In situ Raman Spectroscopy of Oxide Films on Zirconium Alloy in Simulated PWR Primary Water Condition

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1. Introduction

Zirconium and its alloy have low thermal neutron capture cross section and excellent mechanical properties; therefore, they are used as nuclear fuel cladding materials in nuclear power plants. The phase of zirconium oxide is related to the mechanical properties and corrosion behaviors of zirconium oxide. To assure the safety of nuclear power plants, therefore, the mechanical property of zirconium fuel cladding and oxidation characteristic should be comprehensively understood.

Investigation based on Raman spectroscopy and transmission electron microscopy (TEM) showed that two phases of zirconium oxide - monoclinic and tetragonal phases - exist [1]. The tetragonal zirconium oxide is dominant near the oxide/metal interface, where the compressive stress is relatively higher than the middle of the zirconium oxide. As oxidation time increases, the proportion of monoclinic zirconium oxide increases while that of tetragonal zirconium oxide decreases [2].

It has been reported that in pre-transition zirconium oxide, the volume fraction of tetragonal zirconium oxide increased near the oxide/metal (O/M) interface, and the substoichiometric zirconium oxide layer was observed.[21] The diffusion of oxygen ion through the oxide layer is the rate-limiting process during the pre-transition oxidation process, and this diffusion mainly occurs in the grain boundaries[4]. The two layered oxide structure is formed in pre-transition oxide for the zirconium alloy in high-temperature water environment. It is known that the corrosion rate is related to the volume fraction of zirconium oxide and the pores in the oxides [5]; therefore, the aim of this paper is to investigate the oxidation behavior in the pre-transition zirconium oxide in high-temperature water chemistry.

In this work, Raman spectroscopy was used for in situ investigations for characterizing the phase of zirconium oxide. In situ Raman spectroscopy is a well-suited technique for investigating in detail the characteristics of oxide films in a high-temperature corrosion environment. In previous studies [6,7], an in situ Raman system was developed for investigating the oxides on nickel-based alloys and low alloy steels in high-temperature water environment. Also, the early stage oxidation behavior of zirconium alloy with different dissolved hydrogen concentration environments in high temperature water was treated in the authors' previous study [8]. In this study, a specific zirconium alloy was oxidized and investigated with in situ Raman spectroscopy for 100 d oxidation, which

is close to the first transition time of the zirconium alloy oxidation. The ex situ investigation methods such as transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) were used to further characterize the zirconium oxide structure.

2. Experimental

2.1 Materials and specimen preparation

A plate of the zirconium alloy, provided by KEPCO Nuclear Fuel Co., Ltd., was used for the oxidation experiment in the primary water chemistry of pressurized water reactor. The chemical composition of the zirconium alloy is presented in Table. 1.

Table. 1 Chemical composition of zirconium alloy

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

The dimensions of the plate zirconium alloy specimen for in situ Raman specimens were $40 \times 40 \times 0.65$ mm^3 and the specimens were polished before oxidation. First, grits 400 to 800 SiC papers were used to polish the specimen. Next, diamond pastes of up to 1 μm and colloidal SiO_2 were used for minimizing the mechanical transformation of specimens.

2.2 Experimental system

For simulating the primary water chemistry of a pressurized water reactor, a loop and an autoclave for high temperature and pressure conditions were used. The detailed explanation about the system is illustrated in the authors' previous study [8].

Using this system, the conditions of the simulated primary water environment were set as follows: temperature of 360 ℃, pressure of 19 MPa, dissolved oxygen concentration of below 5 ppb, and boric acid and lithium hydroxide concentrations of 1200 ppm and 2 ppm, respectively. These conditions were maintained during the oxidation process, for a total of 100 d.

The Raman spectroscopy measurements were made using a RamanRXN^{TM}, manufactured by Kaiser optical systems Inc., which used 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 μm^2 and the power density at the specimen was less than 10 mW/cm^2 to prevent the damage on the specimen. The in situ Raman system consists of four parts, and

these include 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. A detailed explanation about Raman system is shown in earlier studies [6,7]. The optical probe for in situ Raman was installed in the autoclave within a distance under 1 mm, which is lower than the maximum focal length of laser beam.

