Kinetics of Zr-alloy Cladding Oxidation in a Mixture of Air and Steam at 1200°C

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1. Introduction

In high burn-up PWR reactors, zirconium-based alloys are widely used as cladding material for fuel rods. This is because Zr alloys have a low neutron absorption cross-section, good corrosion resistance in various operating conditions, and satisfying mechanical properties. As demonstrated by the Fukushima accident in reactor 4, the integrity of the fuels stored in a wet storage pool is an important issue. To analyze the problem, we have to know the details related to the oxidation kinetics of the fuel claddings in a mixture of air and steam at high temperatures. Many oxidation experiments of Zr alloys with air and steam have been studied, but there have been not enough available data about performance in a mixture of air and steam. The goal of the study is to obtain fundamental data to develop a calculation tool for the analysis of failure in the wet storage pool accident.

2. Experiment

2.1 Materials.

Zircaloy-4 and Zirlo tubes used in commercial nuclear power plants were used in this study. Cladding tubes were cut by a cutter to be 10~12mm long with 2 holes (Φ3.1mm hole) near the top. They were cleaned and etched before the test.[1]

Table I: Chemical composition of specimen

(wt%)	Zr	Nb	Sn	Fe	Cr
Zry-4	bal.	-	1.35	0.2	0.1
Zirlo	bal.	1.0	1.0	0.1	-

2.2 Experimental procedures

The apparatus for this study is shown in figure 1. It consists of a furnace containing an alumina furnace tube and electronic heater. To make the setting the air-steam partial pressure, each air contents in Ar gas was different. Assuming that the temperature is 30℃, then the vapor pressure is 32.824 mmHg and saturated vapor pressure is 760mmHg. Table Ⅱ.shows the air to steam ratio and the percentage Ar.

Table Ⅱ: Each air content in Ar gas.

Air : Steam	9:1	7:3	5:5	3:7	1:9
Air content in Ar (%)	40	10	4.2	2	0.5

Ar gas was passed through a bubbler (30℃ maintenance) supplying the Ar gas with heavy moisture. In the tube furnace, there is an alumina tube in the center and the heater surrounds the tube. The furnace maintained a fixed temperature (1200℃), and we put the specimens in the center of the tube. After an experimental time passed, the specimen was pulled out. The weight of each specimen was measured before and after the experiment. The microstructures of the polished surface of the specimen were observed using an optical microscope.

Fig. 1. Apparatus (tube furnace) for high temperature oxidation of Zr alloys.

3. Results

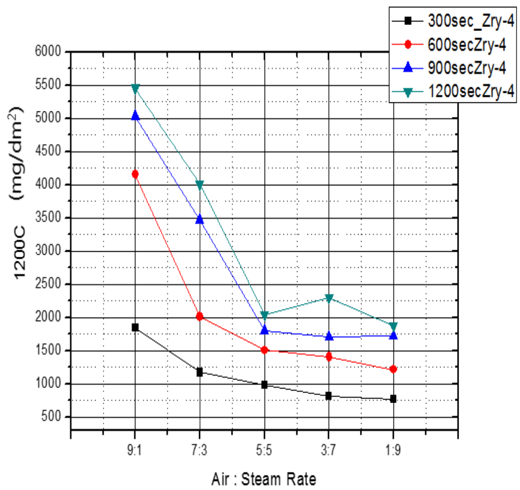

Fig. 2. Experimental results of the weight gain of Zry-4 at 1200°C in each condition.

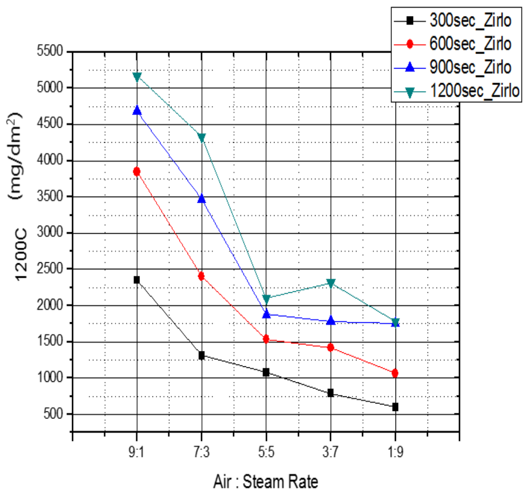

Fig. 3. Experimental results of the weight gain of Zirlo at 1200°C in each condition.

The experimental temperature was 1200℃ and 7 different steam-air mixture conditions were used this study. (air : steam=10:0, 9:1, 7:3, 5:5, 3:7, 1:9, 0:10). The oxidation rate in air is higher than that in steam. The nitride was found in the oxidized cladding only in air.

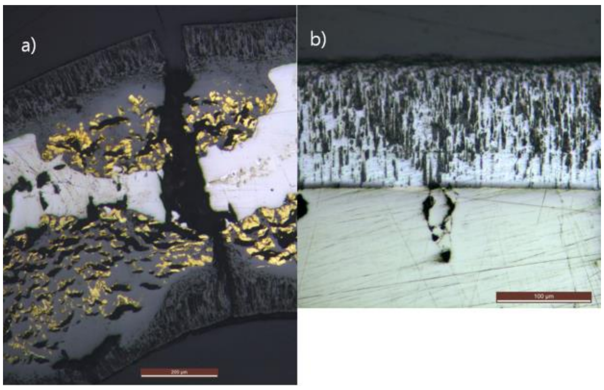

Fig. 4 Zry-4 specimen oxidized in (a) air and (b) steam at 1200℃

Cracks in oxide film act as funnels and nitrogen causes the creation of nitride. The oxide film near the nitride seems unprotected equiaxial oxide layer not columnar oxide layer [2, 3]. These nitrides in the metal layer destroy the protective oxide layers and increase oxidation rate. In the reaction of Zr with oxygen, the theory is that it generates oxide film, not nitride because free energy is lower than in a reaction of Zr with nitrogen. Thus, oxygen cannot penetrate the metal because of the oxide layer and the formation of nitride can be described by the nitrogen reaching the metal layer through the oxide layer. Oxidation rate and the amount of nitrogen reaching the metal layer will be proportional to the partial pressure of nitrogen. Results also show that as the air content (nitrogen content) in the mixture increased, the oxidation rate also increased and became close to that in the air. It formed an oxide film for a short time and cracks formed nitride as a funnel with nitrogen and increased the oxidation rate. A large amount of the nitride observed in higher content air that could be based about penetration phenomenon of nitrogen.

4. Conclusion

The oxidation in the mixture of steam and air was higher than when under steam, but slower than when under air. The higher the amount of air in Ar gas, the closer the oxidation rate approached the oxidation rate in air. When we determined the engineering oxidation model under steam-air mixture conditions at high temperature, the fixation seems more proper that oxidation rate is proportional to air content in the mixture of steam and air, so that makes oxidation rate of steam-air mixture conditions approach oxidation rate in air . In addition, the higher the air concentration, the more nitrides were found inside the metal. The amount of nitrogen that reached metal layer was proportional to the partial pressure of nitrogen. This may be evidence for the oxide permeability of nitrogen.

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