High-Temperature Oxidation Behavior of Zirconium Alloys in Simulated Spent Fuel Pool Accident Conditions

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1. Introduction

Spent nuclear fuel is mainly stored in a wet storage method by immersing it in a water pool to remove decay heat and shield against radiation. Zirconium alloys, which has excellent thermal resistance and corrosion resistance, are mainly used as the material for spent fuel rods. The likelihood of an accident in a spent nuclear fuel storage pool is considered low; however, the possibility of incidents, such as coolant leakage caused by natural disasters or other external factors, cannot be entirely dismissed. In such an accident situation, the spent fuel rods exposed to the atmosphere may generate heat and the coolant may evaporate, forming a steam atmosphere. These conditions can lead to oxidation of the fuel rod cladding and welded joints and cause catastrophic failures such as fuel exposure.

This study experimentally investigated the high-temperature oxidation behavior of zirconium alloys under conditions simulating potential accident scenarios. In actual accident conditions, heat generated by nuclear fuel is directly transferred, resulting in self-heating phenomena. Therefore, an induction heater was adopted as the heating method. During the experiment, the real-time weight increase of the specimen was monitored and subsequently converted to weight change per unit area for analysis.

2. Experimental

The Zircaloy-4 specimen used for the oxidation experiments measured 20 mm × 8 mm × 3.5 mm, and was prepared with a drilled hole at the top for connection to the balance during the experiment. The specimen composition is shown in Table 1. Prior to the oxidation experiment, the specimen was polished using 1200-grit SiC sandpaper as a pretreatment.

Alloy	Composition (wt%)					ppm	ppm	ppm
	Zr	Sn	Fe	Cr	O	C	Nb	H
Zy-4	Balance	1.32	0.21	0.11	0.12	125	<40	<3

Table 1. Composition of Zircaloy-4

To simulate the cooling water leakage scenario of an actual storage pool, an experiment was designed, and the experimental schematic along with the actual device is shown in Fig. 1. First, the specimen was suspended from the lower hook of the microbalance and placed inside a glass tube, where its weight change was measured in real time. To replicate the self-heating environment, an induction coil was used for heating, and the temperature was monitored using an infrared thermometer. The experiment was conducted at temperatures of 800°C, 900°C, 1000°C, and 1100°C, with each test lasting 2 hours.

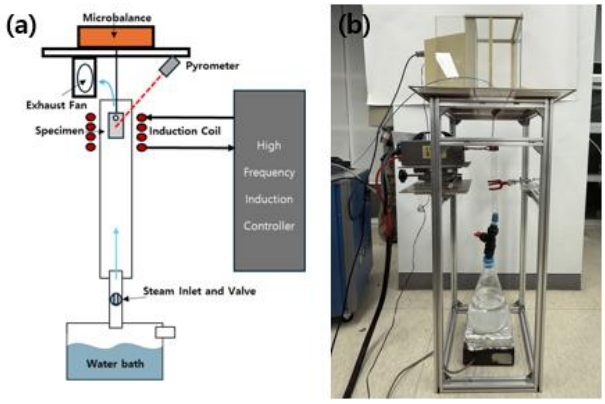

Fig. 1. (a) Schematic diagram of the experiment (b) Actual experimental apparatus

The oxidation experiments were carried in two different atmospheres. In the first, an open water vapor atmosphere was created by heating a flask containing water on a hotplate, with water vapor injected through a glass tube connected to the flask's opening. The vapor passed over the specimen and was expelled from the top of the glass tube, assisted by a fan. In the second experiment, conducted in a normal atmosphere, the specimen was heated without the vaporization process.

XRD (Cu-Kα radiation) was used to analyze the composition of the oxides formed on the oxidized specimens. The surface morphology and microstructural changes of the oxide scales were investigated using scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS). In addition, cross-sections of the specimens were prepared to analyze oxide thickness and compositional variations at different depths.

3. Results and Discussion

Fig. 2 shows the oxidation behavior of specimens in air and steam at different temperatures, with overall trends indicating that higher temperatures lead to increased oxidation, and steam accelerates oxidation compared to air. At 800°C, oxidation is minimal, with air and steam showing nearly identical weight changes. At 900°C, the curves overlap for the first 5000 seconds, after which oxidation in steam increases sharply, diverging from air. At 1000°C and 1100°C, oxidation progresses rapidly, with steam consistently resulting in greater weight gain. Unlike at 1000°C, where the oxidation rate slows after an initial rapid increase, 1100°C shows a continuous rise, suggesting sustained oxide growth.

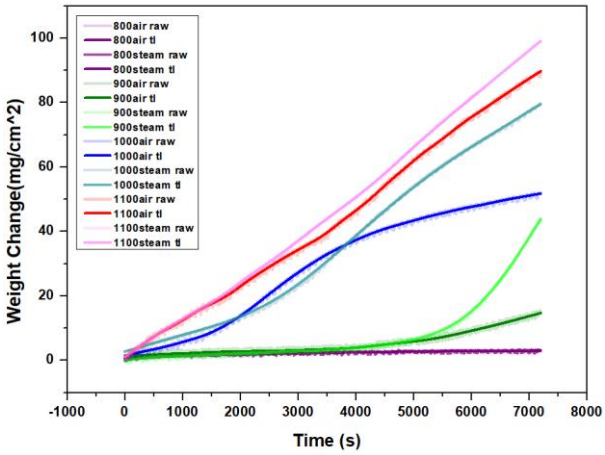

Fig. 2. Oxidation behaviors of Zircaloy-4 at 800℃, 900℃, 1000℃, and 1100℃

After the oxidation experiment, the surface condition of the specimen was examined using SEM, and the images in Fig. 3. were taken. At 800℃, no significant changes were observed other than precipitates on the surface. However, cracks began to appear at 900℃, and their size increased with rising temperature.

