In-situ Oxide Analysis on the surface of Zr-alloy in PWR Primary Water Environment using Raman Spectroscopy

Jong Jin Kim[1], Seung Hyun Kim[1] and Ji Hyun Kim[1]

[1]Interdisicplinary School of Green Energy, Ulsan National Institute of Science and technology(UNIST)
UNIST gil-50, Ulju-gun, Ulsan. 689-798, Republic of Korea

[*]Corresponding author: kimjh@unist.ac.kr

1. Introduction

Zirconium based alloys are widely used as the cladding materials in a light water reactors (LWR). It is because that the Zirconium alloys have good mechanical properties and small neutron absorption cross section. The oxidation of the Zr-alloys used in nuclear power plants is main issue to ensure its safety.

Zirconium-oxide consists in three crystalline forms; the monoclinic α-phase at low temperature, the tetragonal β -phase above 1400K and the cubic γ-phase above 2600K [1]. Generally, the crystalline zirconium-oxide exists in the monoclinic phase at room temperature. However, the cubic phase can be stabilized at lower temperature by the enhanced formation of vacancies in the anion sublattice [2].

The changes in the crystalline forms of the Zirconium oxide show different mechanical properties and corrosion resistance. Therefore, the investigation of oxidation behavior of Zr-alloys in nuclear power plants is necessary to operate the nuclear power plant in safe way.

The Raman spectroscopy is the measurement of the inelastic scattered wavelength and intensity from the each molecule. The Raman spectroscopy can identify the oxidation products and oxide films on surface of the metal and alloys by 'in-siu' investigation. It can give a clear result of oxidation formation as function of time. There are several studies about in-situ method of aqueous corrosion were conducted for metals and alloys at elevated temperature in pure water and LWR environments [3-7].

Especially, Maslar et. al [8] conducted the in situ Raman spectroscopic investigation for Zirconium-niobium alloy corrosion under hydrothermal condition. The Zr-Nb alloy coupon was exposed to air-saturated water at a pressure of 15.5 MPa and temperatures ranging from 22 ~ 407℃. The phase transformation was observed and the different corrosion product was observed before and after ZrO_2 film formation.

In this study, the in-situ Raman Spectroscopy has been applied in order to analyze the oxidation behavior and phase transformation of the surface film on zirconium alloys which is used as cladding materials of fuel rod in primary water conditions of pressurized water reactors.

2. Methods and Results

2.1 Sample

A 10mm dia. and 0.6mm thickness disk type Zirlo specimen, fabricated by KEPCO Nuclear Fuel Company (KNFC) was sued in this study. Table 1. shows the chemical composition of Zirlo used in this study.

Table 1. Chemical compositions of Zirlo used in this study.(wt%)

	Nb	Sn	Fe	Cr	Zr
Zirlo	1.8	1.2	0.1	-	Bal.

2.2 Hydrothermal cell

The cell for the in situ observation in primary water environment which is high pressure and temperature condition, was developed The half-inch union cross of compression fitting is used as a main optical cell, which is connected to a half-inch union tee for simulated PWR primary water circulation. The half-inch union tee plays a role of water inlet and outlet with coaxial configuration with 1/4 inch inner tubing. Spring type preheater and box type main heater can heating up to 320℃.The sample stage was made by oxidized Zr-rod and alloy718 to avoid galvanic coupling. And the spring energized seal was used to seal the laser rod from the hydrothermal cell.

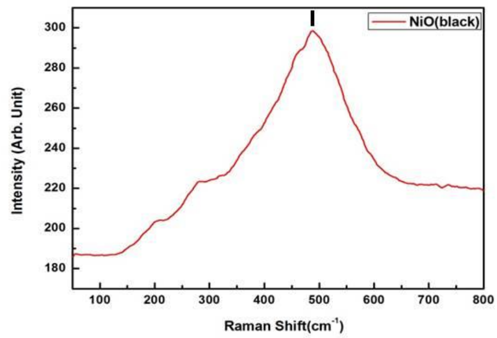
.2.3 In-situ Raman system

The Raman spectroscopy system adopted in this study is consisted of a spectrometer, optical components including filters and an 532nm excitation laser source. It was manufactured by Kaiser Optical Systems, Inc. The Krypton ion laser with 532nm wavelength was used in this study. The Raman system was equipped with holo graphic bandpass-filter and the volume transmission grating had dispersion at 5000 grooves/mm with spectral resolution 5cm^{-1}.

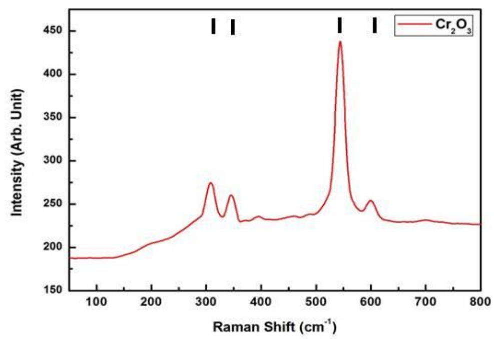
An in-situ Raman spectroscopy was performed on Zirlo specimen in primary water environment that includes dissolved hydrogen of ~30ppm, dissolved oxygen of less than 5ppb, and pH maintained between 6.9 ~ 7.1 using 1,200ppm of B(as $_{H3BO4}$) and 2ppm Li (as LiOH).

Before the in-situ experiment, the reference spectra obtained from reference powders such as NiO, CrO and $NiCr_2O_4$ to validate our system. The results show good agreement with reference data [6,7] as shown in figure 1..

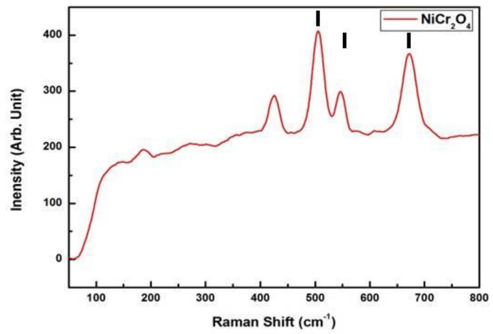
The test was performed during heating up to 320℃ and cooled down. At 320℃, the test was conducted during 50h.



(a) NiO



(b) Cr_2O_3



(c) $NiCr_2O_4$

3. Summary

The hydrothermal cell was developed for In-situ Raman spectroscopy analysis on surface oxide films of Zirlo specimen in primary water condition. The in-situ analysis was conducted with three conditions: heated up to 320℃, 50h at 320℃ and cooled down. The results regarding oxidation behavior and change in phase will be discussed.

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