Investigation of flow condition on the oxidation of Zircaloy-4 in air at 850 and 1100℃

Yunhwan Maeng [a], Sanggil Park[b], Jaeyoung Lee [a*]
[a]*School of Mechanical and Control Engineering, Handong Global Univ., Pohang, 791-708, Korea*
[b]*ACT Co. Ltd., Techno 9 Ro, Yuseong-gu, Daejeon, 34027, Korea*
[*]*Corresponding author: jylee7@handong.edu*

1. Introduction

An oxidation behavior of the Zircaloy-4 was experimentally studied by varying a flow rate and partial pressure of air. Tests were conducted at two distinct temperatures in which a kinetic transition was occurred, or not: 850℃ and 1100℃. The effects of flow rate and partial pressure of air was studied by a measurement of mass gain using thermogravimetric analyzer (TGA). After experiments, samples were observed with macrophotography and metallography using optical microscopy. The effect of flow rate and partial pressure of air were qualitatively analyzed with those methods. This paper is based on a revised and considerably extended presentation given at the 21st International Quench Workshop [1].

2. Backgrounds

An oxidation test of Zircaloy-4 cladding samples was conducted at two different temperature; 850℃ and 1100℃. The difference between two temperatures is whether the breakaway (transition) phenomenon occurs or not. However at temperature ranges above 1050℃, breakaway was not occurred [2-6].

3. Experimental Details

In this section, Zircaloy-4 cladding samples and experimental devices were introduced. Experimental procedure is illustrated by temperature programming. For the additional analysis, samples were used for macrophotography and metallography.

3.1 Zircaloy-4 Sample

Zircaloy-4 cladding tubes were cut into 10mm segments and both ends of samples were grinded. The inner diameter of the samples were 9.25mm and the outer diameter of the samples were 10.75mm. After cutting and grinding, samples were cleaned using ultra sonication cleaner for 10minutes. In this process, samples were submerged by acetone.

3.2 Experimental Setup & Procedure

The mass gain during test procedure was measured in-situ by TGA (NETZSCH STA-409) device [7]. In the furnace, samples were located on the ring-shaped alumina plate. In pre-experiment procedure, TGA device (including furnace) was evacuated and argon was refilled to reduce impurities. Argon gas was flowing continuously through the furnace in roles of carrier gas and protective gas. Experiments can be initiated when the oxygen concentration reached steady state. The oxygen concentration was measured ZIROX oxygen concentration measurement system [8]. This device measures oxygen concentration by the off-gas from the furnace.

During test, temperature inside the furnace changes as programmed sequence already set. At the first step, temperature increases by 30K/min to the initially set value. However, because of the overshoot, 10minutes of thermal stabilization phase was assigned at the second step. At the third step, temperature could be stabilized and isothermal region begins. Air flows into the furnace and the oxidation reaction occurs during isothermal region. When the isothermal region finishes, temperature inside the furnace decreased and the experiments also finish. When the temperature inside the furnace decreased to approximately 100℃ range, samples were kept safely for the additional analysis.

3.3 Test Matrix

Two different test matrices were planned to study an effect of flow conditions on the oxidation of Zircaloy-4 cladding in air.
i) For the effect of flow rate, flow rates of air and argon were changed with maintaining the constant partial pressure of air (15%).
ii) For the purpose of confirming the effect of partial pressure of air (P_{O_2}), air flow rate was kept constant and argon flow rate was changed. The air flow rate was set to two values; 3l/h & 18l/h, relatively low and high flow rates. The detail explanation of test matrices are illustrated in Table I and Table II.

Table I: Test Matrix for an effect of flow rate (FA)

Temp (℃)	Air (l/h)	Ar (l/h)	Total gas (l/h)	Test ID
850 / 1100	3	1	4	FA1
	6	2	8	FA2
	12	4	16	FA4
	18	6	24	FA6
	24	8	32	FA8
	30	10	40	FA10

Table II: Test Matrix for an effect of partial pressure (APP)

Temp (℃)	Air (l/h)	Ar (l/h)	P_{O_2} (%)	Test ID
850 / 1100	3	1	15.0	A3PP1
		2	12.0	A3PP2
		4	8.6	A3PP4
		6	6.7	A3PP6
		8	5.5	A3PP8
		10	4.6	A3PP10
	18	1	18.9	A18PP1
		2	18.0	A18PP2
		4	16.4	A18PP4
		6	15.0	A18PP6
		8	13.8	A18PP8
		10	12.9	A18PP10

3.4 Post-test Analysis

After experiments, samples were used for additive analysis using macrophotography and metallography. In order to observe deformation on the surface of samples by the oxidation at different flow conditions and temperatures, macrophotography was used. In addition, for the purpose of further observation such like the growth of an oxide scale and the formation of nitride, metallography was used by optical microscopy.

