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Phase transformation of oxide film in zirconium alloy in high temperature hydrogenated water

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ABSTRACT

The effect of the variation of the dissolved hydrogen concentration on the oxide phase transformation under high-temperature hydrogenated water conditions was investigated using in situ Raman spectroscopy. The Raman spectrum in 50 cm³/kg of dissolved hydrogen concentration indicated the formation of monoclinic and tetragonal zirconium oxide at the water–substrate interface. As the dissolved hydrogen concentration decreased to 30 cm³/kg, the Raman peaks corresponding to the zirconium oxide phase changed, indicating an oxide phase transformation. And, the results of SEM and TEM analyses were compared with those of in situ analyses obtained for the oxide structure formed on the zirconium alloy.

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1. Introduction

Zirconium alloys are frequently used as fuel cladding materials in nuclear power reactors, as these materials have very low thermal neutron capture cross-sections as well as desirable mechanical properties. However, the Fukushima accident demonstrates the importance of understanding the oxidation behavior of zirconium alloys, as they shield the radioactive materials (i.e., uranium, fission gas) and the degradation of the zirconium cladding directly contributes to severe accidents in nuclear power plants. Furthermore, zirconium oxide forms at the water–metal interface, and its structure and phase determine its mechanical properties [1–18]. Therefore, to ensure the safety of the nuclear power reactors, the corrosion mechanism and sustainability of the zirconium based alloy materials must be understood.

It has been reported that the diffusion of O²⁻ ions via anion vacancies is the key factor of the oxide growth on zirconium alloys [19,20]. In the early stages of the oxidation, the carrier transport is a rate-determining process, while the oxygen anion diffusion influences the oxidation rate later in the oxidation process [21]. The zirconium alloy oxidation kinetics can be divided in two steps:

pre-transition and post-transition. In the pre-transition period, the rate of oxidation can be parabolic or cubic, and a cyclic growth of the oxide is observed [22,23]. Then, after breakaway phenomena, the oxide growth rate assumes a linear shape due to reduced oxygen diffusion. The oxygen diffusion is reduced by the formation of nanosized cracks at or near the oxide/metal interface [24]. In addition, the oxide growth rate is influenced by the grain boundaries, which can act like the short circuit of the oxygen ion diffusion paths [25].

Investigations based on transmission electron microscopy (TEM) and Raman spectroscopy showed that there are two phases of zirconium oxide on zirconium alloys, namely, monoclinic and tetragonal [18,26–29]. The grain shapes of zirconium oxide are directly related to the zirconium oxide phase. Notably, the values of the macroscopic compressive stress near the oxide/metal interface are very high, but extend over a short distance [18]. Thus, in the region near the oxide/metal interface, the tetragonal phase is dominant; as the distance from the oxide/metal interface increases, the proportion of tetragonal zirconium oxide decreases, while that of monoclinic zirconium oxide increases [8,30–32]. The decrease of the tetragonal phase portion means that an oxide phase transformation occurs, from tetragonal to monoclinic. The tetragonal-to-monoclinic transformation has the characteristics of a martensitic transformation [33], and many previous results show that the formation of the tetragonal phase in zirconium oxide and

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its transformation to the monoclinic phase are highly related to the corrosion resistance of zirconium alloys [6,8,23,34–35].

The comprehension of the mechanism by which the water enhances the zirconium oxide tetragonal-to-monoclinic transformation is a major unsolved issue [36]. Previous experimental results show that the hydroxyl ions (OH^- ions) originated from the water ionization diffuse into the zirconium oxide lattice and fill the oxygen vacancies, lowering the vacancy concentration and destabilizing the tetragonal phase [37–40]. The mechanism behind the phase transformation of zirconium oxide in water is the following [37]. Water is chemically absorbed on the ZrO_2 surface and, by reacting with O^{2-} ions, forms OH^- ions on the ZrO_2 surface. Then, the OH^- ions penetrate the inner part by grain boundary diffusion and fill the oxygen vacancies within the grains. Finally, the tetragonal to monoclinic transformation occurs as a result of the decrease of the oxygen vacancy concentration.

The dissolved hydrogen concentration is a major issue in water chemistry, especially, in primary water chemistry of pressurized water reactors (PWRs), as the change in the dissolved hydrogen concentration can affect the corrosion mechanism of the nickel base alloy [41–43]. The effect of the dissolved hydrogen concentration on the oxide formation has been investigated by previous studies [44,45]; however, there are few studies concerning the influence of the dissolved hydrogen concentration on zirconium oxide and oxide phase transformation in a primary water environment. Therefore, in this study, the effect of the dissolved hydrogen concentration on the phase transformation of zirconium oxide is analyzed.

