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Influence of dissolved hydrogen on the early stage corrosion behavior of zirconium alloys in simulated light water reactor coolant conditions

Taeho Kim, Kyoung Joon Choi, Seung Chang Yoo, Yunju Lee, Ji Hyun Kim*

Department of Nuclear Engineering, School of Mechanical, Aerospace, and Nuclear Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Eonyang-eup, Ulju-gun, Ulsan 44919, Republic of Korea

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ABSTRACT

The dissolved hydrogen concentration in the water phase represents a key factor for corrosion characteristic of zirconium alloy. A zirconium alloy was oxidized for 100 d at two different concentrations, 2.49 and 4.15 mg/kg. In situ Raman peaks of the specific oxide phases changed, indicating the occurrence of phase transformation. Moreover, the result of transmission electron microscopy was compared with in situ analysis of the oxide structure formed on the zirconium alloy. The phase stability of the oxide could be influenced by the dissolved hydrogen, and it the phase transformation from tetragonal to monoclinic is influenced by dissolved hydrogen.

1. Introduction

Zirconium alloys are used as fuel cladding materials in nuclear power plants, owing to their low thermal neutron capture cross section and good corrosion resistance under high-temperature aqueous conditions [1]. Zirconium fuel cladding plays an important role in the nuclear power plants, because it protects the environment from radioactive materials including enriched uranium, fission products, and fission gas. However, the degradation of zirconium alloys in harsh conditions could cause severe accidents in nuclear power plants and also prevents high burn-up operation of the reactor [2,3]. The importance of the corrosion characteristics of zirconium alloy, including high-temperature corrosion and steam oxidation, has become a major focus of nuclear power plant operation.

It has been reported that an inward diffusion of oxygen ions from the surface to the oxide/metal interface takes place during the corrosion process [4]. In the early stages of oxidation, a thin and dense layer of tetragonal zirconium oxide with a small and equiaxed grain was formed as a result of the high compressive stress near the oxide/metal interface [5,6]. It was also reported that the protective barrier oxide was formed before the transition, and the tetragonal zirconium oxides become columnar to minimize the stress accumulation [7]. As the oxidation time increases, the thickness of the zirconium oxide layer also increases, and the compressive stress decreases with the distance from the metal/oxide interface, resulting in the phase transformation of zirconium oxide from tetragonal to monoclinic [8–11].

The oxide/metal interface region plays an important role in the mechanism of zirconium oxidation, because the diffusion of oxygen or

hydroxyl ions takes place in this region [12]. Moreover, the characteristics of the oxide/metal interface, such as the absence of cracks and the slower rate of oxygen diffusion in this region, critically affect the corrosion rate [13]. The zirconium oxide layer near the oxide/metal interface region mostly consists of the tetragonal phase, and it has been reported that this phase can be stabilized by four different factors: grain size, compressive stress, solute elements acting as a stabilizer, and oxygen vacancies [14–20]. Therefore, as the corrosion behavior of zirconium alloys is strongly influenced by the amount of tetragonal zirconium oxide phase present, controlling the phase transformation processes through the above factors can be used to limit the corrosion of the alloy.

To mitigate corrosion in structural materials (including nickel-based alloys and stainless steel) used in nuclear power plants, a number of recent studies focused on the control of the water chemistry in the primary coolant loop [21,22]. In particular, the concentration of hydrogen dissolved in primary coolant is maintained as 2.49 mg/kg at standard temperature and pressure for decreasing the dissolved oxygen concentration. Furthermore, previous research revealed that the high dissolved hydrogen level could influence on the susceptibility of stress corrosion cracking and crack growth rate of the structural materials for the pressurized water reactor [23–25]. But there is not enough data available on the effect of high dissolved hydrogen concentration on zirconium oxide and its phase transformations. Previous studies have addressed the role of oxygen ions and water species in the phase transformation of zirconium oxide in high-temperature water [26,27]. Nonetheless, the relationship among dissolved hydrogen, zirconium oxide phase, and corrosion behavior of zirconium alloys remains to be investigated.

* Corresponding author.

E-mail address: kimjh@unist.ac.kr (J.H. Kim).

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Our previous studies [28,29] investigated the effect of dissolved hydrogen on a zirconium alloy oxidized for 150 h, but the analysis was limited to the corrosion behavior in the early-stage oxidation. Moreover, the corrosion behavior of zirconium alloys in high-temperature hydrogenated water has not been fully explored so far, even though the influence of the water chemistry on the corrosion mechanism of these alloys has been widely investigated [30,31]. Therefore, in this work we investigated the influence of the dissolved hydrogen concentration on the corrosion behavior of zirconium oxide during long-term oxidation. Therefore, the experimental conditions were set as two different hydrogen levels: 2.49 mg/kg at standard temperature and pressure, as representative of normal pressurized water reactors, and 4.15 mg/kg at standard temperature and pressure, as representative of high concentrations of dissolved hydrogen. In situ Raman spectroscopy was employed to determine the phase composition of zirconium oxide during oxidation with two different dissolved hydrogen concentrations. In addition, transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) analyses were employed to investigate the microstructure of zirconium oxide. In order to characterize the corrosion resistance corresponding to different dissolved hydrogen concentrations, the thickness of the zirconium oxide layer was measured after each corrosion test.

