High Temperature Oxidation of a Zirconium Base Alloy in Steam

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1. Introduction

Zr-base alloys are used as cladding materials for nuclear fuel in light and heavy water reactors. Zircaloy-4 (Zry-4) has been used satisfactorily as a cladding material in pressurized water reactors. Nowadays, light water reactors tend to extend their fuel cycle length with high burn-up of nuclear fuel to get the improved economy. Zry-4 may not satisfy the required safety margin for the high burn-up fuel, and more corrosion-resistant Zr-base cladding materials are being developed. One direction for the development of new Zr-base alloys is addition of Nb in alloying elements.

At high temperatures, the exothermic reaction of Zr-base alloys with steam is always a concern for the safety of nuclear power plants during accidents like a loss-of-coolant accident. The Nuclear Regulatory Commission still uses the same criteria, which are applied to conventional Sn-added Zr claddings, for the safety analysis of newly developed Nb-added Zr base alloys. So, it is needed to check the difference in the kinetics of high-temperature oxidation in between Nb-added and Sn-added Zr alloys. In the present paper, we compare the characteristics of Sn-added Zr-alloy (Zry-4) and those of Nb-added alloy (Zr-1%Nb alloy), especially at high temperature oxidation.

2. Experimentals

We selected two types of specimens, i.e., Zry-4 as a Sn-added alloy and Zr-1%Nb alloy as a Nb-added alloy in the experiments. Zry-4 tubes are the commercial tubes of Westinghouse, and used in the as-supply state. The tubes were cut to specimens of the height of about 15mm. Each specimen was degreased and pickled in aqueous HF/HNO$_3$ solution, then cleansed in hot and cold water. The main alloying elements of Zry-4 are Sn, Fe and Cr, while those of Zr-1%Nb alloy are Nb, Sn, and Fe.

High temperature oxidation tests were done under 1 atm steam in a vertical heater, where a specimen is hung by a Pt-wire. When the goal temperature is obtained and the steam flow through the alumina tube inside heater becomes stabilized, the specimen is inserted into the center of the tube and pulled out of the tube after the desired oxidation is reached. The temperature range is in between 700 and 1200°C. The steam flow rate is about 10g/min.

The steam flow rate is about 10g/min. The steam-pressure dependency of Zr-alloys on the oxidation at high temperatures was also observed. The dependency was obtained by an experimental setup that consists of two vessels and two resistance heaters (Fig.1). The outer vessel is used for maintaining high-pressure steam during the experiment. The vessel is heated up to 400°C, and the steam pressure is controlled by the amount of water inside the vessel up to 150bar steam. Once the steam pressure is stabilized, the resistance heater surrounding the specimen inside the inner vessel is on. The specimen is heated up to the set-up temperature (700-900 ^{o}C) rapidly by the resistance heater. The heat up rate of the specimen is about 3 ^{o}C/sec, and oxidation time was set to 1500sec.
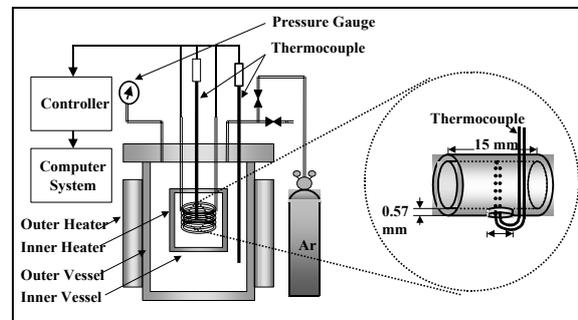
Figure 1. Experimental setup for high-pressure steam oxidation

After oxidation test, the specimen is molded, grounded and polished for the optical microscopic observation. For the micro-structural evaluation, sometimes the polished section was wipe-polished by etchant. The thickness of oxide and that of alpha-layer are determined by the photos from optical microscope.

3. Results and Discussion

The oxidation test at 1 atm steam is shown in Fig.2. The symbols (solid lines) indicate the weight gains of Zr-1%Nb alloy specimens with time and the dashed lines are those of Zry-4. Below 900°C, transition points are observed in both alloys. Parabolic rate law is always applicable before transition in Zr-1%Nb alloy. The weight gain of Zr-1%Nb alloy at atmospheric steam can be formulated by the following equations.