For the metallography, samples were embedded in epoxy resin and hardened. After then, cutting, grinding and chemical conditioning were conducted so the cross section of the samples were clearly observed.

4. Results

An effect of flow rate and partial pressure of air were confirmed by experimental results. After experiments, samples were analyzed by macrophotography and metallography methods.

4.1 An Effect of Air Flow Rate (FA)

As could be seen from Fig. 1, when the test temperature was 850℃, the mass gain and the oxidation kinetics were increased as the flow rate of air+Ar gas. As already mentioned from 2nd chapter, the breakaway phenomenon occurs at the temperature ranges lower than 1050℃ so the oxidation kinetics accelerates from parabolic rate to linear rate. The time when the breakaway phenomenon occurred at oxidation kinetics were also affected by the flow rate. The breakaway times were delayed as the flow rate increased.

The effect of flow rate showed different trend by changing temperature. When the test temperature increased from 850℃ to 1100℃, this trend was reversed. As could be seen from Fig. 2, the mass gain and the oxidation kinetics increased as the flow rate increased at 1100℃. However, an oxygen starvation condition could be assumed from the FA1 samples. It showed linear oxidation rate less than other test samples showing parabolic oxidation rate.

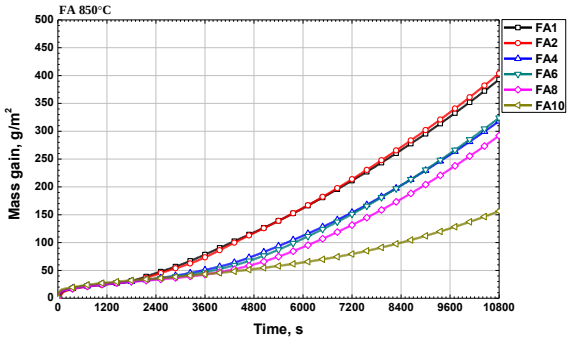


Fig. 1. Experimental results of FA 850℃ test series

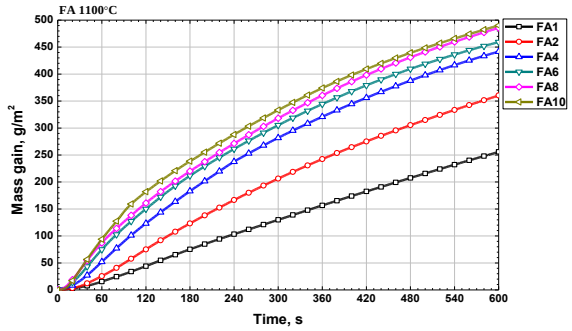


Fig. 2. Experimental results of FA 1100℃ test series

4.2 An Effect of Air Partial Pressure (APP; A03PP & A18PP)

APP test series was divided by air flow rate and temperature. From the Fig. 3 and Fig. 4, when the test temperature was 850℃ and air flow rate was 3l/h, the experimental results showed different trend by changing test duration. From the Fig. 3, the experimental results conducted for 50minutes, the oxidation kinetics increased as the partial pressure of air increased. However, when the test duration increased from 50minutes to 180minutes, these trends was not observed.

From the Fig. 4, it could be assumed that the mass gain and the oxidation kinetics increased as the partial pressure of air increased within the ranges between A03PP1 and A03PP6. However, A03PP8 and A03PP10 were deviated from these trends. In addition, A03PP10 showed linear oxidation rate after breakaway. It might be assumed that it was from an oxygen starvation condition because of the accelerated oxidation kinetics after breakaway.

