

High Temperature Oxidation Behavior of the Zirconium Alloys in Air and Oxygen

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1. Introduction

The zirconium alloy is a common name of the alloy, which consist of 97~98% zirconium and 2~3% of other components (Zn, Fe, Cr, Ni, Nb, etc.). The benefits of zirconium alloy as the cladding material of nuclear fuel are the corrosion resistance similar to stainless-steel, small absorption cross-section of the thermal neutron, easy to be processed because of a number of slip system, low residual stress and thermal stress caused by a low elastic coefficient, and less expanded by heat. However, the cladding material of zirconium alloy responds to the high temperature water and generates the hydrogen, and then it is absorbed into the cladding again about 20% of the original quantity, so that the generated hydride has critical influence to secure the integrity of nuclear fuel cladding material when the Loss Of Coolant Accident (LOCA) occurs.

Therefore, various types of cladding, which can endure these severe conditions, are under development, and experiments to secure the integrity of the cladding when the LOCA occurs are conducted. For this, the NRC has suggested a new regulation 10CFR50.46c in April, 2014, and also the regulation guide DG-1261[1], which is used to measure the starting point of the breakaway oxidation phenomenon and suitable for the new standard, has been suggested together. At the acceptance criteria of cooling system for emergency reactor core of newly suggested 10CFR50.46c, the usage of NRC certificated methods is required for researches about the breakaway oxidation of cladding, so that it is also necessary in the study of new zirconium alloys that a progressed by the Korea Nuclear Fuel company (KNF).

However, the data to expect the alloy behavior when accidents such as the LOCA happen is quite limited so far, and most of experiments focus on the oxidation behavior of cladding in the steam atmosphere. In practice, there are many cases of the air ingress to the reactor core. M. Bottcher[2] has suggested various scenarios of ingress to the external surface of cladding. Air ingress is possible under shutdown conditions when the reactor coolant system is open to the containment atmosphere. Air oxidation of the remaining outer core regions after reactor pressure vessel failure in the late phase of core degradation during severe accidents, etc. Because of this situation, the oxidation of cladding material is accelerated and finally the embrittlement happens when the cladding material is exposed by high-

temperature air for a long time, so that it is connected to the break.

The goal of this study is to observe the oxidation behavior of new zirconium alloy claddings M1-5 and M2-5 provided by KNF and the commercial cladding Zry-4, and measure the starting point of breakaway. For this, successive high temperature oxidation has been applied to the specimen charged by hydrogen at the atmospheric pressure, with air and oxygen atmosphere using the TGA, and the breakaway starting point is measured through the measurement of increased quantity of specimen oxide.

2. Materials and methods

2.1. Specimen Preparation

The specimen applied for this research is the metal board type of Zr based new alloy cladding materials M1-5 and M2-5 that are being currently developed by KNF. Though the chemical composition of new alloy cladding material (Table 1) cannot be described because of patent issues, M1-5 is Zr based Nb-Sn-Cr type and M2-5 is Zr based Nb-Cu type.

Table 1. Chemical composition of Zirconium alloy specimens.

	Nb	Sn	Fe	Cr	Cu	Zr
M1-5	O	O		O		Base
M2-5	O				O	Base
Zry-4	-	1.38	0.2	0.1	-	Base

2.1.1. Processing the specimen

The size of the specimen has been cut as both 10mm width, and height, 1mm thickness, and a hole with 1.4 ϕ diameter has been pierced to be hooked on the TGA.

2.1.2. Specimen cleaning

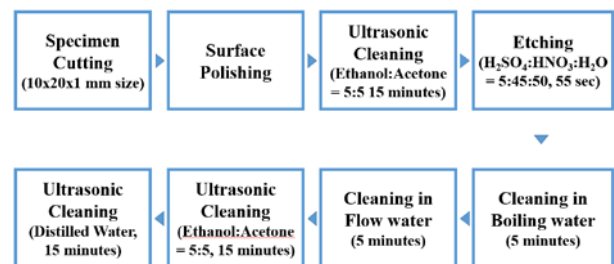


Figure 1. Preparatory procedure of specimens.

Before the beginning of the experiment, the specimen cleaning has been prepared following to the specimen guide of ASTM[3]. The preparation procedure is as shown in figure 1. When the etching was processed, the magnetic stirrer has been used to prevent being pinhole-corroded by acid and the specimen has been cleaned to remove the hydrofluoric acid. Leistikow and Schanz[4] etched specimen with the acid containing nitric acid and hydrofluoric acid, and then finally cleaned with boiling water, and the specimen used by Mardon[5] has been cleaned by acetone. In the study of ANL[6], the specimen has been ultrasonic cleaned with ethanol and then cleaned with water. In the experiment of Baek and Jeong[7], the solution of 5% HF + 45% HNO₃ + 50% H₂O has been used for etching and finally ultrasonic cleaned by the mixture of ethanol and acetone.