Before transition, the weight gain (ΔW) becomes;
$$\Delta W = K_p \sqrt{t}$$
where $K_p = 7.139 \times 10^4 \exp\left(\dfrac{-10,665.7}{T(K)}\right)$

and ΔW : mg/dm2, t : sec.

After the transition point (below 900°C), the weight gain becomes;

$$\Delta W = Wt + K_1(t - t_T)$$

where

$$Wt = 1.286 \times 10^7 \exp\left(\frac{-11,964}{T(K)}\right)$$

$$K_1 = 1.51 \times 10^2 \exp\left(\frac{-8,303}{T(K)}\right)$$

$$t_T = 3.23 \times 10^4 \exp\left(\frac{-2,579}{T(K)}\right)$$

The above kinetic equation is denoted as solid lines in Fig.2. The oxidation kinetics of Zr-1%Nb alloy is somewhat different from those of Zry-4.[1-2]
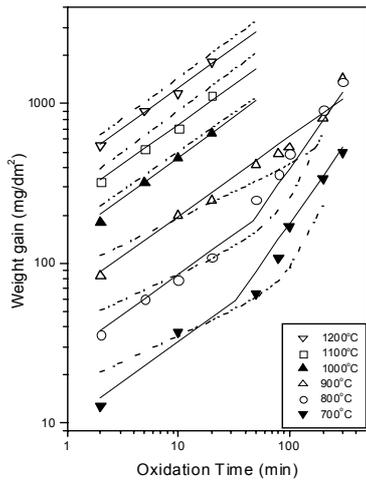
Figure 2. Weight gain of Zr-1%Nb alloy in Steam. (dashed lines:Zry-4)

The results of oxidation enhancement by high-pressure steam are shown in Fig.3 and 4. The oxidation time is set 1500sec. The oxidation enhancement depends exponentially on the steam pressure. The dependency of Zr-1%Nb alloy is much smaller than that of Zry-4 (Fig.4).[3-4]
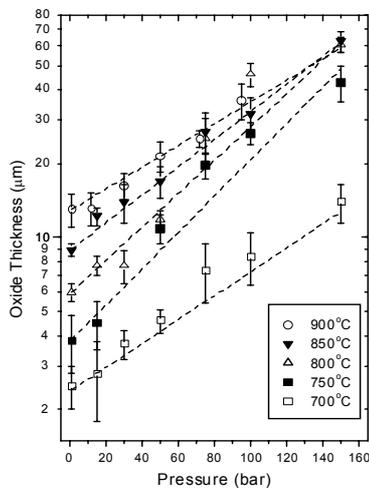
Figure 3. Steam pressure effects on the oxidation of Zry-4.
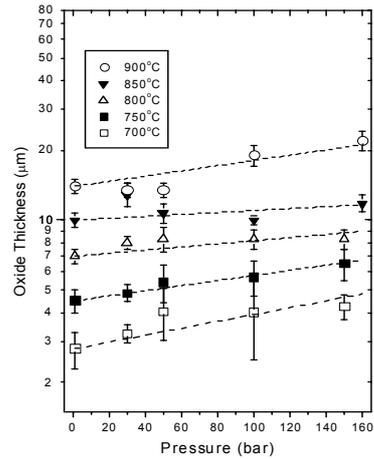
Figure 4. Steam pressure effects on the oxidation of Zr-1%Nb alloy.

4. Conclusion

High temperature steam oxidation behaviors of Zr-1%Nb alloy and Zry-4 were compared. Oxidation kinetics of Zr-1%Nb alloy at atmospheric steam pressure, follows parabolic-rate law, instead of cubic-rate as was observed in Zry-4 below 900 °C. The oxidation rate of the Zr-alloy is comparable to that of Zry-4 below 900 °C , however, is slightly lower than Zry-4 above 1000 °C.

Steam pressure effects on high temperature oxidation of both Zr-1%Nb alloy and Zry-4 were measured. Zry-4 was very sensitive to the steam pressure, and the oxidation rate increases exponentially with applied steam pressure. Contrary to Zry-4, Zr-1%Nb alloy was less sensitive to the high-pressure steam.

Acknowledgment

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