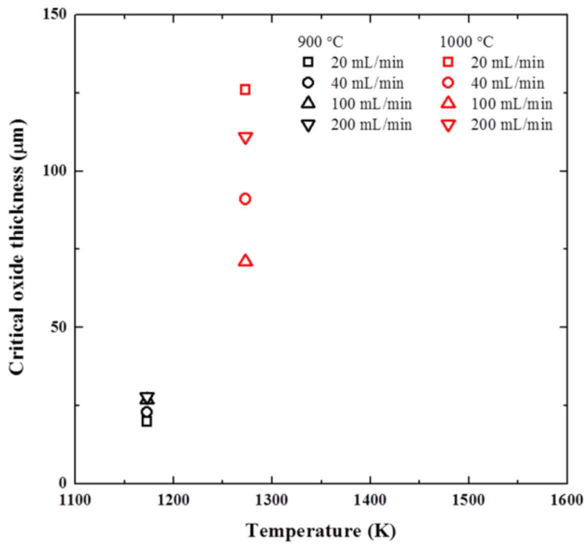


Fig. 3 Results of critical oxide thickness under various air flow rate conditions

## 4. Conclusions

In this study, we performed the series of air oxidation tests to find its flow rate effect on the zirconium breakaway. The time to breakaway was delayed and the critical oxide thickness was increased as increased the air flow rate at 900℃. The trend was similar with previous results presented in [4]. On the other hands, it was hard to find such tendency at 1000℃. It might be assumed that the oxidation starvation condition preferably formed at 1000℃ compared to 900℃, which means reaction kinetics was more complicated because of higher reactivity of the nitrogen.

Further experimental and analytical study is ongoing to develop the new air oxidation breakaway model, which incorporate the effect of air flow rate.

**ACKNOWLDGEMENT**

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