Analysis of oxide layers on zirconium alloys by Raman spectroscopy of oxygen 18

Pavel SIALINI¹, Petr SAJDL², Vera VRTILKOVA³

¹ UCT Prague, Prague, Czech Republic, sialinip@vscht.cz
² UCT Prague, Prague, Czech Republic, sajdlp@vscht.cz
³ UJP Prague, Prague, Czech Republic, vrtilkova@ujp.cz

Abstract
Analysis of oxide layers on zirconium alloys by Raman spectroscopy of oxygen 18 was carried out with purpose to find out the form of diffusion of oxygen throw the oxide layer on the tube surface. Experiments consisted of long-term exposure of samples to create the oxide layers, after it the samples were exposed in hot water with O18 under high pressure. Samples were analyzed by Raman spectroscopy and the result was the distribution of oxygen 18 in the original oxide layer. Differences were found in behavior of alloys with niobium and with tin.

Keywords
Zirconium alloys, oxygen diffusion, Raman spectroscopy
Introduction

The largest application of zirconium alloys lies in nuclear power engineering, where they are used as a protection material fuel. Among the most commonly used alloys for protection of the fuel pellets belong zirconium alloys with tin and zirconium alloys with niobium. Among features which destine alloys for application in nuclear power engineering belong their chemical stability and mechanical resistance. A very important feature is then the low capture cross section for thermal neutrons, which are required to maintain the fission reaction in the reactor core.[1,2]

Numerous adverse effects act on the coating material are in the reactor core. These negative effects are especially high temperatures and pressures (about 320 °C and 15.5 MPa for PWRs). Another important negative factor is the radiation exposure of the material. The above factors also influence the environment in which the alloy is exposed, which leads to decomposition reactions of water to form oxygen and hydrogen. These elements can further negatively affect the material.[2,3]

The chemical resistance of zirconium alloys is due to the formation of a protective oxide layer on the surface of the metal material that prevents further deterioration and oxidation of the alloy. Oxygen diffusion through the formed oxide layer can occur in such a way that the oxygen atoms diffuse either along the grain boundaries or through the crystals of the already formed oxide to the oxide / metal interface, where further metal oxidation takes place.[3,4] Diffusion of oxygen to the interface oxide / metal is not fully understood. One way to investigate oxide layer is the use of an aqueous medium when water molecules present in the oxygen isotope $^{18}$O. In the experiment, when the oxidation of the alloy due $\text{H}_2^{18}$O can examine oxide layer by means of Raman Spectroscopy, which can distinguish individual isotopes of oxygen.[5] Manufacture isotopic environment of sufficient purity is very expensive. This implies an effort to minimize the amount of media used in the experiments. This is related to the development of equipment for small volumes of media used during exposure and thus reduces the high cost of the experiment.

Experimental

For the experiment, tubes were made of zirconium alloy E110 (containing 1 wt. % Nb) were used, pre-exposed at 360 °C and 18.0 MPa, these conditions correspond to the chemical composition of the VVER1000 reactor. The samples were exposed in an experimental apparatus for small volumes of exposition medium (Figure 1), where the samples were placed in an exposure cell with exposure to isotope-purified $\text{H}_2^{18}$O medium with a minimum purity of 98%. Information about samples and exposure parameters are summarized in Tab. 1.

Tab. 1. Parameters of samples and experiments

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>1136273</th>
<th>3136048</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-exposure [days]</td>
<td>1325</td>
<td>1280</td>
</tr>
<tr>
<td>Medium</td>
<td>H$_{2}^{18}$O</td>
<td>H$_{2}^{18}$O</td>
</tr>
<tr>
<td>Volume [cm$^3$]</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Target temperature [°C]</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>Exposition time [hours]</td>
<td>336</td>
<td>336</td>
</tr>
<tr>
<td>Pressure during exposition [MPa]</td>
<td>1.2</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The thickness of the newly formed oxide layer of the sample of known area was determined from the increase of its weight when all the weight gain of the sample is regarded as the weight increase due to oxygen that is bound to the newly formed crystals of oxide of Zirconium.