2.3 Experimental procedure

In this study, in situ Raman spectroscopic measurement was performed on zirconium alloy specimen in primary water environment. The temperature was measured by thermocouples positioned close to the specimen in the autoclave, and the zirconium alloy plate specimen was oxidized under primary water chemistry conditions for 100 d. 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.

The in situ Raman spectra were measured after 30, 50, 80, and 100 d from start-up. During each Raman spectrum measurement, the in situ Raman spectrum was recorded over a period of 30 min and it was repeated 2 times for increasing the signal-to-noise ratio. The ex situ investigation, it was performed to characterize the oxide layer of specimens using several instruments like SEM, EDS, and TEM. For TEM analysis, focused ion beam (FIB) method is used for making analysis sample. To prevent the surface contamination from impurities and ion beam damage during the FIB process, the specimen surface was coated with sputtered carbon before gallium ion milling. Finally, the in situ and ex situ results were compared for a comprehensive understanding of the zirconium oxide characteristic.

3. Results and Discussion

3.1. In situ Raman spectroscopy of zirconium alloy in simulated PWR primary water

Figure 1 shows the in situ Raman spectra of the zirconium alloy specimen oxidized for 100 d while the DH concentration was maintained at 30 cm³/kg. The baseline correction method was applied to remove the baseline drift caused by fluorescence. From this method, it is possible to obtain the better Raman spectrum. The strong intensity peaks, originating from sapphire window and boric acid, are marked in the spectrum.

The Raman peaks at 414, 430, 575, and 747 cm^{-1} could be attributed to sapphire window and these are produced by the tip of the Raman laser optical probe. Also, the peak observed in the range of $860 - 870$ cm^{-1} corresponds to the boric acid which is dissolved in the simulated primary water [7,9,10]. The line in black is the Raman spectrum of the zirconium alloy specimen oxidized after 30 d, and the lines in blue, red, and purple are the spectra after 50, 80, and 100 d, respectively.
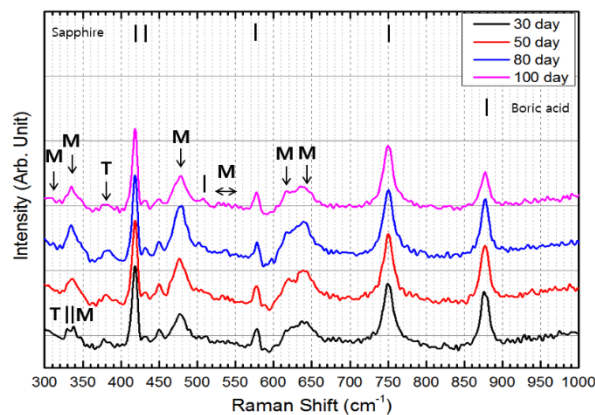

Figure 1. In situ Raman spectra of oxidized zirconium alloy specimen at four different oxidation times in primary water containing 30 cm³/kg of dissolved hydrogen concentration

After 30 d oxidation, the tetragonal zirconium oxide peaks are about 330 and 380 cm^{-1}. When the oxidation time increases to 50 d, the tetragonal zirconium oxide peak at 330 cm^{-1} is merged with the monoclinic zirconium oxide. Also, the tetragonal zirconium oxide peak which is positioned about 380 cm^{-1} became weak. The monoclinic zirconium oxide peak about $620 - 640$ cm^{-1} is shown in 30 d; however, it is not distinct, compared to 50, 80, and 100 d Raman spectra. As oxidation time increases, Raman peaks of monoclinic zirconium oxide become obvious, and this stands for the development of monoclinic zirconium oxide phase.

3.2 Oxide Film Characterization Formed on the Zirconium Alloy

In this study, the oxide films on zirconium alloy specimens, oxidized for 30, 50, 80, and 100 d at 30 cm³/kg, dissolved hydrogen concentrations, and were investigated by high-resolution TEM. The results were as follows. Figure 2 shows the TEM images of oxidized zirconium alloy's cross section after 30 d oxidation.