2. Experimental

2.1. Materials and specimen preparation

A plate of Zr–Nb–Sn alloy specimen, provided by KEPCO Nuclear Fuel Co., Ltd., was used in this study for simulating corrosion in an aqueous environment corresponding to the primary coolant loop of a pressurized water reactor. The detailed chemical composition of the Zr–Nb–Sn alloy is presented in Table 1. The dimensions of the Zr–Nb–Sn plate were 40 mm × 40 mm × 0.65 mm. The plate was ground with SiC paper up to 800 grit, polished with a diamond paste of at least 1 μm, and polished with 0.05 μm colloidal silica to produce a flat surface with minimal mechanical deformation.

2.2. Water chemistry control

In order to simulate the water chemistry in the primary coolant loop of a pressurized reactor, an autoclave and a loop were used to maintain a high temperature and pressure, as illustrated in Fig. 1 [29]. Using this system, the temperature and pressure of the simulated primary water of the pressurized water reactor were set to 360 °C and 20 MPa, respectively, using the main and pre-heaters and a high-pressure pump. Deionized water with a resistivity of 18 MΩ cm was mixed with appropriate chemicals to produce the primary coolant solution, which contained 1200 mg/kg B³⁺ from boric acid and 2 mg/kg Li⁺ from lithium hydroxide.

Corrosion tests in the simulated primary water coolant were conducted at two different concentrations of dissolved hydrogen: 2.49 mg/kg, representative of a primary water coolant under normal conditions, and 4.19 mg/kg, representative of a primary water coolant with high levels of dissolved hydrogen. The dissolved hydrogen content of the inlet water was strictly controlled by bubbling a mixture of argon and hydrogen gas in the water reservoir column. The dissolved hydrogen concentration was precisely measured with an Orbisphere™ sensor. Corrosion tests were conducted for 100 d for each dissolved hydrogen

Table 1

Chemical composition of the Zr–Nb–Sn alloy for this study.

Element	Nb	Sn	Fe	Hf	C	O	N	Zr
Composition (wt.%)	0.96	0.76	0.18	0.002	0.1	0.62	0.03	Balance

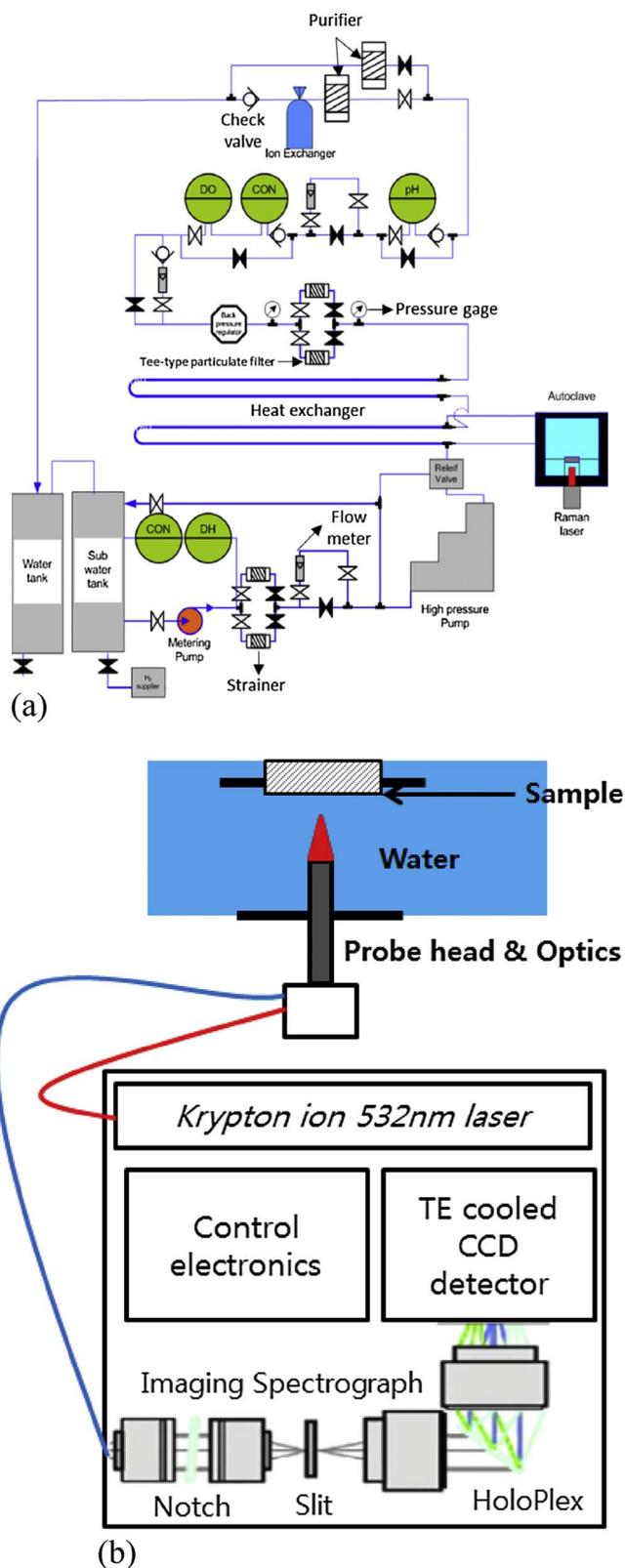


Fig. 1. Schematic illustration of the experimental system used for the zirconium alloy oxidation tests [29]. (a) Scheme of the system used for the in situ Raman spectroscopic analysis. (b) Region surrounding the Zr–Nb–Sn alloy sample in the autoclave and schematic illustration of the Raman analysis system.

level. The dissolved oxygen content was maintained to less than 5 μg/kg throughout the tests, to exclude any effect of dissolved oxygen on the present results.

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