$$X = \frac{10^{4}}{2 \cdot S} \cdot \frac{M_{ZrO_{2}}}{\rho_{ZrO_{2}}} \cdot \frac{\Delta m}{M_{O_{2}}}$$

Where($\Delta m$) is increase in weight, ($S$) is the surface area of the sample, the density ofZrO$_2$(ρ$_{ZrO_2}$) (M$_{O_2}$), the molecular weight of oxygen(M$_{ZrO_2}$) molecular weight of zirconia.[4]

The Raman spectra were measured by Thermo Scientific's Raman Dispersion Spectrometer - and a DXR Microscope model equipped with an Olympus confocal microscope. The excitation source was a Nd: YAG laser with a wavelength of 532 nm and an input power of 10 mW. A grid of 900 bevels.mm$^{-1}$ was used. The multichannel thermoelectric cooled CCD camera was used as a detector. Samples were measured at 100x magnification with a measurement track of approx. 1 μm$^2$. Samples were measured through an aperture of 50 μm pinhole. Measurement at 8 mW, measuring time 5 s and with 5 spectra.
accumulations. Samples were measured as cross-sections, each area was mapped to the area of a corrosion layer of approx. 50 μm² with 1 μm pitch in both directions. The incidence of monoclinic m-Zr\textsuperscript{18}O\textsubscript{2} (together with m-Zr\textsuperscript{16}O\textsubscript{2}), and the occurrence of tetragonal t-ZrO\textsubscript{2} were studied in the samples.

Different forms of zirconium oxides differ in their Raman spectra. A sample comparison of some measured spectra is shown in Figure 1. In the first two spectra, it can be seen that the \textsuperscript{18}O content mainly affects the vibration bands of the oxide between 350-650 cm\textsuperscript{-1}, there is a marked shift of 15-30 cm\textsuperscript{-1} over the \textsuperscript{16}O analogue (in the direction of lower wavelengths). According to the calibration described in the literature, according to the belt positions ~ 475 cm\textsuperscript{-1} (Fig. 2), the ratio of \textsuperscript{18}O in the corrosion layer is estimated. [5]

The third spectrum then corresponds to the tetragonal modification of ZrO\textsubscript{2}. Generally, it has very low intensity with a pair of visible bands at 283 and 444 cm\textsuperscript{-1} and t-ZrO\textsubscript{2} can not always be clearly distinguished, however, the 283 cm\textsuperscript{-1} strip is outside the region of the distinctive m-ZrO\textsubscript{2} bands, so it can serve as a relatively good indicator of this forms. In addition to these three forms of ZrO\textsubscript{2}, amorphous carbon was found on most samples.

**Fig. 2** Comparison of typical Raman spectra of individual measured phases. The blue spectrum corresponds to the standard Zr\textsuperscript{16}O\textsubscript{2}, the red contains a high proportion of \textsuperscript{18}O. The green spectrum is typical for t-ZrO\textsubscript{2}, the last Raman spectrum then shows typical bands of amorphous carbon. [5]
Results and discussion

The increase of the newly formed corrosion layer [X] on the samples, which was determined from increase in weight [Δm] by the formula (1), is shown in Tab. 2.

**Tab. 2. Prepared layer of oxides of Zr**

<table>
<thead>
<tr>
<th>sample</th>
<th>1</th>
<th>362</th>
<th>73</th>
<th>31</th>
<th>3604</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Δm</td>
<td>0.7</td>
<td>0.7</td>
<td>2.7</td>
<td>3.4</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td>X</td>
<td>0.8</td>
<td>0.9</td>
<td>2.8</td>
<td>3.8</td>
<td>4.7</td>
<td>4.6</td>
</tr>
</tbody>
</table>
A smaller increase in weight and thus the oxide layer was due to the lower resistance of the oxidic layer during the experiment to disrupt this layer and peel off.

**Sample 1**

To monitor the distribution of the oxidic forms, a correlation contour graph was drawn for the individual phases, which showed the similarity of the measured spectra with a spectrum corresponding to the given pure phase (for sample 1 see Figure 4). For example, $^{18}$O is not a percentage representation in the sense of the above-mentioned calibration.

