Investigation of flow effect on breakaway time under the isothermal oxygen atmosphere at 1000℃

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1. Introduction

Nuclear power plants (NPPs) prevent the release of radioactive materials to the public through the concept of physical defence-in-depth. Since the oxidation of cladding that occurs in a severe accident threatens the integrity of the cladding, which is the second barrier of physical defence-in-depth, many studies have been conducted so far [1-5]. For the safety and accident management of nuclear power plants, it is very important to determine the time of cladding failure in case of a severe accident. In safety analysis codes such as MELCOR, the oxidation model established through TGA (Thermogravimetric Analysis) experiment is used. However, these models are functions of only time and do not reflect the flow effects of oxidants such as steam, air, and oxygen. Oxidant flow rate is expected to have a significant influence on the oxidation behavior because it affects the reaction heat of oxidation and the initial temperature rise of the cladding. Therefore, in this study, an isothermal oxygen oxidation experiment was performed at 1000°C under various flow conditions to observe the effect of flow rate on the initial reaction heat and its effect on oxidation kinetics and breakaway time.

2. Experimental Setup

Isothermal oxidation tests at 1000°C with varying oxygen flow rates from 20 to 200 mL/min were performed with Zircaloy-4 tube specimens using a commercial thermogravimetric analysis (TGA). Abrupt temperature escalation, which leads to abrupt increasing mass gain in the beginning of the oxidation reaction, was expected, due to an intensive exothermic reaction between oxygen and Zr metal. Mass gain and mass-gain-rate data obtained from TGA were used to describe the oxidation behaviors. In addition, an investigation of macrographs supporting TG analyses was performed in this study. The preparation of specimens and experimental procedures was as follows: The cladding specimens were prepared by cutting a long original Zircaloy-4 tube, and two holes with 1 mm outer diameters were drilled into the upper part of the tube, from which thermobalance was suspended. The dimension of the specimen was 10 mm long, with a 9.5 mm outer diameter and a 7.9 mm inner diameter. The fabricated test specimen is represented in Figure 1.

After the specimens were prepared, the surfaces of the samples were polished and cleaned in an ultrasonicator using acetone. The commercial SETARAM TGA was used as a thermobalance for the cladding oxidation tests. The inside of the test section temperature of the TGA was controlled by an s-type thermocouple inside TGA furnace.

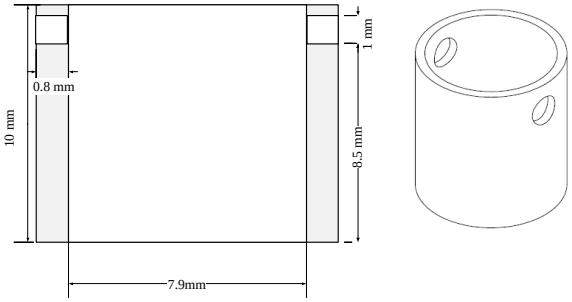

Fig. 1. Preparation diagram of specimen inside the TGA

The tube was hung in a TGA using a series of platinum (Pt) wires. All the tests were started after the mass-gain data were stabilized. Argon was injected to remove impurities inside the TGA for 90 min while room temperature was maintained, and the temperature was raised to 1000 °C under an argon atmosphere. After the desired temperature was obtained, the temperature was stabilized for 10 min. Then, oxygen was injected as an oxidant and varied from 20 to 200 mL/min, according to the planned tests. The most frequent oxidation time was 2 h, and several cases were conducted for an additional 4 h. The direction of gas flow was top to bottom, based on the samples (gravity direction). After oxidation, the supply of oxygen was stopped, and the temperature was reduced as far as possible under an argon atmosphere. The post-test samples were photographed and embedded in a mixture of resin and hardener. In addition, the samples were ground and polished for metallography. Macrographs were taken of samples after 2 and 4 h of oxidation.

3. Results and Discussions

In this section, the results of isothermal oxidation experiments at 1000℃ are presented. A breakaway time delay phenomenon was discovered in the high-flow-rate region of this test. These results were interpreted from the point of view of reaction heat.

3.1 Results of Isothermal oxidation Experiments

To investigate the oxidation kinetics, TG mass gain and gain-rate data were employed. Figure 2 and 3

shows the results of mass gain and the mass gain rate in terms of oxygen flow rate.