After 30 d oxidation, the oxide thickness increased to 0.88 μm. For investigating the phase of zirconium oxide at specific position, the Fast Fourier transform (FFT) analysis was conducted from positions "A" and "B" which are marked with a red box in Figure 2. The middle oxide which can be represented as A is analyzed as monoclinic, and the O/M interface, which can be represented as "B" is analyzed as tetragonal zirconium oxide phase. It is well-matched with in situ Raman spectroscopy results. The oxide thickness is below 1 μm; therefore, the tetragonal zirconium oxide peak can be shown in Raman spectrum after 30 d. Figure 3 shows the TEM-EDS analysis results, and it shows that the oxide thickness is around 800 nm. Also the Nb precipitations are shown in the zirconium oxide and the zirconium alloy matrix.
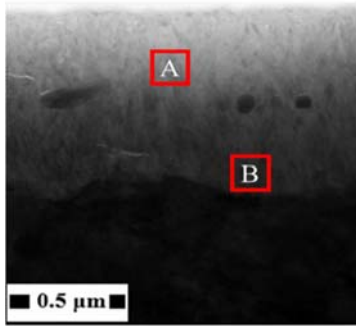
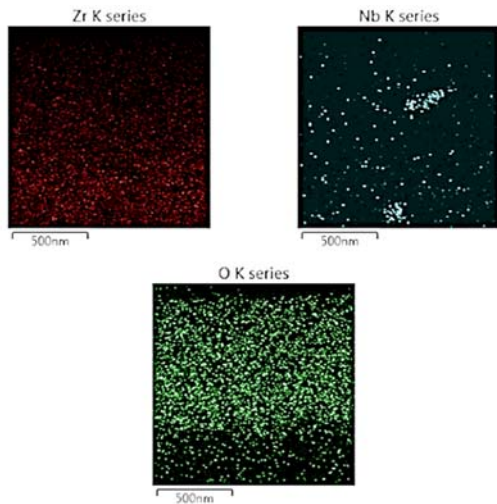Figure 2. TEM image of oxidized zirconium alloy after 30 d oxidation

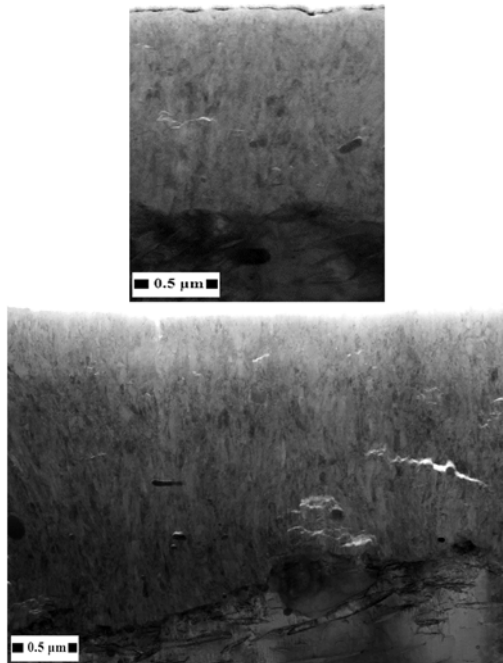Figure 3. TEM-EDS analysis results of oxidized zirconium alloy after 30 d oxidation

Figure 4. TEM image of oxidized zirconium alloy after 50 d (upper), and 80 d (lower) oxidation

Figure 4 is the TEM image of oxidized zirconium alloy after 50 and 80 d, respectively. The oxide thickness is increased from 1.46 μm to 2.27 μm as oxidation time increases from 50 d to 80 d. The FFT analysis was conducted in several regions including top and middle oxide layers and O/M interface. Top and middle oxides are analyzed as monoclinic, and O/M interface is tetragonal oxide. Tetragonal zirconium oxide is not found in the Raman spectra after 50 and 80 d oxidation because the thickness of zirconium oxide is thicker than the penetration depth of Raman laser.

The oxide thickness is increased to 2.44 μm as oxidation time increases to 100 d. The d-spacing of positions "A," "B," and "C" are explained, and the zirconium oxide phases located at these three sites are determined using JCPDS diffraction reference data (37-1484, 42-114, 50-1087; zirconium oxide).
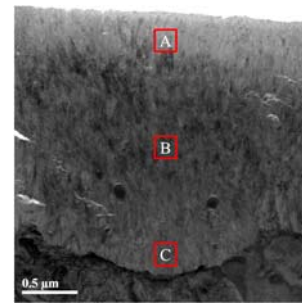

