Investigation of effect of air flow rate on Zircaloy-4 oxidation kinetics and breakaway phenomenon in air at 850℃

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1. Introduction

This paper analyzed an effect of flow rate on oxidation kinetics of Zircaloy-4 in air at 850ºC. In case of the oxidation of Zircaloy-4 in air at 850ºC, acceleration of oxidation kinetics from parabolic to linear (breakaway phenomenon) occurs. Oxidation and breakaway kinetics of the Zircaloy-4 in air was experimentally studied by changing a flow rate of argon/air mixture. Tests were conducted at 850℃ under constant ratio of argon and air. The effects of flow rate on the oxidation and breakaway kinetics was observed. This paper is based on a revised and considerably extended presentation given at the 21st International Quench Workshop [1].

2. Experimental Details

Preparation of the Zircaloy-4 cladding samples, experimental devices and procedure are introduced. After the tests, picture of the sample was taken and embedded in epoxy resin for macrophotography and metallography.

2.1 Zircaloy-4 Sample

Zircaloy-4 cladding tubes were cut into 10mm segments and both ends of samples were grinded. The inner and outer diameter of the sample was 9.25mm and 10.75mm respectively. After cutting and grinding, samples were cleaned by acetone in ultrasonic bath for 10minutes.

2.2 Experimental Setup & Procedure

Change of mass of the samples during test procedure was measured in-situ by TGA (NETZSCH STA-409) device [2]. In the furnace, samples were located on the ring-shaped alumina crucible. 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 [3]. 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 post-test analysis.

2.3 Test Matrix

Test matrices were planned to study an effect of flow rate on the oxidation of Zircaloy-4 cladding in air. Flow rates of air and argon mixture were changed from 4l/h to 40l/h. However, the ratio of air and argon flow rate was kept constant as 3:1. The concentration of oxygen was also kept constant as 15%. The test duration was set to 180 minutes.

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	3	1	4	FA1
	6	2	8	FA2
	12	4	16	FA4
	18	6	24	FA6
	24	8	32	FA8
	30	10	40	FA10

* Air:Ar = 3:1. Concentration of oxygen is 15%

2.4 Post-test Analysis

After tests, picture of the samples were taken for the macrophotography. After the macrophotography, samples were embedded in epoxy resin and hardened. After then, cutting, grinding and chemical conditioning were conducted for the metallography.

3. Results

As could be seen from Fig. 1, the mass gain and the oxidation kinetics increased as the flow rate decreased. The oxidation kinetics accelerates from parabolic rate to linear rate at specific time (time to transition) as could be seen from Fig. 2. The time to transition was found from derivatives of test samples by finding the lowest value. The time to transition was also affected by the flow rate and increased linearly by increasing flow rate. This tendency could be seen from Fig. 3. However, the critical oxide thickness to transition was from 15μm to 19μm and it was not significantly affected by flow rate.

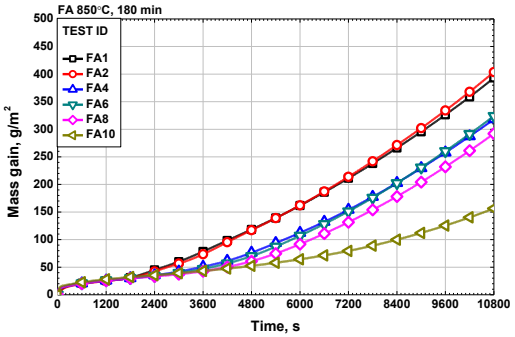


Fig. 1. Experimental results of FA 850℃ test series

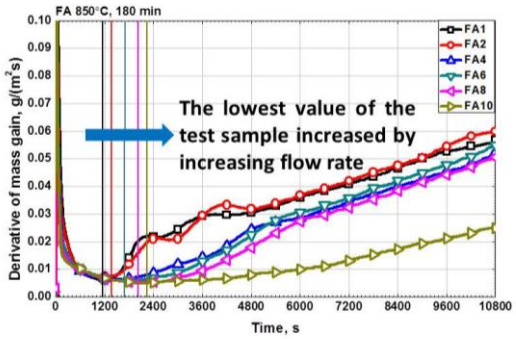


Fig. 2. Derivatives of FA 850°C test series

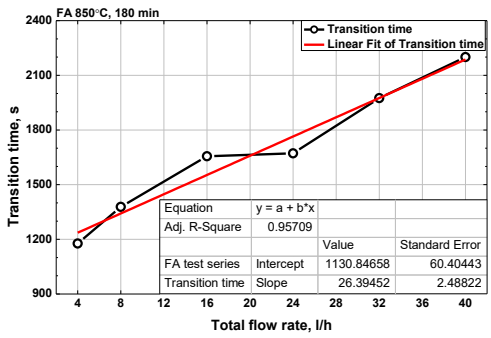


Fig. 3. Time to transition and linear fitting curve of FA 850°C test series

4. Analysis

The effect of flow rate on the oxidation kinetics of Zircaloy-4 in air was analyzed with residence time and percent flow efficiency.

4.1 Residence Time

Residence can be identified by following equation:

$$T_{res} = \frac{L}{V} \quad (1)$$

L is the sample length, and V is the flow velocity of purge gas. If flow rate decreased, then residence time increased and hence the probability that oxygen diffused from flowing gas to the sample would increase.