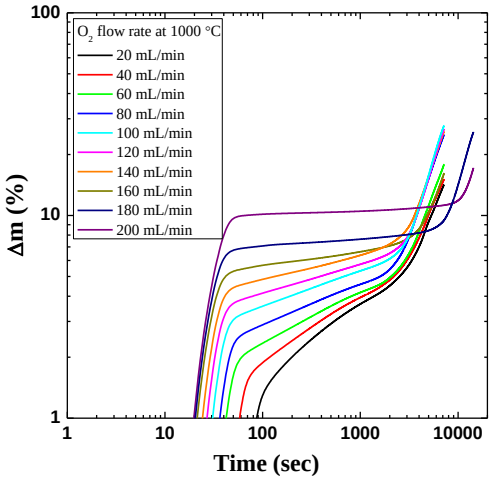

Fig. 2. TG mass gain results (log-log diagram)

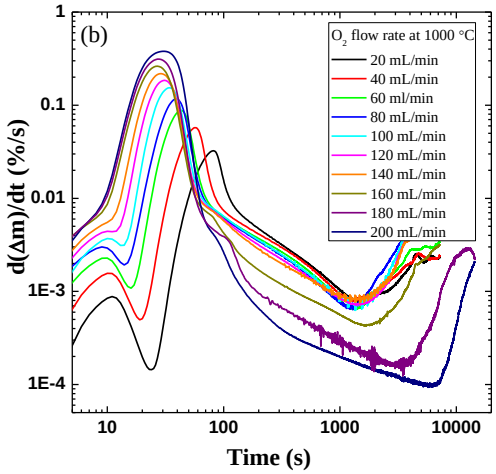

Fig. 3. TG mass gain rate results (log-log diagram)

It can be identified from Figure 2 that the overall mass gain trend seemed to follow general oxidation kinetics. The sharp mass gain was measured by the oxygen inflow because oxygen was reacted with pure Zr metal. As an oxide layer grew, the mass gain became slower and followed almost (sub-)parabolic and/or cubic reaction laws. After reaching critical oxide thickness, the reaction rate accelerated and became linear or higher; a phenomenon termed breakaway or reaction transition. However, there are differences between both the extent of the reaction rate at each regime and the breakaway time, as identified in Figure 3. The reaction rate in the early stages was raised slightly, and then the first minimum point was reached. This might be caused by the early oxygen starvation and this moment. Furthermore, the minimum value was progressively reduced, and this trend almost disappeared at the highest flow rates. The reaction rate increased sharply at the oxygen inflow period, and its degree of escalations became higher as the oxygen flow rate increased. This trend might be influenced by both higher peak temperature [1,4,6] and enhancement of diffusivity [5]. After this abrupt increase in reaction rate, the trend changed adversely, and it decreased. The extent of this decrease increased as the flow rate increased. This might be caused by the formation of a thicker oxide layer, which acted as a diffusion barrier at the early stages. On the other hand, the breakaway is determined by the minimum point after the maximum value in Figure 3, which was delayed from the 160 mL/min flow rate. The results are presented in Figure 4.