The spectra most similar to the respective phase are thus in Fig. 4 to red, the most diverse blue. In the case of $m$-Zr$^{18}$O$_2$ (Fig. 4A) it can be seen that this form occurs mainly in longitudinal deposits, mainly in the central part of the corrosion layer (but closer to the metal interface). Oxide with $^{16}$O (Fig. 4B) is a major form here, as expected with the previous $^{18}$O form. The tetragonal t-ZrO$_2$ (Fig. 4D) was, as with most samples, found longitudinally directly at the interface of the corrosion layer and the metal at a thickness of ~ 1-2 μm. The thickness of the corrosion layer at the site was approx. 20μm.

On the map, the whole image is shifted by a few micrometers due to a slight shift of the sample when photographed with an optical camera, and it is no bigger problem for qualitative assessment of chemigrams.

![Fig. 5 Mixed image from optical camera and correlation chemigram on mapped sample 1. A - m-Zr$^{18}$O$_2$. B - m-Zr$^{16}$O$_2$. C - only optical photo. D - t - ZrO$_2$.](image)

**Sample 8**

For sample 8, the $m$-Zr$^{18}$O$_2$ region (Fig. 5A) looks different. It appears there to be a band close to the metal interface, but the approximate distance from this interface is not much
larger than that of sample 1, the difference is mainly in the width of the corrosion layer, which is practically doubled (about 40 μm) and in the outer part of which is already exclusively propagated m-Zr\textsuperscript{16}O\textsubscript{2} (Fig. 5B).

The tetragonal t-ZrO\textsubscript{2} (Fig. 5D) is again situated directly at the interface of the corrosion layer and the metal at a thickness of ~ 1-2 μm.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig_6.png}
\caption{Mixed image from optical camera and correlation chemigram on mapped sample 8. A-m-Zr\textsuperscript{18}O\textsubscript{2}. B-m-Zr\textsuperscript{16}O\textsubscript{2}. C-only optical photo. D-t-ZrO\textsubscript{2}}
\end{figure}

**Sample 31**

For sample 31, an area was selected around two distinct cracks. The thickness of the layer was in the measured area 30-35 μm. Unfortunately, m-Zr\textsuperscript{18}O\textsubscript{2} was not observed here (Fig. 6A), the dominant band ~ 475 cm\textsuperscript{-1} characteristic of m-Zr\textsuperscript{16}O\textsubscript{2} was shown in all corrosion spectra (Fig. 6B). In cracks, the spectrum was not significantly different, so it was probably only when the sample was prepared (cutting, polishing), etragonal t-ZrO\textsubscript{2} (Fig. 6D) at the metal-oxide interface was found.
Sample 73

For sample 73, the m-Zr\textsuperscript{18}O\textsubscript{2} (Fig. 7A) was found in two lanes roughly mid-layer (20 μm). One of the strips (closer to the outside) roughly coincides with the "scratch" visible on the optical image, probably more likely a coincidence (the scratch looks more like a residue than an internal crack). The m-Zr\textsuperscript{16}O\textsubscript{2} phase (Fig. 7B) again fills the remaining sites. The tetragonal t-ZrO\textsubscript{2} (Fig. 7D) is well defined at the interface of the corrosion layer and the metal (again ~ 1-2 μm).
Fig. 8 Mixed image from optical camera and correlation chemigram on mapped sample 73. 
A-m-Zr$^{18}$O$_2$. B-m-Zr$^{16}$O$_2$. C-only optical photo. D-t-ZrO$_2$

Sample 362

For sample 362, the m-Zr$^{18}$O$_2$ (Fig. 8A) was already found in three lanes practically across the thickness of the corrosion layer (about 20 μm thick). The m-Zr$^{16}$O$_2$ phase (Fig. 8B) again on the rest of the space - between the Zr$^{18}$O$_2$ strip, the outer edge and the m-Zr$^{18}$O$_2$ and t-ZrO$_2$, which is standard on the corrosion-metal interface (Fig. 8D).
Fig. 9 Mixed image from optical camera and correlation chemigram on mapped sample 362.  
A-\textit{m-Zr}^{18}\text{O}_2. B-\textit{m-Zr}^{16}\text{O}_2. C-only optical photo. D-\textit{t-ZrO}_2.