2.1.4. Effect of Hydrogen and Hydrogen Charge

The effect of absorbed hydrogen to the cladding during normal operation accelerates the diffusion of oxygen inside residual beta layer(prior-β) when the high temperature oxidation happens during the LOCA[8]. Moreover, it increases the oxygen solubility in the metal so that it brings about more active oxidation. Continuous oxygen supply at the high temperature reduces the thickness of the Zr residual beta layer(prior-β), which manages the mechanical integrity of the nuclear fuel cladding, and the ductility is also reduced as the oxygen is absorbed. The hydrogen accelerates the embrittlement on the β layer caused by oxygen.

In NUREG/CR-6967[6], it has been confirmed that if the cladding has been oxidized in the steam atmosphere for about 4,000 seconds at the temperature of 970 °C - 1,000 °C, the hydrogen more than 400 wppm would be absorbed so that it caused the ductility reduction. Also, the duration of breakaway oxidation to maintain the integrity of cladding ductility is defined as the duration to absorb the hydrogen of 200 wppm.

Therefore, to charge the hydrogen, hydride layer has been artificially created on the surface of specimen through the cathodic hydrogen charging method[9], and then the created hydrogen on the surface has been absorbed into the metal by heat treatment for 24 minutes at 360 °C.

2.2. Experiment Method

2.2.1. Successive Measurement of Oxide Increase

To measure the starting point of breakaway oxidation of new zirconium alloy M1-5 and M2-5, the hydrogen charged specimen has been oxidized at the temperature of 950°C and 1,000°C using the successive measuring oxidation facility (SETSYS Evolution TGA-DTA/DSC of SETARAM Instrumentation). The specimen has been oxidized for 5,000 seconds after reaching to targeted temperature and the weight has been continuously

measured by duration. The specimen has been connected into the device by fine scales and platinum wire, and the alumina tube has been covered on the platinum wire and zirconium alloy to prevent the reaction from direct contact at the high temperature. In addition, the ultrapure argon and 0.1% hydrogen mix gas has been applied to prevent the oxidation while the oxidation device was reached to targeted temperature. After the oxidation device reaches to the targeted temperature, amount of oxidation has been measured by providing the air or oxygen. After the experiment, the oxidation behavior was investigated through the analysis of the weight gain. Also the microstructure of the cross section was analyzed using OM after each experiment.

3. Results and discussion

3.1. Oxidation Behavior of Zirconium Alloys in Oxygen and Air Atmosphere

In figure 2-5, the oxide increase by duration has been schematized as a graph. It was confirmed that the oxidation amount was high in the order of M1-5, Zry-4 and M2-5 under the high-temperature air condition, and Zry-4, M1-5 and M2-5 in the oxygen condition. However, in air condition, the differences of oxidation amount was drastically decreased when temperature went high up to 1,000 °C. To confirm this, the metallographic images compiled in figure 6 gives a closer view into the thickness and structure of the oxide layers. The thickness of the oxide film of each specimen is summarized in table 2. According to the previous research [1], when a zirconium alloy is oxidized in the air, it forms a columnar oxide layer at the initial stage. However, when the oxide film grows to some extent, a nitride (ZrN) is formed in the oxide film and the metal boundary layer, and it accelerates oxidation. As a result of the analysis of the microstructure using a optical microscope, the nitride is hardly recognized at 950 °C., but the nitride is apparent at 1,000 °C. and the diffusion of air is accelerated by the spalling on the surface of the oxide film to cause the nitride (ZrN) .

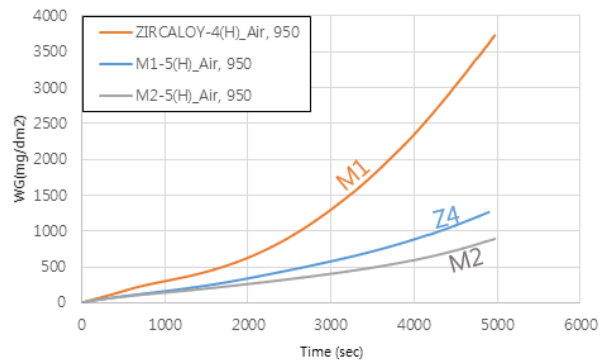


Figure 2. Weight gains and the onset time of Breakaway oxidation of zirconium alloy specimens at atmospheric pressure and air atmosphere under 950 °C for 5,000 seconds.