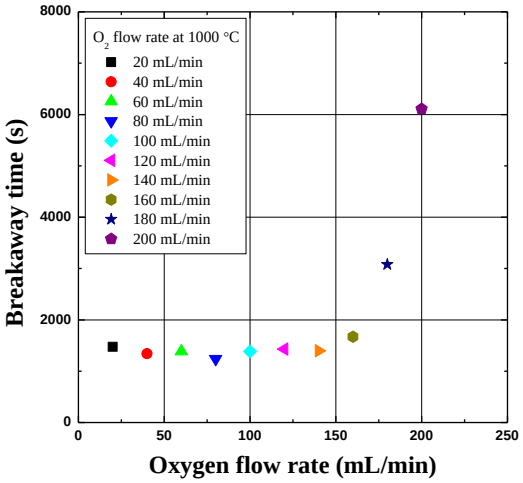

Fig. 4. Breakaway time results

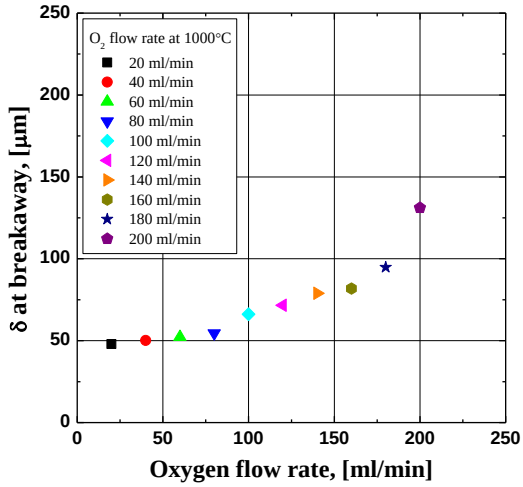

Fig. 5. Oxide thickness at the breakaway

The average transition time was approximately 1379 s to reach 140 mL/min, while the breakaway time was retarded in the higher flow rate region as, shown in Figure 4. The oxide thickness at the breakaway was calculated from the TG mass gain data, considering it was dense zirconia, and ignoring the mass gain of the oxygen dissolved in the Zr metal [1]. The thickness increased as the flow rate increased, but it showed an

abrupt increase in the 160 to 200 mL/min region (Figure 5).

3.2 Reaction Heat Measurement

Measurement of the reaction heat was performed by measuring the temperature around the cladding specimen in order to identify the reason for the breakaway time delay. In Figure 6, the history of the temperature escalations during the early stage of the reaction between oxygen and fresh metal in terms of the increasing flow rate are shown.

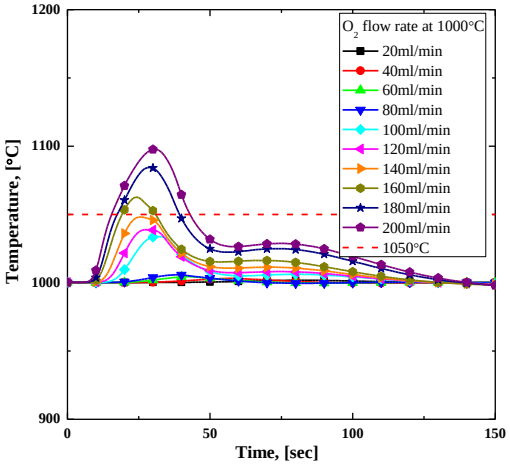

Fig. 6. Results of the temperature escalation in the early stage of the oxidation reaction

The peak temperature increases with the increase in the oxygen flow rate due to rise in the oxygen flow rate per the outer surface of the metal [1], as shown in Figure 6. The interesting point is the delay point corresponding to the peak temperature that exceeds 1050°C. As reported earlier in [1,4,6], at temperatures above 1050 °C, dense columnar oxides are favorably formed. This observation is used as a standard to distinguish the breakaway time delay.

3.3 Macrograph results

To identify the oxide appearance of the post-test samples, investigation of the macrographs was conducted. Figure 7 shows the macrographs of the post-test specimens. Shown in Figure 7a–j, photos were captured after 2 h of isothermal test under 180 mL/min, while those in Figure 7k,l were obtained after 4 h tests under 200 mL/min, respectively. At a first glance, there are numerous cracks on the external surfaces of the samples, and the color of the oxides appears to be light until 140 mL/min (Figure 7a–g). On the other hands, cracks are not observed, and a dark-colored oxide is observed for 180 and 200 mL/min conditions (Figure 7i,j, respectively), while a mixture of light- and dark-colored oxides were observed with no apparent cracks for 160 mL/min. The change in oxide colors from dark to light coincided with the kinetic transition, which was reported in previous studies [7]. Moreover, the cracks are generated when the accumulated stresses in the oxide scale are released progressively during the oxide phase transition from tetragonal to monoclinic [3,6,8]. These descriptions support the change in oxide color from dark to light in both 180 and 200 mL/min cases, as oxygen exposure time is increased from 2 to 4 h, which can be assumed as the occurrence of the breakaway (Figure 7i–l). Additionally, the investigation of the macrographs is in good agreement with the previously reported TG mass gain.