As an air flow rate increased to 18l/h, it was similar with the experimental results when the air flow rate was 3l/h as could be seen from the Fig. 5 and Fig. 6. An effect of partial pressure of air was not clearly observed from Fig. 5 and Fig. 6

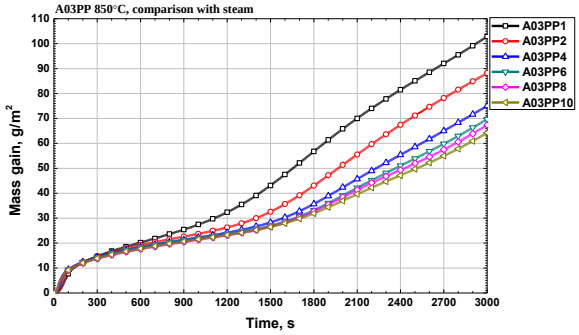


Fig. 3. Experimental results of A03PP 850℃ test series (50minutes of test duration)

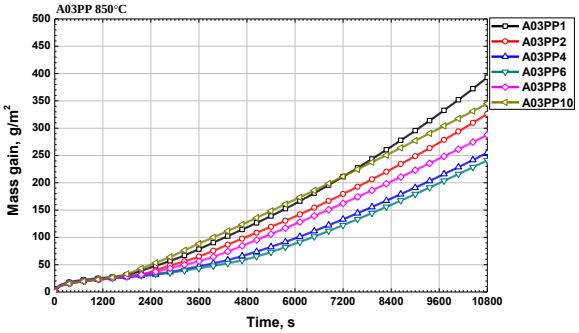


Fig. 4. Experimental results of A03PP 850℃ test series (180minutes of test duration)

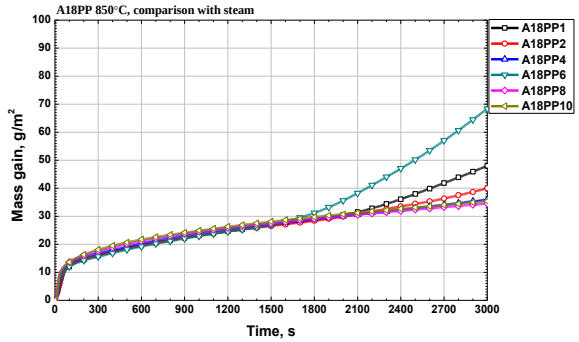


Fig. 5. Experimental results of A18PP 850℃ test series (50minutes of test duration)

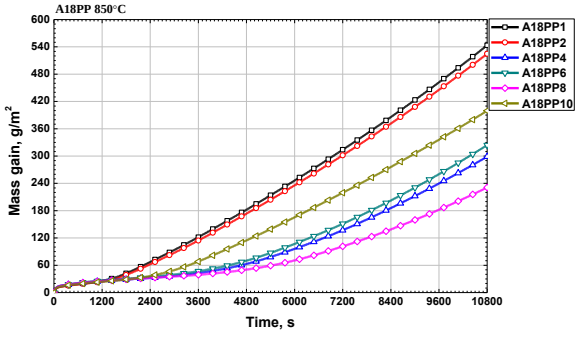


Fig. 6. Experimental results of A18PP 850℃ test series (180minutes of test duration)

However, at 1100℃, an effect of partial pressure of air was observed more clearly than the experiments conducted at 850℃. At the relatively low air flow rate (3l/h), the mass gain and the oxidation kinetics increased as the partial pressure of air also increased as could be seen from Fig. 7. However, at the relatively high air flow (18l/h), the oxidation kinetics of the samples were similar regardless of partial pressure of air from Fig. 8. It might be assumed that the oxidation kinetics was not affected significantly by partial pressure of air when the air flow rate was high.