Most of the reported experimental work on zirconium oxide entails ex situ experiments [46–50]. Removing the specimen from the oxidation environment can, however, modify the phase and structure of the oxide formed on the zirconium alloy. Therefore, in this work, Raman spectroscopy was used for in situ investigations, as the observational system can operate at the elevated temperatures and high pressures of the aqueous environment. In situ Raman spectroscopy can identify the oxide phase and oxidation products on a metal surface, providing a comprehensive understanding of the oxidation mechanisms. The method measures the wavelength and intensity of the inelastically scattered light resulting from the excitation of the molecules when the test sample is irradiated with a laser. The discrete shift in the energy of the scattered light from that of the incident light is characteristic of the scattering material [51,52].

In previous studies [51–53], an in situ Raman system was designed to analyze oxides on nickel-based alloys and low-alloy steels in primary water environments. Here, a specific zirconium alloy was oxidized in situ at two different dissolved hydrogen concentrations, $50 \text{ cm}^3/\text{kg}$ and $30 \text{ cm}^3/\text{kg}$. In situ Raman spectroscopy was used to characterize the oxide phases at the zirconium–water interface, and the effects of the dissolved hydrogen concentration on the characteristics of the zirconium oxide were investigated. Subsequently, ex situ investigation methods such as scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM) were used to further characterize the oxide structure of the zirconium alloy.

2. Experimental

2.1. Materials and specimen preparation

A plate of the zirconium alloy ZIRLO [15,50–51], provided by KEPSCO Nuclear Fuel Co., Ltd. was used in this study, for oxidation in the primary water environment. The chemical composition of ZIRLO is presented in Table 1. The dimensions of the specimen

Table 1
Chemical composition of ZIRLO.

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

were $40 \text{ mm} \times 40 \text{ mm} \times 0.65 \text{ mm}$, and the plate was polished before oxidation.

First, SiC papers with grits 400–800 were used to polish the specimen. Next, diamond pastes of up to $1 \mu\text{m}$ were used. Finally, to minimize the mechanical transformation of the ZIRLO specimen, a $0.05 \mu\text{m}$ colloidal SiO_2 paste was used for polishing.

2.2. Experimental system

To simulate the primary water chemistry of a pressurized water reactor, a loop for the high temperature and high pressure conditions and an autoclave were used. A schematic of the complete system used for the in situ Raman spectroscopic analysis is shown in Fig. 1(a), and the region near the specimen in the autoclave is shown in Fig. 1(b). Using this system, the conditions of the simulated primary water were set as follows: temperature of 325°C using the main and pre-heaters, pressure of 18 MPa using a high pressure pump, a dissolved oxygen (DO) concentration of less than 5 ppb, and lithium hydroxide and boric acid concentrations of 2 and 1200 ppm, respectively. This was maintained during the oxidation process. The water chemistry data during oxidation, including the electrical conductivity of inlet and outlet water, the dissolved oxygen and hydrogen concentrations, and autoclave pressure and temperature, are shown in Fig. 2. The dissolved hydrogen concentration was precisely measured by an OrbisphereTM dissolved hydrogen sensor.

2.3. In situ Raman spectroscopic system

The Raman spectroscopy measurements were performed using a RamanRXNTM, manufactured by Kaiser Optical Systems, Inc., which uses a 532-nm-wavelength krypton ion laser with a maximum power of 100 mW. The irradiation area in the specimen of the Raman system was $100 \mu\text{m}^2$; the power density at the specimen was held below $10 \text{ mW}/\text{cm}^2$ to prevent damaging the specimen. The in situ Raman system consisted of four parts, including the immersion optics for moving the laser toward the sample, a notch filter for signal processing, a band-pass filter, and a charge-coupled device detector. Detailed explanations of the Raman system are presented in earlier studies [47,48]. The optical probe for in situ Raman investigation was installed in the autoclave within 1 mm of the sample, below the maximum focal length of the laser beam.

2.4. Experimental procedure

In this study, in situ Raman spectroscopic measurement was performed on ZIRLO specimen in a primary water environment. The temperature was measured by thermocouples positioned close to the specimen in the autoclave, and the ZIRLO plate specimen was oxidized under primary water chemistry conditions for 150 h. Tests were conducted in an autoclave system specially constructed for the present study. Careful consideration was given to ensuring extremely rigorous chemistry control, and near-theoretical water conductivity was achieved routinely.

Dissolved hydrogen concentration was maintained at $50 \text{ cm}^3/\text{kg}$ during the first 120 h of oxidation and then was decreased to $30 \text{ cm}^3/\text{kg}$. A detailed description is shown in Fig. 2. At the dissolved hydrogen concentration of $50 \text{ cm}^3/\text{kg}$, in situ Raman spectra were obtained after 60 h and 120 h. The Raman spectra were also measured at the dissolved hydrogen concentration

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