



## Monitoring the oxidation of nuclear fuel cladding using Raman spectroscopy



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### ABSTRACT

In order to observe Zircaloy-4 (Zr-4) cladding oxidation within a spent fuel canister, cladding oxidized in air at 500 °C was investigated by micro-Raman spectroscopy to measure the oxide layer thickness. Systematic Raman scans were performed to study the relationship between typical Raman spectra and various oxide layer thicknesses. The thicknesses of the oxide layers developed for various exposure times were measured by cross-sectional Scanning Electron Microscopy (SEM). The results of this work reveal that each oxide layer thickness has a corresponding typical Raman spectrum. Detailed analysis suggests that the Raman scattering peaks around wave numbers of 180 cm<sup>-1</sup> and 630 cm<sup>-1</sup> are the best choices for accurately determining the oxide layer thickness. After Gaussian–Lorentzian deconvolution, these two peaks can be quantitatively represented by four peaks. The intensities of the deconvoluted peaks increase consistently as the oxide layer becomes thicker and sufficiently strong signals are produced, allowing one to distinguish the bare and oxidized cladding samples, as well as samples with different oxide layer thicknesses. Hence, a process that converts sample oxide layer thickness to optical signals can be achieved.

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### 1. Introduction

Monitoring of spent fuel cladding can assist with the assurance of the integrity of the fuel within the storage canister, ensure the safety of the fuel within the cask during transportation, and assess fuel as it comes out of a spent fuel pool. The oxidation of Zircaloy-4 (Zr-4) cladding has been studied at different temperatures and the oxidation process has been simulated in various experimental settings [1–4]. In this paper we propose a system that can provide real-time, in situ monitoring of this oxidation.

Raman spectroscopy is able to reveal vibrational mechanisms inside materials in different phases. By combining this technique with microscopy, it is possible to measure the properties of very small material changes, including the oxide layer thickness. One advantage of this approach is that it can be non-destructive and non-contact, which assures the integrity of the material being evaluated and permits long distance detection [5]. For this application, a high luminosity laser source and high sensitivity charge-coupled

device (CCD), as used in a typical micro-Raman spectroscopy device, will permit high resolution (even submicron scale) thickness determination.

Raman spectroscopy has been widely employed to study the properties of zirconium oxide. The crystal structure/phase of zirconium oxide can be distinguished from a typical Raman spectrum. It has been shown that the vibration status of the amorphous, tetragonal and monoclinic polymorphs can be reflected from the peak intensity and profile [6–9]. Based on the Raman spectra, the lattice mechanism can be used to identify zirconium oxide from other oxide materials [10]. Meanwhile, some research has focused on the Raman spectra to detect Zircaloy cladding oxidation. The Raman spectra could provide detail to observe the formation of a textured oxide layer constituted in the Zircaloy cladding corrosion process [11]. Very recently, results of experiments suggest that Raman investigation of Zircaloy oxidation kinetic processes is also possible. Both pre- and post-breakaway oxide scales formed on Zircaloy can be reflected in corresponding Raman scattering peaks [12]. This previous research has resulted in the foundation for further Raman scattering investigation on Zr-4 cladding health condition and characteristics.

The purpose of this work is to investigate the Zr-4 cladding oxide layer thickness by micro-Raman spectroscopy. The relationship between the Raman spectrum and the corresponding oxide

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thickness on Zr-4 cladding will be discussed and a method to convert zirconium oxide thickness into scattering optical signals will be analyzed.

## 2. Experimental

### 2.1. Sample oxidation

The tested Zr-4 cladding samples were cut by saw from 1 mm thick Zr-4 cladding into 1 cm × 1 cm samples. The Zr-4 samples were ground and polished by a Struers TegraForce-5 polish machine on one side using Allied High Tech SiC papers from 120 grit to 1200 grit to remove the native surface oxide layer and provide a smooth sample surface. The morphology of the oxide may be affected by the cold-worked nature of the polished surface. Future work will have to address the comparison of our oxide thickness sensor for cold-worked and stress-relieved samples. The samples were loaded in a quartz tube with a 5 cm diameter and were oxidized in a Thermo Scientific F79335-70 furnace chamber at 500 °C in flowing air. Because the oxide layer thickness increases with the oxidation time [13], samples were oxidized for 5 h, 10 h, 20 h, 50 h and 100 h respectively in order to produce different oxide layer thicknesses for measurement with the Raman technique. These oxidation times were chosen such that the thickness of the grown oxide layer can be clearly distinguished in further study. After oxidation, the polished side of each oxidized sample was ready for further Raman laser scattering investigation.

### 2.2. Raman spectrum investigation

The Raman spectra of the oxidized samples were measured with a Thermal Scientific DXR micro-Raman spectrometer. The excitation laser source is a DXR 532 nm green laser and the output power was 10 mW. The spectra were acquired by a 50 μm aperture. The objective of the microscope was chosen as 10× and the laser beam produced a spot size diameter of 2.1 μm. Raman spectra are collected from the entire 2.1 μm diameter spot. The scans implemented a 900 lines/mm grating to obtain full range spectra and find the interested spectrum range requiring further study. Systematic scans were carried out for several spots, randomly selected at different locations. Then, the representative spectra were examined to identify the peaks that would provide the best potential for identifying the oxide layer thickness. These representative Raman spectra can effectively detect the sample properties of interest.