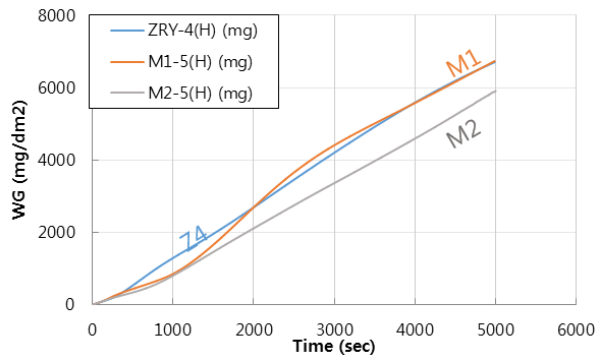


Figure 3. Weight gains and the onset time of Breakaway oxidation of zirconium alloy specimens at atmospheric pressure and air atmosphere under 1,000 °C for 5,000 seconds.

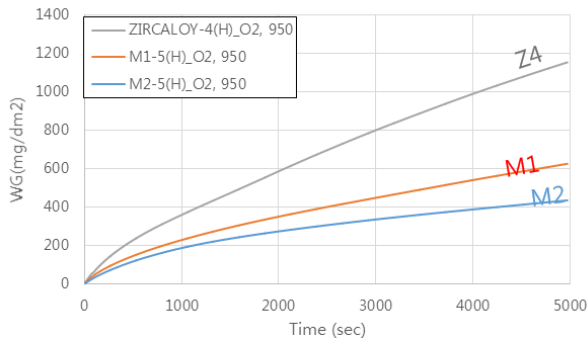


Figure 4. Weight gains and the onset time of Breakaway oxidation of zirconium alloy specimens at atmospheric pressure and oxygen atmosphere under 950 °C for 5,000 seconds.

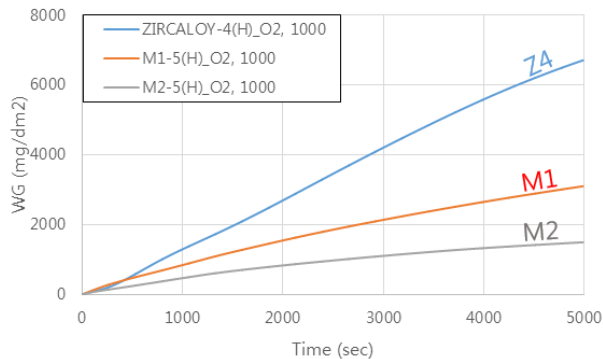


Figure 5. Weight gains and the onset time of Breakaway oxidation of zirconium alloy specimens at atmospheric pressure and oxygen atmosphere under 1,000 °C for 5,000 seconds.

Table 2. Weight gain and oxide thickness of oxidized zirconium alloy specimens for 5,000 seconds under atmospheric pressure air and oxygen conditions of 950 °C, 1,000 °C

Specimens		Conditions			
		Air, 950 °C	Air, 1,000 °C	Oxygen, 950 °C	Oxygen, 1,000 °C
Zry-4	Weight gain (mg/dm ²)	1265.28	6706.41	435.35	6706.41
	Oxide thickness (um)	72.09	348.31	97.59	129.21
M1-5	Weight gain (mg/dm ²)	3730.59	6738.80	626.03	3099.60
	Oxide thickness (um)	312.58	382.52	69.36	61.54
M2-5	Weight gain (mg/dm ²)	892.53	5910.48	1154.21	1494.23
	Oxide thickness (um)	26.52	373.03	27.55	30.60