It is hard to generalize that the oxidation kinetics increases by increasing residence time or decreasing flow velocity. However, it might be assumed that the percentage of oxygen by reaction in the specific control volume increases if residence time increases.

4.2 Percent Flow Efficiency

Percent flow efficiency can be defined as the ratio between the experimental reaction rate and flow rate of reacting material. The percent flow efficiency can be defined as [4]:

$$E = l(dn/dt)(A/F) \times 100\ [\%] \quad (2)$$

A is geometric surface area in cm^2, F is flow rate in molecules of O_2 per second, dn/dt is rate of reaction in terms of atoms of metal $\cdot cm^{-2} \cdot sec^{-1}$, l is stoichiometric ratio for the given oxide.

The percent flow efficiency increased by decreasing flow rate, as could be seen from Fig. 4. It could be explained with residence time of test samples. The residence time of the FA test series is described at Table II. According to Table II and Fig. 4, the percent flow efficiency increased as residence time also increased.

Table II: Residence time of FA 850°C test series

Test ID	Total flow rate	Effective residence time
FA1	4	4.423s
FA2	8	2.211s
FA4	16	1.106s
FA6	24	0.737s
FA8	32	0.553s
FA10	40	0.442s

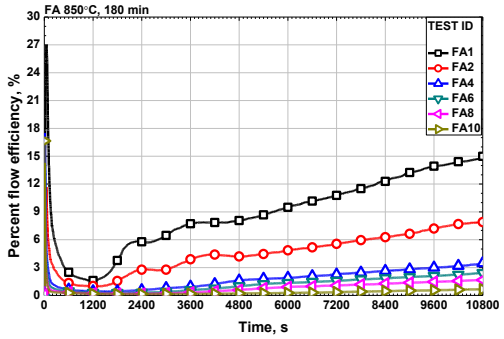
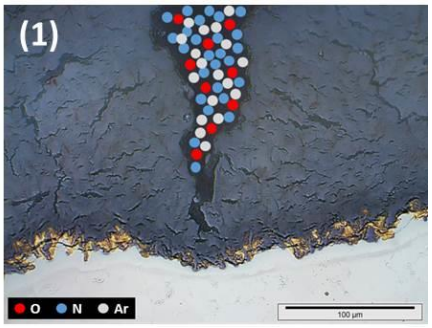


Fig. 4. Percent flow efficiency of the FA850ºC test series

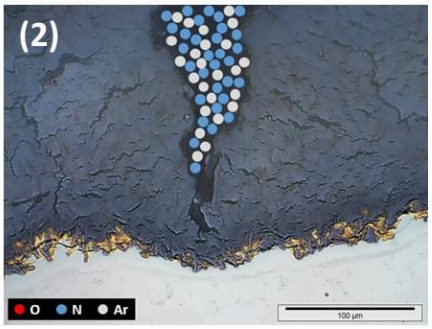
5. Discussion

Because of the breakaway phenomenon, considerable radial cracks formed on the oxide structure and hence the acceleration of the oxidation kinetics occurred. At post-breakaway regime, an interdiffusion of the oxygen from flowing gas to not-reacted zirconium part of the sample would be occurred because of the breakaway phenomenon.

At pre-breakaway regime without considerable radial cracks, the mechanism of the oxidation kinetics could be explained by oxygen diffusion through the protective oxide scale. However, at post-breakaway regime, because of the formation of radial cracks, interdiffusion occurred and hence the oxidation kinetics would be more complex. In addition, from the geometrical change from the breakaway phenomenon, flow of gas would be affected and hence the diffusion of oxygen would be affected. This process is described at Fig. 5.

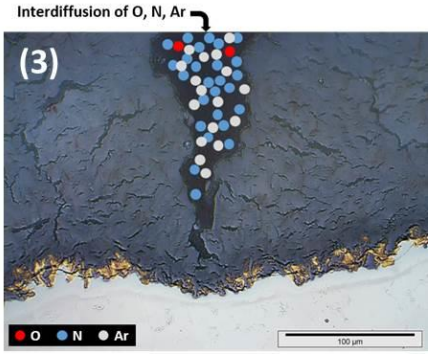


(1) At initial phase, mixed atmosphere would be located at crack tips maintaining equivalent concentration with purge gas



(2) Oxygen would react firstly with zirconium metal because of its high reactivity.

At crack tips, concentrations of nitrogen and argon increases and oxygen starvation might be occurred.



(3) Oxygen in flowing gas diffuses into the crack tips, oxide scale and metallic part.

Fig. 5. Process of interdiffusion of oxygen at crack tips

6. Conclusion & Outlook

The effects of flow conditions on the oxidation kinetics of Zircaloy-4 samples were explained with residence time and percent flow efficiency. In addition, several issues were observed from this study, interdiffusion at breakaway and deformation of oxide structure by breakaway phenomenon. However, additional subjects are remained. For example, an effect of nitrogen, such like an effect of flow rate on the mechanism of nitriding, was not yet considered.

For the purpose of understanding on mechanism of zirconium oxidation in air, further study is required.

ACKNOWLEDGEMENT

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