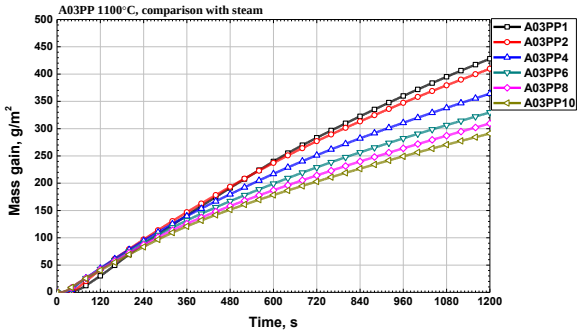


Fig. 7. Experimental results of the A03PP 1100℃ test series

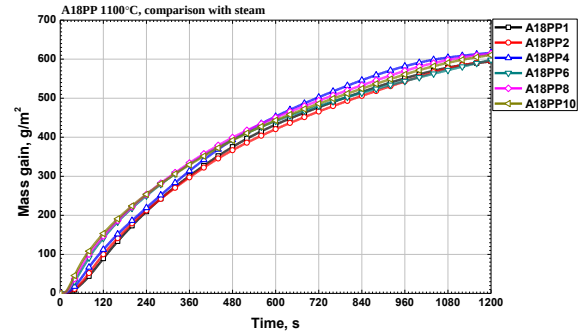


Fig. 8. Experimental results of the A18PP 1100℃ test series

5. Analysis

An experimental results at 850℃ in the present study did now showed certain trend between the oxidation kinetics and partial pressure of air. It might be assumed that an uncertainty exhibited on the oxidation kinetics observed from the experiments conducted at 850℃ is caused by different thermal-hydraulic boundary conditions and local, random and stochastic properties of breakaway phenomenon. An uncertainty on the oxidation kinetics caused by breakaway phenomenon was already suggested at [9].

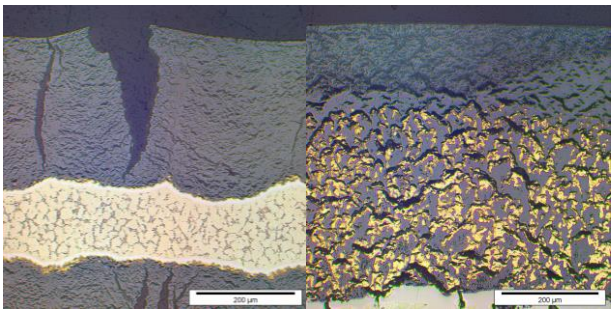
After experiments, various changes in samples were observed using macrophotography. After experiments conducted at 850℃, volume of the samples were expended and the spalling was observed at the surface. However, after experiments conducted at 1100℃, volume of the samples also changed but the degree of volume expansion was smaller than samples at 850℃. Thickness of sample was increased and the surface changed to black and gray color. Surfaces of the samples and growth of oxide scale were different by test temperature and flow conditions as could be seen from Fig. 9 and Fig. 10.

Bare 850℃ 1100℃

Fig. 9. Comparison between macrophotographs of the samples

At the metallographic images of Fig. 10, different structures of breakaway (850℃) and non-breakaway (1100℃) oxide scales were observed and compared. After experiments conducted at 850℃, the formations of golden-yellow colored nitrides were observed at the interface between the oxide scale and zirconium metallic part. The oxide scale was damaged by macro radial cracks so the protectiveness of the oxide scale was lost. These radial cracks permits oxygen/steam in atmosphere to access through the zirconium metallic part with reducing diffusion path through the oxide scale. Therefore, it accelerates the oxidation kinetics

However, after experiments conducted at 1100℃, considerable amounts of nitrides, circumferential cracks and pores were observed. Circumferential cracks were also observed at 850℃ but the magnitude of cracks in 1100℃ oxide scale was larger than that observed from 850℃ Oxide scale.



850℃ 1100℃

Fig. 10. Comparison between metallographic images of the samples

6. Conclusions

The effects of flow conditions on the oxidation kinetics of Zircaloy-4 samples were qualitatively studied. The flow rate and the partial pressure of air were changed and their effects was different when the temperature was changed. Especially, results of experiments conducted at 850℃ showed unclear trend with oxygen partial pressure. It may be assumed that these behaviors caused by an onset of different thermal-hydraulic boundary condition and stochastic aspect of breakaway phenomenon. Relatively rapid oxidation kinetics and different morphology of oxide scales were observed from experiments conducted at 1100℃.

Therefore, quantitative analysis and additional study are required to apply the effect of flow conditions on the further understanding and improvement of zirconium oxidation model. In addition, it should be considered and validated how thermal-hydraulic conditions varies by flow conditions and how those conditions could be reflected by experimental conditions.

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