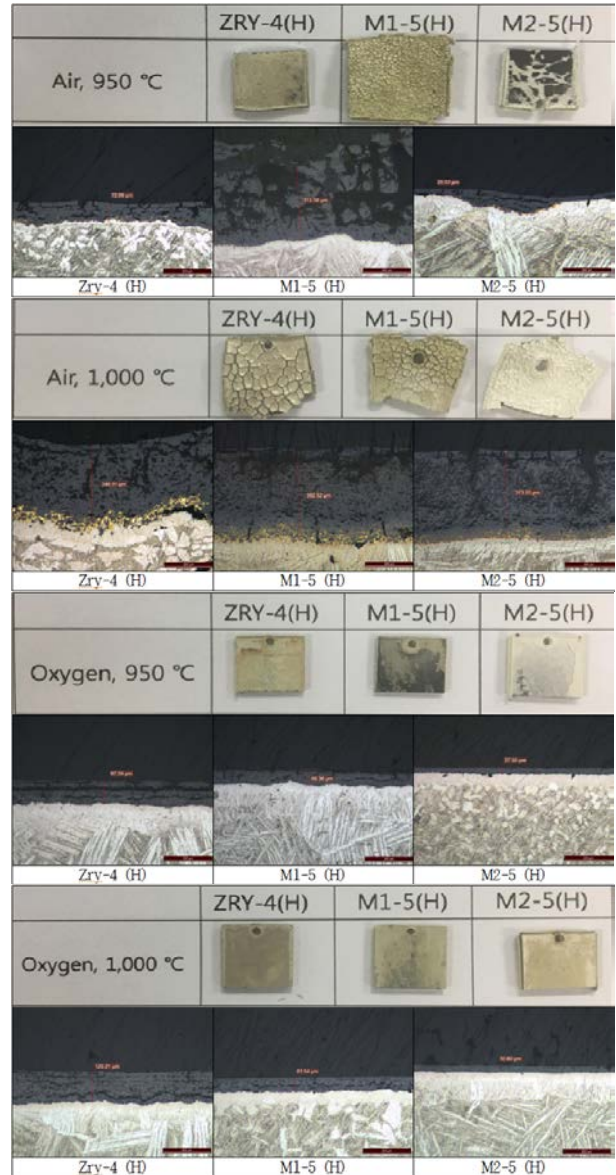


Figure 6. Metallographic images and post-test appearance of zirconium alloy specimens after isothermal oxidation at of 950 and 1,000 °C in air and oxygen.

The corrosion behavior in the high temperature oxygen atmosphere was examined in the order of M2-5, Zry-4 and M1-5. This can be explained by the influence of the constituent elements in the alloy on the oxidation. Especially, the difference of corrosion resistance according to the contents of Nb and Sn has been studied in domestic and foreign countries. However, in the case of new alloys, the detailed composition is not known due to the patent problem, but the big difference between M1-5 and M2-5 is existence of Sn. Therefore, we investigated the difference of Breakaway oxidation time according to Sn content.

In the study of Baek and Jeong [7], the Sn content in the alloy has been explained to be directly influential to the starting point of breakaway. According to the starting point of breakaway at each wt% of Sn (figure 7), the starting point is more delayed as the Sn is less

contained. Likewise, M2-5 that is without Sn has shown later starting point of breakaway than other alloy with Sn, in this study.

However, the wt% of Sn cannot be concluded as a reason that M1-5 has shown faster breakaway than Zry-4, since the exact content of Sn in M1-5 is unknown.

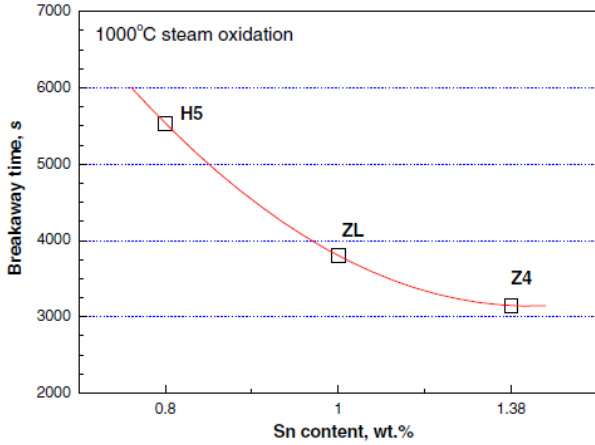


Figure 7. Breakaway oxidation time of H5, ZL and Z4 alloys at 1,000 °C [7].

3.2. Effects of Hydrogen on High Temperature Oxidation Behavior in Air Atmosphere

As described above, the pure oxygen atmosphere has been expected to lead faster oxidation because of the hydrogen effect inside the metal. As shown in figure 4-5, however, there was no breakaway within 5000 seconds in the oxygen atmosphere. As the trend of graph explained, the starting point of breakaway can be observed, if the duration of oxidation is longer, but it exceeds the maximum observation duration of 5000 seconds suggested by the NRC, so that it cannot satisfy the purpose of this study. Moreover, another reason with direct influence has been supposed rather than the increase of oxygen solubility caused by the hydrogen, since the oxidation behavior in the oxygen atmosphere was different from which it had been expected on the experiment planning step. And it has been assumed as the influence of nitrogen in the air.

