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Enhanced high-temperature oxidation resistance of a zirconium alloy cladding by high-temperature preformed oxide on the cladding

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ABSTRACT

Using a zirconium alloy, pre-oxidation was conducted at 1200 °C in a steam environment, and the pre-oxidised specimens were oxidised at 1012, 1100, and 1200 °C. The preformed oxide enhanced the oxidation resistance significantly during the subsequent oxidation at 1012 and 1100 °C. In addition, the preformed oxide enhanced the breakaway oxidation resistance greatly at 1012 °C. The microstructures of the preformed oxide were analysed using TEM and EPMA. The oxidation resistance enhancement may be related to the large columnar grain width of the preformed oxide and Zr-Sn type precipitates formed at the grain boundaries.

1. Introduction

Zirconium alloys are widely used as fuel cladding materials in nuclear power plants. Although the zirconium alloys show good performance during normal operation, they have some disadvantages during accident conditions such as a loss-of-coolant accident (LOCA). During a LOCA, coolant transforms to steam, and the temperature of the cladding increases rapidly. According to a LOCA scenario in a pressurised water reactor (PWR), the peak cladding temperature (PCT) could increase to approximately 1080 °C [1]. In this temperature range, the oxidation rate of the cladding becomes so high that the cladding can easily become brittle, and a phenomenon called breakaway oxidation can easily occur, which leads to an increased oxidation rate and rapid hydrogen absorption. In addition, after the Fukushima accident, more concerns have arisen over the accident resistance of the current zirconium alloys. To solve this problem, various ideas have been proposed to enhance the accident resistance of the cladding, and they were incorporated into the development of the accident-tolerant fuel (ATF). The ATF can be divided into three general categories [2]: zirconium alloys with improved oxidation resistance and strength, non-zirconium material with high strength and oxidation resistance, and alternative fuel forms.

The advantage of the first ATF category is that we can still utilise the zirconium alloys that have shown good performances during normal operation. One of the approaches is to create highly adherent oxidation-resistant coating layers on the surface of the zirconium alloys. Numerous coating materials such as Cr, SiO₂, Si, Ti₂AlC, and polycrystalline diamond are currently being studied [3–8], and these studies show that coating can be a promising solution. Another method that

can be applied to the current zirconium alloy cladding to enhance the oxidation resistance is pre-oxidation. Recently, it was reported that the nanostructured preformed oxide layer formed by anodization enhances the oxidation resistance significantly [9]. Moreover, it has already been shown that the preformed oxide layer decreases the extent of oxidation during simulated LOCA conditions [10–12]. It was proposed that the effect of the preformed oxide layer is due to the redistribution of oxygen from the oxide layer to the metal substrate [12]. This postulated redistribution of oxygen occurs with a reduction of the oxide thickness, and the oxygen concentration within the oxide layer is decreased [12–15]. As a result, the oxidation reaction is delayed until the oxygen concentration within the oxide layer returns to its usual level.

In this paper, a new approach to improve the effect of the preformed oxide is reported. So far, most of the previous studies have concentrated on the preformed oxide formed at normal operating temperatures (~360 °C) [11–13]. However, in our investigation, we found that the preformed oxide that was formed at a higher temperature (1200 °C) enhances the oxidation resistance much more significantly than the preformed oxide that was formed at the normal operating temperature. The enhancement of the oxidation resistance by the preformed oxide was verified by testing the pre-oxidised specimens at 1012, 1100, and 1200 °C under steam conditions. The enhancement of the oxidation resistance was confirmed by checking the onset of the breakaway oxidation and comparing the amount of oxidations with those of the non-pre-oxidised specimens. Then, the preformed oxide was examined using optical microscopy (OM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron probe micro-analysis (EPMA).

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Table 1
Chemical composition of the zirconium alloy used in this study.

Element	Zr	Nb	Sn	Fe
Composition, wt.%	Balance	0.96	0.99	0.12

2. Material and methods

2.1. Specimen preparation

The chemical composition of the zirconium alloy used in this study is given in Table 1. Each specimen was cut from cladding tubes; the length was 40 mm, the outer diameter was 9.5 mm, and the thickness was 0.57 mm. After cutting, the edges of the specimens were carefully ground using silicon carbide paper (320 grit). Then, the specimens were cleaned using Alconox, ethanol, and acetone in an ultrasonic cleaner.

2.2. Oxidation test

After the specimens were prepared, pre-oxidation and subsequent oxidation were performed in the test system shown in Fig. 1 by the same method [16]. A specimen was placed between the alumina specimen holders to prevent a reaction between the specimen and the Inconel holder during oxidation tests. Steam was generated from the bottom of the equipment by a steam generator, and it flowed through the inside and outside of the specimen, so that both sides of the specimen were oxidised. The steam flow rate was controlled to be about $3.5 \text{ mg}/(\text{cm}^2 \text{ s})$.

