Accelerating Oxidation on High Temperature and High Pressure Steam of Zirconium Alloy

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1. Introduction

Nowadays, the operation of high burnup of nuclear fuels with their extended cycle is needed for the better economy of nuclear power generation. Enhanced safety of nuclear fuels should be guaranteed against the failure during their high burnup. New cladding materials keep being developed to meet the increased safety of high burnup fuels. Zry-4 evolves to low-Sn Zry-4 that has lower Sn contents in alloy elements, and Nb added alloys are developed and used recently. But most of studies for verification of safety of fuels at high temperatures have been conducted only at one atmosphere of steam, excluding the effect of high steam pressure. As shown in the TMI accident, zircaloy claddings can be oxidized at high temperatures under high steam pressure. Cox [1], Pawel [2], and Bramwell [3] studied about the pressure effects on the oxidation behavior of Zr alloys. They found the high pressures steam enhanced the oxidation of Zry-4. But these studies were limited to the specimens of Zry-4 tubes only. Therefore, we investigated the effects of high steam pressure on high-temperature oxidation of Zr-alloys, especially the dependency of alloy elements and manufacturing processes.

2. Experimental

2.1 Specimens

The specimens used in this study are Zry-4 and Nb-added alloy (A alloy) tubes use in commercial nuclear power plants. In addition to the tubes, sheet specimens containing alloy elements of Zry-4, 1% Nb, and 1.5% Nb were prepared respectively to find the effect of manufacturing processes. Cladding tubes were cut to the height of 6mm~7mm, and sheet specimens to the dimension of 10 by 10mm^2. They were ground, polished, pickled, and cleaned.

2.2 Apparatus and experimental method

Figure 1 shows the equipment used in this study. The equipment can oxidize a specimen uniformly in steam at pressures from 0.1 to 15.0MPa, and temperatures from 700 to 900℃. The system consists of two vessels and two resistance heaters. The outer vessel is used for maintaining high-pressure steam during the experiment. It is heated up to 400℃, and the steam pressure is controlled by the amount of water inside.

After the stabilization of steam pressure, the resistance heater surrounding the specimen inside the inner vessel turns on. The specimen is heated to the set-up temperature for the fixed duration of time. After oxidation, we let the specimen cooled and then recovered. We measure the weight increase due to oxidation. We analyze the microstructures of specimens by OM and SEM.

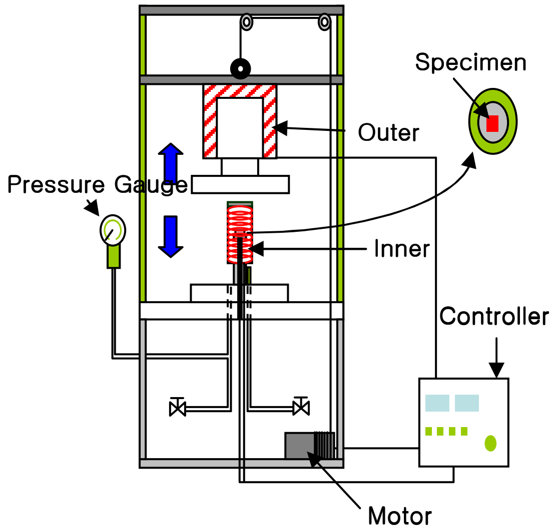

Figure 1. Test apparatus.

3. Result and discussion

The results of the experiments performed at 800℃ are shown in figure 2. Accelerated oxidation by high steam pressure was noticed for Zry-4 tubes. The high-Sn Zry-4 showed the equal amount of oxidation to those of the previous work [4]. However, the low-Sn Zry-4 shows a decreased enhancement by high pressure steam. And Nb containing ally (A alloy) shows little or no effect. These results imply that the composition and contents of alloying elements can influence the oxidation behavior under high pressure steam. Nb seems to block the acceleration of oxidation by high pressure steam.

Figure 3 shows the amount of oxidation under the condition, 800℃-10.0MPa/1500seconds. The results indicate that the metallurgical process also affects the oxidation enhancement by the steam pressures.

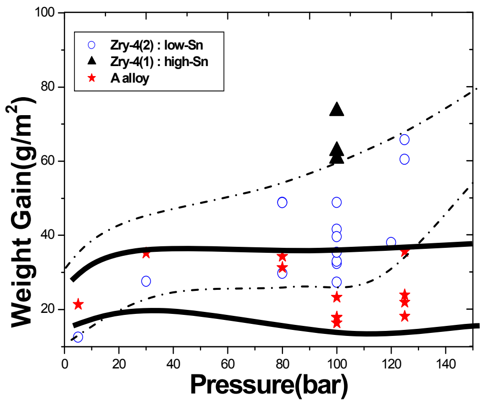

Figure 2. The weight gain versus steam pressure at 800℃.

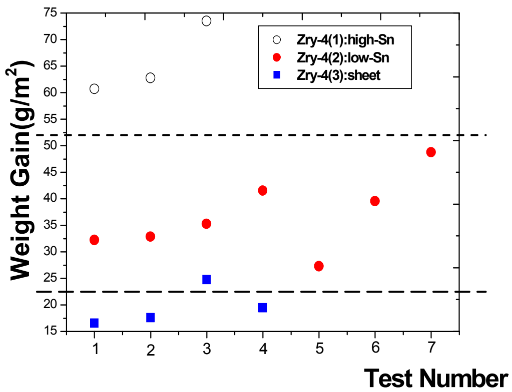

Figure 3. The weight gains at 800℃, 10MPa steam.

The metal microstructures of the low-Sn Zry-4 tube and the Zry-4 sheet before oxidation are examined. Manufacturing processes definitely change the metallic microstructure, and the microstructure difference between the two is clearly noticeable. These microstructure differences affect the oxidation behavior of Zr alloys under high pressure steam. Further characterization of those metallic specimens is in progress.

Figure 4 shows the OM pictures of cross sections of the high-Sn Zry-4 and the low-Sn Zry-4 specimens. There are many cracks observed in the high-Sn Zry-4 specimen that experienced accelerated oxidation. These cracks, generated during oxidation, enhance oxidation. However, the oxide layer of low-Sn Zry-4 looks to have much less cracks. High pressure steam seems to make a role of generating macro-cracks in oxide during oxidation.

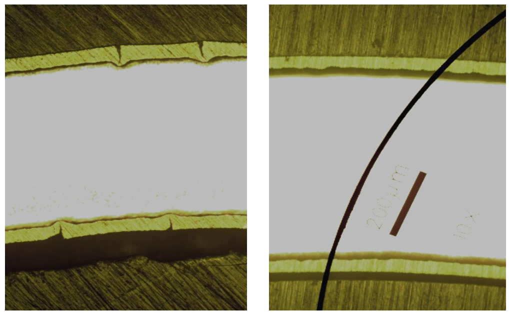

Figure 4. Cross sectional view of specimens oxidized at 800℃, 10.0MPa
(Left : high-Sn Zry-4, Right : low-Sn Zry-4)

4. Conclusion

Steam pressure effects on high temperature oxidation of Zr-alloy were studied. The oxidation of high-Sn Zry-4 was accelerated by high steam pressure. But low-Sn Zry-4 was decreased enhancement of oxidation. And Nb containing alloy has little or no effect of high steam pressure. Also microstructure differences affect the oxidation behavior under high pressure steam. Therefore, Acceleration of oxidation depends on alloy composition, contents, and manufacturing process.

Acknowledgment

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