3.2.3. Effects of Nitride in Zr-based alloys

As shown in Fig. 3.15-3.17, the accelerated oxidation effect due to hydrogen was not observed at 950 °C, unlike the expected results. Rather, depending on the specimen, the specimen without hydrogen was found to have a large amount of oxidation.

On the other hand, at 1,000 °C, the specimens loaded with hydrogen were about twice as oxidized as the specimens without hydrogen. These results indicate that at 950 °C, the accelerated oxidation effect due to nitrogen in the air is more dominant than the accelerated

oxidation effect due to hydrogen, and the acceleration effect due to hydrogen is predominant at 1,000 °C.

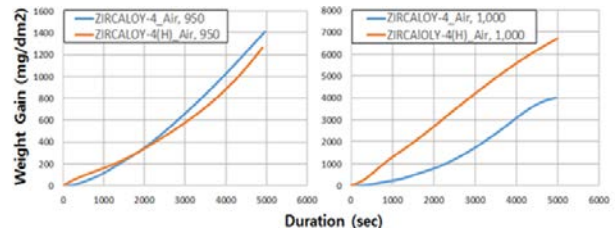


Figure 8. Weight gain differences of Zry-4 specimens with and without hydrogen after isothermal oxidation at of 950 and 1,000 °C in air.

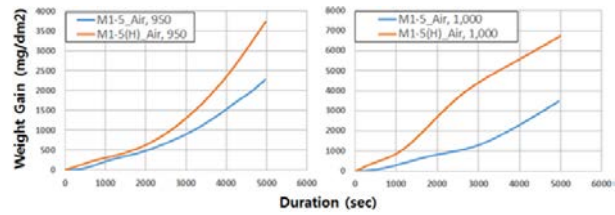


Figure 9. Weight gain differences of M1-5 specimens with and without hydrogen after isothermal oxidation at of 950 and 1,000 °C in air.

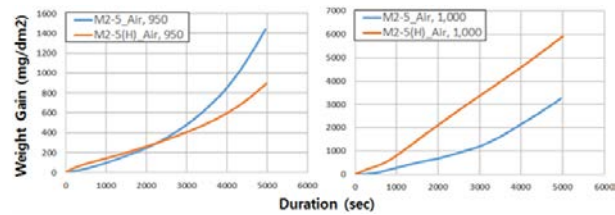


Figure 10. Weight gain differences of M2-5 specimens with and without hydrogen after isothermal oxidation at of 950 and 1,000 °C in air.

In order to find the breakaway starting point, the secondary differential value of the weight gain graph was confirmed, and the starting point is summarized in Table 3.

Table 3. The onset time of Breakaway oxidation of zirconium alloy specimens with and without hydrogen after isothermal oxidation at of 950 and 1,000 °C in air.

	Air, 950 °C		Air, 1,000 °C	
	Hydride (200 ppm)	Non Hydride	Hydride (200 ppm)	Non Hydride
Z4	4,511 sec	4,777 sec	250 sec	305 sec
M1	4,856 sec	4,913 sec	982 sec	3,010 sec
M2	4,861 sec	4,715 sec	677 sec	2,087 sec

4. Conclusions

In this study, the oxidation behavior of new alloys (M1-5, M2-5) and commercial cladding material (Zry-4) has been reviewed in the air and oxygen atmosphere. According to the results of the experiment, M2-5 has shown later starting point of breakaway oxidation than

M1-5 and Zry-4. This means that M2-5 has superior corrosion resistance comparing to other two cladding material. The reason is related to the composition of the alloy. Especially, the content of Sn is directly influential.

According to the results oxide thickness is higher in air with lower oxygen concentration. That is cause by the generation of nitride. In order to verify this, the experiment result has been compared to the leading research conducted in the steam atmosphere, and the starting point of breakaway oxidation occurred faster in this study. Therefore, further research in the nitrogen atmosphere is on the future plan to determine the impact of nitrogen to the breakaway.

The accelerated oxidation effect due to hydrogen was not observed at 950 °C, unlike the expected results. Rather, depending on the specimen, the specimen without hydrogen was found to have a large amount of oxidation. On the other hand, at 1,000 °C, the specimens loaded with hydrogen were about twice as oxidized as the specimens without hydrogen. These results indicate that at 950 °C, the accelerated oxidation effect due to nitrogen in the air is more dominant than the accelerated oxidation effect due to hydrogen, and the acceleration effect due to hydrogen is predominant at 1,000 °C.

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