\textbf{Sample 3604}

For sample 3604, the overall intensity of the spectra was very low, and the spectra itself was rather degraded by fluorescence and high amorphous carbon bands - the measurement would therefore have to be repeated. The traces of \textit{m-Zr}^{18}\text{O}_2 (Fig. 9A) were found only in one band near the oxide-metal interface. Most of the surface showed only the presence of \textit{m-Zr}^{16}\text{O}_2 (Fig. 9B). Less intense \textit{t-ZrO}_2 was not detected at all.
As previously mentioned, for m-Zr$^{18}$O$_2$ the bandage shift is typically in the range of 350-650 cm$^{-1}$. For the relative quantitative representation of this phase, a bandwidth ratio of about 457 cm$^{-1}$ to the sum of intensities I (457 cm$^{-1}$) + I (477 cm$^{-1}$) was obtained wherein the band about 477 cm$^{-1}$ corresponds to the same analog vibration mode m-Zr$^{16}$O$_2$ (subtracting the intensity is indicated in Fig. 1). This ratio was plotted in the contour maps in Fig. 2-7. The qualitative dependence corresponded to the correlation chemigrams from the previous report, the intensity ratio ranged from 0.1 (practically without $^{18}$O) to 0.8 (100% Zr$^{18}$O$_2$).

In the case of contour maps for this ratio, it is only meaningful to consider the area where only the different m-ZrO$_2$ phases are found, so it is not worthwhile to notice this ratio outside the main area of the corrosion layer (shown in Figure 2 - 7 with a black rectangle).

In addition, lines corresponding to a typical flow from the oxide-metal interface to the edge of the oxide layer were plotted in each map, which were plotted in Fig. 8 with constant intensity scaling to compare the individual m-Zr$^{18}$O$_2$ profiles. Here we can see the m-Zr$^{18}$O$_2$ strap structure in samples with a thinner corrosion layer (~ 20 μm) at the measuring site. In the case of thicker samples, these well-defined $^{18}$O-rich belts were not recorded.
Fig. 11 Example of reading the intensities on the spectra of two boundary forms of ZrO2 and one mixed form of Zr \((^{16}\text{O}_{1-x}^{18}\text{O}_x)\) \_2 (lower spectrum)

Fig. 12 The image from the optical camera and the chemigram intensity ratio \(I (457) / (I (457) + I (477))\) on mapped sample 1
Fig. 13 The image from the optical camera and the chemigram intensity ratio $I(457)/(I(457)+I(477))$ on the mapped sample 8

Fig. 14 The image from the optical camera and the chemigram intensity ratio $I(457)/(I(457)+I(477))$ on the mapped sample 31

Fig. 15 The image from the optical camera and the chemigram intensity ratio $I(457)/(I(457)+I(477))$ on mapped sample 73
Fig. 16 The image from the optical camera and the chemigram intensity ratio $I(457)/(I(457) + I(477))$ on the mapped sample 362

Fig. 17 The image from the optical camera and the chemigram intensity ratio $I(457)/(I(457) + I(477))$ on the mapped sample 3604
Fig. 18 - Comparison of typical Intensity Ratio $I_{457}/(I_{457} + I_{477})$. Parameter $d$ indicates the distance from the oxide-metal interface.
Conclusion
On the samples, an oxide layer containing $^{18}$O was prepared in the experimental apparatus. Generally speaking, heterogeneous distribution of $^{18}$O in the corrosion layer of ZrO$_2$ was observed in all samples. The measured spectra usually correspond to almost the entire concentration range of 0-100% $^{18}$O

Acknowledgment
Financial support from specific university research (MSMT No 20-SVV/2018)

References
5. GUERAIN, M.; MERMOUX M.; DURIEZ C. The use of micro-Raman imaging to measure 18O tracer distribution in thermally grown zirconia scales. Corrosion Science [online]. September 2015, (Volume 98), Pages 140-149