### 2.3. Scanning Electron Microscopy (SEM) examination

After the Raman spectrum measurement, the oxidized Zr-4 samples were prepared for cross-section measurement by SEM in order to provide an independent measure of the oxide layer thickness. Because of the different properties of phenolic (used for mounting the samples), zirconium oxide, and Zr-4, these three materials can be easily distinguished by different white-black color due to the contrast. Zirconium oxide is a high dielectric constant material, so compared with Zr-4, the zirconium oxide layer has a darker gray color in SEM images and the boundary between the oxide layer and the Zr-4 was obvious. Following this procedure, the zirconium oxide region could be identified in the cross-section SEM images. In the cross-section SEM images of each oxidized sample, the scale measurement function in the SmartSEM software was carried out to measure the zirconium oxide layer thickness accurately at different positions of cross-section.

## 3. Results

### 3.1. Raman spectra

Raman scans were performed at different spots on bare Zr-4, as well as samples oxidized for 5, 10, 20, 50, and 100 h. The characteristic Raman scattering peaks appear between wave number of 160 cm<sup>-1</sup> and 800 cm<sup>-1</sup>. Fig. 1 shows the selected representative Raman spectra in this wave number range. In this figure, a baseline has been subtracted from each spectrum, allowing all the spectra to be put at the same level for selection of the best peaks for measuring the oxide layer thickness. As the Raman spectra reveal, the characteristic Raman scattering peaks become more obvious as the sample's oxidation time increases. In the spectrum from the non-oxidized sample, there is only one peak around 480 cm<sup>-1</sup> with a very weak intensity. The spectrum from the 5 h sample exhibits the 480 cm<sup>-1</sup> peak, which is similar to the bare sample. Meanwhile, two weak peaks around 180 cm<sup>-1</sup> and 630 cm<sup>-1</sup> appear with a broad peak width. In the spectrum from the 10 h sample, the peaks at 180 cm<sup>-1</sup>, 480 cm<sup>-1</sup> and 630 cm<sup>-1</sup> become stronger and wider. In addition, two peaks at 340 cm<sup>-1</sup> and 380 cm<sup>-1</sup> appear. The spectrum from the 20 h sample is similar to that of the 10 h sample, but the intensity of each peak increases slightly. The peaks at 180 cm<sup>-1</sup> and 630 cm<sup>-1</sup> begin to split into two sub-peaks at 175 cm<sup>-1</sup> and 187 cm<sup>-1</sup> for the 180 cm<sup>-1</sup> peak and 613 cm<sup>-1</sup> and 638 cm<sup>-1</sup> for the 630 cm<sup>-1</sup> peak. In the spectrum from the 50 h sample, all these peaks still exist at the same positions, but with much stronger intensities. New peaks at 220 cm<sup>-1</sup>, 540 cm<sup>-1</sup> and 580 cm<sup>-1</sup> also appear within this spectrum. The spectrum from the 100 h sample contains all the peaks in the 50 h sample's spectrum, but each of them displays an increase in intensity. Furthermore, there are two new peaks at 280 cm<sup>-1</sup> and 300 cm<sup>-1</sup> with weak intensities.

As the oxidation time increases, thicker oxide layers are grown on top of Zr-4 and in turn the Raman spectrum of this sample can show stronger Raman scattering signals. Comparing all of these Raman spectra in detail, some characteristic peaks are helpful in identifying bare and oxidized samples. As discussed previously, there are 12 characteristic peaks, either appearing or growing, in the spectra of the tested samples. In the spectra of the bare and 5 h samples, the differences are only observed for peaks at

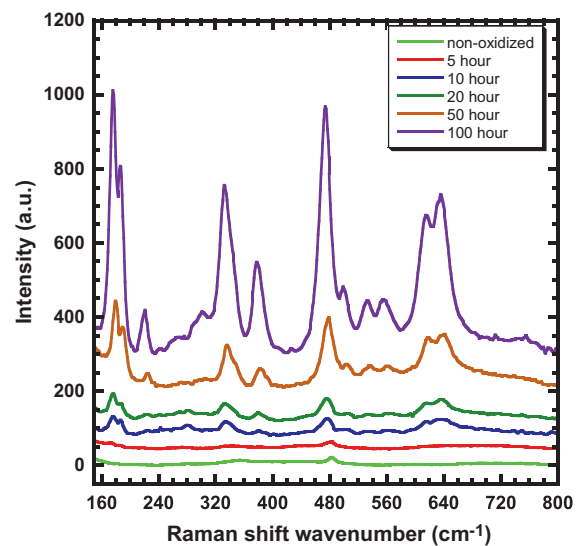


Fig. 1. The selected representative Raman spectra of the non-oxidized, 5 h, 10 h, 20 h, 50 h and 100 h oxidized Zr-4 cladding samples. As the oxidation time increases, there are 12 characteristic peaks appearing in the spectra.

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