Figure 8 shows the breakaway time at each flow rate

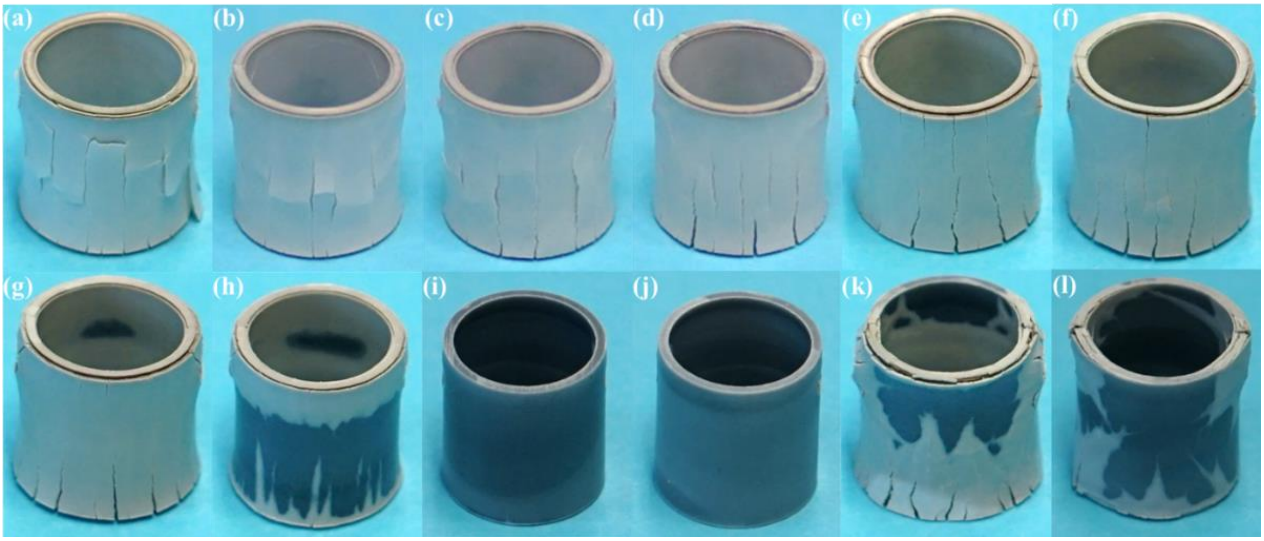

Fig. 7. Macrographs of selected Zircaloy-4 after 2 and 4 h isothermal tests under various oxygen flow rate conditions at 1000 °C: (a) 20 mL/min, (b) 40 mL/min, (c) 60 mL/min, (d) 80 mL/min, (e) 100 mL/min, (f) 120 mL/min, (g) 140 mL/min, (h) 160 mL/min, (i) 180 mL/min, (j) 200 mL/min, (k) 180 mL/min, (l) 200 mL/min; (a–j) 2 h, (k,l): 4 h.