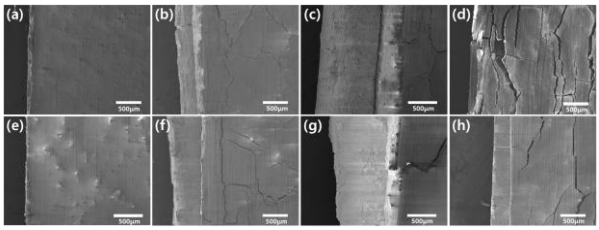

Fig. 3. SEM images of the oxidized specimen surfaces (a) 800°C in air, (b) 900°C in air, (c) 1000°C in air, (d) 1100°C in air, (e) 800°C in steam, (f) 900°C in steam, (g) 1000°C in steam, (h) 1100°C in steam

The post-oxidation specimens in Fig. 4. show visible cracks along the edges, particularly in specimens oxidized at 1000°C and higher, as also observed in Fig. 3(c) and (g). However, for the specimen oxidized at 1100°C (Fig. 4(d) and (h)), the white oxide layer appears more compact, and the gaps are reduced, suggesting partial shrinkage of the oxide scale.

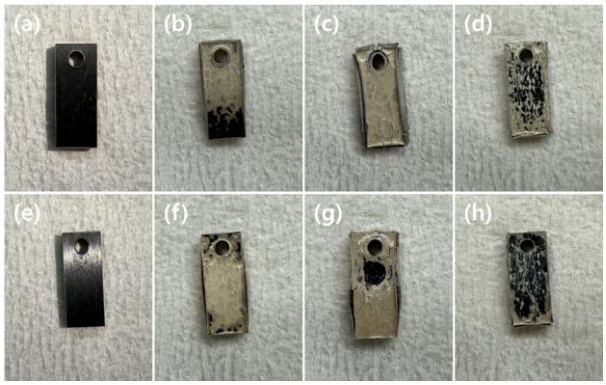

Fig. 4. Images of post-oxidation specimens (a) 800°C in air, (b) 900°C in air, (c) 1000°C in air, (d) 1100°C in air, (e) 800°C in steam, (f) 900°C in steam, (g) 1000°C in steam, (h) 1100°C in steam

The cross-section of the specimen oxidized in a steam atmosphere at 1100°C, which exhibited the largest weight gain, was prepared and analyzed using EDS, as shown in Fig. 5. The oxide layer was observed to be divided into bright and dark regions, with cracks present between them. This suggests that the Zr oxide layer transformed into a tetragonal phase at high temperatures and partially reverted to the monoclinic phase upon cooling [2-3], resulting in a layered structure. The formation of cracks is likely due to the volume difference between these two oxide phases [4]. Unlike previous studies [1][4], which reported the presence of a ZrN layer at the oxide-matrix interface, no such layer was observed in this study. It is assumed that the high-temperature steam environment at 1100°C promoted rapid reoxidation of ZrN, leading to its complete oxidation.

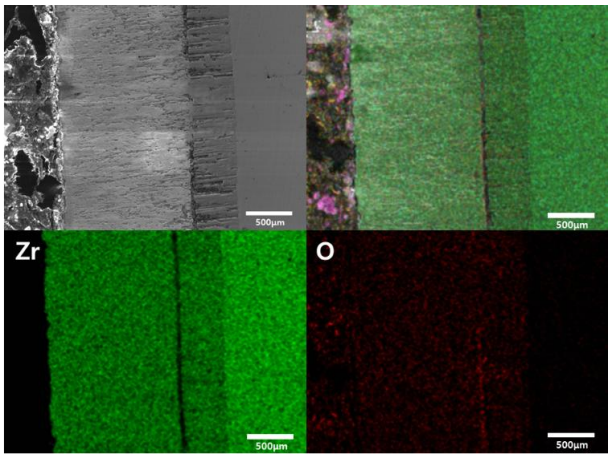

Fig. 5. Cross-sectional SEM image and EDS analysis of a specimen oxidized in a 1100 °C water vapor atmosphere

4. Conclusion

This study experimentally investigated the oxidation behavior of Zircaloy-4 in high-temperature environments, simulating an accident scenario in spent nuclear fuel storage pools. Oxidation experiments were performed using an induction heating method, and weight changes as well as oxidation reaction characteristics in air and steam atmospheres were compared and analyzed.

The oxidation experiment results showed that the oxidation rate increased as the temperature increased, and that the oxidation rate in steam environment was faster than in air. At 800°C, the oxidation reaction hardly occurred, but at 900°C or higher, the oxidation reaction accelerated after a certain period of time, and a higher weight increase was observed in the steam atmosphere in particular. At 1000°C, the oxidation rate slowed down after an initial rapid increase, but it showed a continuous increase at 1100°C.

Surface analysis of the oxidized specimen showed that cracks appeared on the surface at temperatures above 900°C, and the cross-section of the specimen at 1100°C showed that the oxide layer was separated into two layers. This is thought to be because ZrN was reoxidized to tetragonal ZrO_2 at the oxide/metal interface, and cracks occurred due to the volume difference with the existing monoclinic ZrO_2.

In the future, additional cross-sections at other temperatures will be fabricated and analyzed, and the phase structures of the two oxide layers will be confirmed.

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