Before starting an oxidation test, the system was purged with steam for 15 min to make the steam atmosphere, and the steam flow was supplied continuously during the test. Then the specimen was heated using the radiant heating. The temperature histories of the specimens during the oxidation at 1012, 1100, and 1200 °C are shown in Fig. 2. The temperature of the specimen was measured by putting an R-type thermocouple to the surface of the specimen; the thermocouple was fixed in place by using a molybdenum wire. The experiments shown in Fig. 2 were performed only to confirm how the temperatures of the specimens are controlled with respect to the control thermocouple fixed to the Inconel holder. In other words, actual experiments were

performed without putting the R-type thermocouple to the specimen surface since the direct contact with the specimen and the R-type thermocouple can affect oxidation behaviour. During the heating in Fig. 2, the temperatures of the specimens were increased to 320 °C and maintained at 320 °C for 100 s for the stabilization of the specimen temperatures [17]. Then the specimens were heated to the target temperatures with the initial heating rate of 50 °C/s; the heating rates were decreased as the temperatures of the specimens were increased. According to an accident scenario [1], the cladding temperature could be increased to 954 °C within 30 s. To simulate this kind of accident condition, the specimens were heated from 320 °C to the target temperatures within 30 s in our experiments; the average heating rates during the 30 s were about 32, 31, and 27 °C/s during the oxidation at 1012, 1100, and 1200 °C, respectively.

After the heating, the specimens were oxidised isothermally. During the isothermal oxidation periods at 1012, 1100, and 1200 °C, the maximum temperature variations were about 7, 5, and 11 °C, respectively. The oxidation temperatures of the specimens used in this study were defined by averaging the measured temperatures in the isothermal oxidation periods in Fig. 2. When we perform oxidation tests for different times, the isothermal oxidation times were adjusted accordingly. After the tests were finished, the specimens were cooled by the steam flow to the room temperature (25 °C); the initial cooling rate was measured to be about 30 °C/s. Then, the weight gains of the specimens were measured using an electronic mass balance with a precision of 0.1 mg.

2.3. Test matrix and post-analysis

The test matrix for the non-pre-oxidised and pre-oxidised specimens are shown in Table 2. The non-pre-oxidised specimens were oxidised at 1100 and 1200 °C for the listed oxidation times. These tests were performed to compare with the test results of the pre-oxidised specimens. For the pre-oxidised specimen, the pre-oxidation was performed at 1200 °C for 270 s, and nine pre-oxidised specimens were produced. These pre-oxidised specimens were subsequently oxidised at 1012, 1100, and 1200 °C for the listed oxidation times.

After the tests, the preformed oxide was analysed using OM, SEM, TEM, and EPMA. OM and SEM were used to observe whether the preformed oxide is uniform over the entire surface and whether the

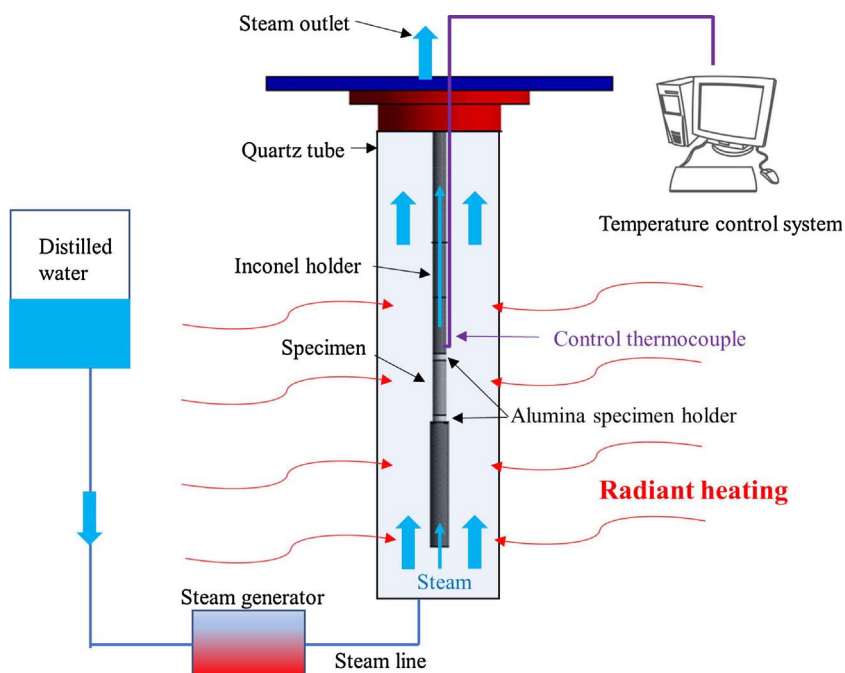


Fig. 1. Schematic of the test system used for the oxidation test [16].

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