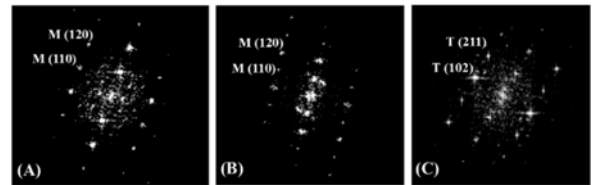Figure 5. TEM image of oxidized zirconium alloy after 100 d oxidation

Figure 6. FFT images of positions "A," "B," and "C" marked in Figure 5

The FFT analysis results show that the oxide phase of positions "A" and "B" are monoclinic zirconium oxide, especially (110) and (120) planes. This means that the top and middle regions of zirconium oxide are monoclinic dominant zirconium oxide. The tetragonal zirconium oxide, which has (102) and (211) planes, is shown in position "C," which represents the O/M interface. It shows that the tetragonal zirconium oxide is always positioned near the O/M interface during the zirconium oxidation process.

Figure 7 shows the TEM-EDS analysis results of oxidized zirconium alloy after 100 d. It shows that the oxide thickness increased to around 2.5 μm and some cracks were positioned in the zirconium oxide layer.

3.3 Phase transformation of zirconium oxide

Previous researches explained that the tetragonal zirconium oxide, which is positioned at the O/M interface, makes effects on the corrosion resistance of the zirconium alloys, and the stress relaxation is the main reason of the zirconium oxide phase transformation [2,11]. The transformation could be completed as the

following sequences. First, the water molecules are absorbed in the zirconium oxide surface. Next, the hydroxyl ions are formed due to the reaction of water and zirconium oxide. These hydroxyl ions are diffused into the inner part of zirconium oxide via the grain boundary of zirconium oxide, while the oxygen vacancies of zirconium oxide are annihilated by the hydroxyl ions. Due to the hydration of water molecule, the hydroxyl ions are made and their concentration could be influenced by the dissolved hydrogen concentration [12]. The concentration of hydroxyl ion is influenced by the dissolved hydrogen concentration, and it could enhance the transformation of zirconium oxide from tetragonal to monoclinic [8].
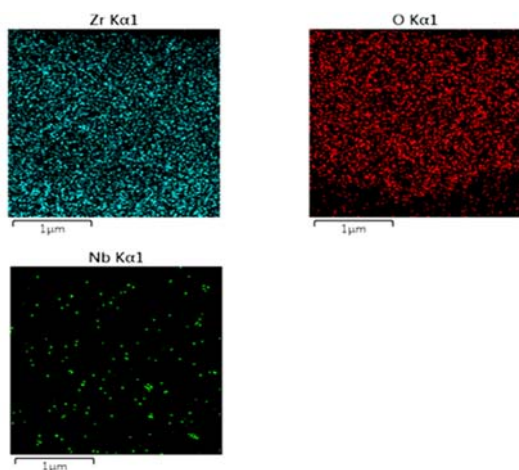

Figure 7. TEM-EDS analysis results of oxidized zirconium alloy after 100 d oxidation

It has been reported that the tetragonal zirconium peak could be identified from the Raman spectroscopy; however, the oxide phase change due to the oxidation time was not treated. It is noticeable that the phase transformation of zirconium alloy could be observed via in situ Raman spectroscopy with the relatively long term oxidation experiment for 100 d. It has been shown by TEM, X-ray diffraction, and Raman spectroscopy that the tetragonal zirconium oxide is near the O/M interface in pre-transition regime while it is hardly measured in the post-transition state. As mentioned above, the in situ Raman spectroscopy reveals that the oxide characteristic and phase transformation of zirconium alloy in high temperature water could be verified.

4. Conclusions

In this study, in situ Raman spectroscopy was conducted for investigating the phase transformation of zirconium alloy in primary water. From this study, the following conclusions are drawn:

1. The zirconium alloy was oxidized in primary water chemistry for 100 d, and the in situ Raman spectra were measured after 30, 50, 80, and 100 d from start-up. At the early stage of oxidation, the tetragonal zirconium oxide peaks showed in Raman spectra.

2. As oxidation time increased, the Raman peaks of tetragonal zirconium oxide were merged or became weaker. However, the monoclinic zirconium oxide peaks became distinct.

3. Ex situ analysis including TEM and FFT showed that the zirconium oxide mostly consisted of the monoclinic phase. The tetragonal zirconium oxide was just found near the O/M interface and this could explain the Raman spectra difference between the 30 d result and others.

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