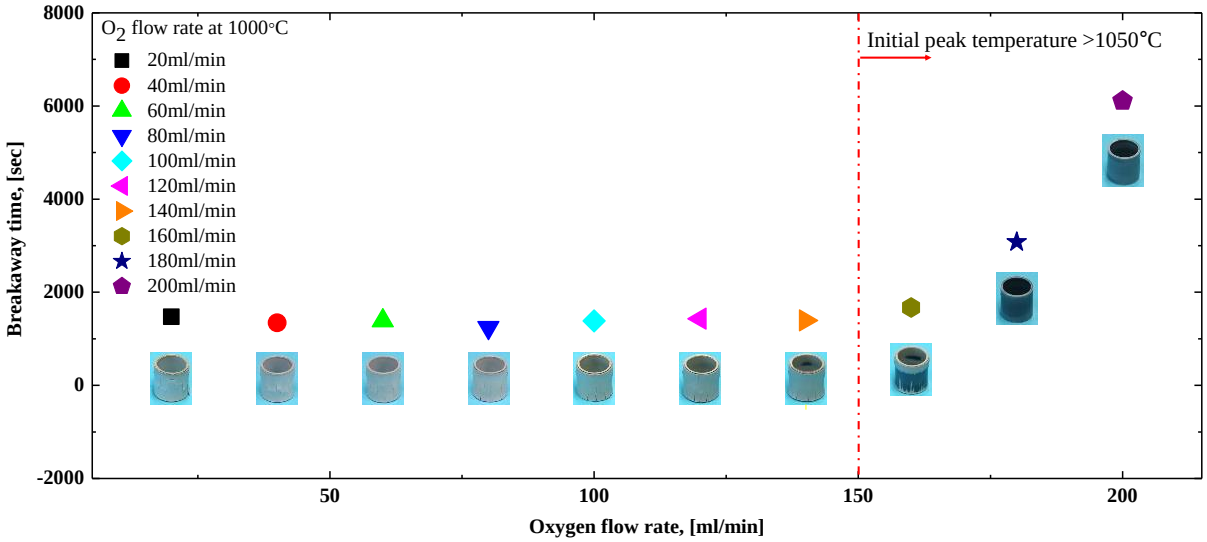

Fig. 8. Relationship between Breakaway delay time and oxide appearance

and the corresponding oxidized specimen. As mentioned earlier, higher reaction heat is generated as oxygen flow rate is increased. When the cladding temperature exceeds 1050°C due to the initial reaction heat, dense columnar oxide of dark color is formed, and it is estimated that the breakaway time is delayed due to the formation of this oxide layer. Figure 8 shows that the breakaway time is closely related to the oxygen flow rate, which means that the flow rate effect should be reflected in the current models.

4. Conclusions

Isothermal oxidation tests at 1000°C were carried out to identify the effect of the oxygen flow rate on oxidation behavior. A breakaway time delay phenomenon was discovered in this study. The breakaway time delay phenomenon seems to depend on the abrupt temperature escalation of the cladding surface in the early stages of the oxidation reaction. It was confirmed that the delay phenomenon starts above peak temperatures exceeding 1050°C. This result is consistent with a previous study showing that dense columnar oxides were favorably formed at over 1050°C. Macrograph observations were also performed to support this result. According to macrographic analysis, there is no oxide color change in cases of high flow rate. This means that there is a breakaway time delay because changes in oxide colors from dark to light coincided with the kinetic transition, which was reported in previous studies. The investigation of the macrographs is in good agreement with the TG mass-gain analyses. Therefore, the breakaway time delay phenomenon was detected in the high oxygen flow region. Consequently, the breakaway time delay phenomenon seems to be related to an abrupt increase in cladding temperature in the early oxidation stage. It is worth emphasizing that the initial temperature escalation should be considered with respect to oxidation behaviors and oxide characteristics, specifically the growth of dense columnar oxide, for a better understanding and prediction of oxide kinetics.

ACKNOWLEDGEMENT

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REFERENCES

[1] Duriez, C.; Dupont, T.; Schmet, B.; Enoch, F. Zircaloy-4 and M5® high temperature oxidation and nitriding in air. J. Nucl. Mater. 2008, 380, 30–45.
[2] Coindreau, O.; Duriez, C.; Ederli, S. Air oxidation of Zircaloy-4 in the 600–1000 °C temperature range: Modeling for ASTEC code application. J. Nucl. Mater. 2010, 405, 207–215.
[3] Steinbrück, M.; Vér, N.; Große, M. Oxidation of Advanced Zirconium Cladding Alloys in Steam at Temperatures in the Range of 600–1200 °C. Oxid. Met. 2011, 76, 215–232.
[4] Steinbrück, M. Prototypical experiments relating to air oxidation of Zircaloy-4 at high temperatures. J. Nucl. Mater. 2009, 392, 531–544.
[5] Grosse, M.; Steinbrueck, M.; Maeng, Y.; Sung, J. Influence of the steam and oxygen flow rate on the reaction of zirconium in steam/nitrogen and oxygen/nitrogen atmospheres. In International Congress on Advances in Nuclear Power Plants (ICAPP); San Francisco, CA, USA, 2016.
[6] Steinbruck, M.; Schaffer, S. High-Temperature Oxidation of Zircaloy-4 in Oxygen–Nitrogen Mixtures. *Oxid. Met.* **2015**, *85*, 245–262.
[7] 8. Negyesi, M.; Amaya, M. The influence of the air fraction in steam on the growth of the columnar oxide and the adjacent α-Zr(O) layer on Zry-4 fuel cladding at 1273 and 1473 K. Ann. Nucl. Energy 2018, 114, 52–65.
[8] Leistikow, S.; Schanz, G. Oxidation kinetics and related phenomena of zircaloy-4 fuel cladding exposed to high temperature steam and hydrogen-steam mixtures under PWR accident conditions. Nucl. Eng. Des. 1987, 103, 65–84.