A new compound of Zr-O-N system identified by Raman investigation

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1. Introduction

Air ingress scenarios could occur in reactor and spent fuel pool accidents. For example, in reactor sequences air could be admitted through the broken reactor vessel at the late phase of a severe accident after the reactor vessel has been breached. In addition, spent fuel assemblies could be directly exposed to air in a postulated complete loss of coolant accident in a spent fuel pool. In air ingress scenarios, nitrogen has an active role on the cladding degradation. Two major roles of nitrogen on the zirconium based cladding degradation were identified: mechanical degradation of the cladding, and the additional chemical heat release.

It has long been known that accelerated oxidation can occur in air due to the nitrogen. In addition, significant uptake of nitrogen can also occur. The nitriding of pre-oxidized zirconium based alloys leads to micro porous and less coherent oxide scales.

Several separate effect tests have been performed at KIT [1] and IRSN [2] to study the air oxidation of zirconium alloy cladding. From their results of post-test investigations, the effect of nitrogen was explained based on the knowledge of Zr-O and Zr-N binary system analyses. Currently, the understanding of nitriding process is phenomenological and only binary compounds, ZrO_2 and ZrN, are involved. In the past, the understanding of nitriding process was based on an assumption of formation of oxide and nitride mixture during the process. No consideration about oxynitride phase was included in the current knowledge of nitriding process. If oxynitride phases are involved during the process, there would be more mechanical and thermal effects than current understanding of nitriding process. In this case, stronger mechanical effect would be expected by more volume mismatches in the oxide/nitride/oxynitride system than in the oxide/nitride system. In addition, more thermal effects are expected by an additional exothermic reaction of oxynitride phases than only of oxide and nitride mixtures.

Recently, Kairid et al. [3] and Idarraga et al. [4] performed Raman investigation on the air-oxidized Zry-4 cladding. From their Raman investigation, they suspected an existence of ternary compounds of zirconium oxynitrides. However, no distinct evidence to prove an existence of ternary compounds of zirconium oxynitrides was provided in their studies.

This study also found the unknown Raman peaks in the oxidized/nitrided samples, this paper will discuss the possibility of existence of oxynitride phases in the chosen sample that showed unknown Raman peaks. The sample from the test in O_2 for 10 sec and subsequent N_2 for 30 min at 1200°C was intensively measured by a Raman spectroscopy to find a cause of unknown peaks.

In addition, several analytical methods were performed to investigate the same sample (or same conditioned sample which were reproduced by same oxidation-nitriding conditions).

It is expected that this study prepares a background to improve the knowledge of the nitriding process that is currently based on formation of a mixture of oxide and nitride.

2. Experimental results and discussions

In order to investigate thoroughly the unknown Raman peaks, the particular regions of interest were chosen from the nitrided sample as shown in Fig 1.

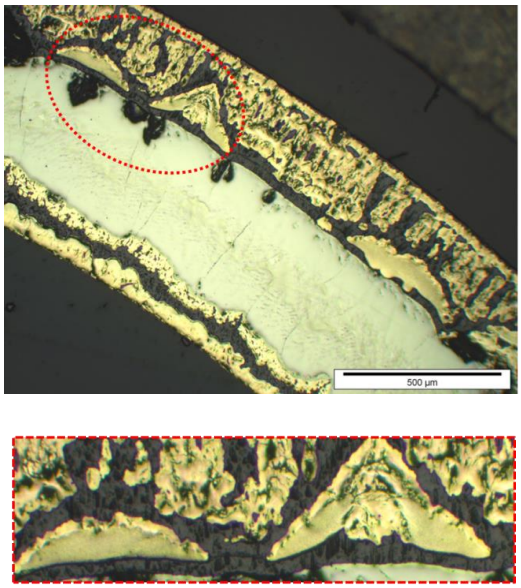


Fig. 1 Particular regions of interests for Raman investigation

The Raman spectra of both selected regions are shown in Fig. 2 and 3, respectively.

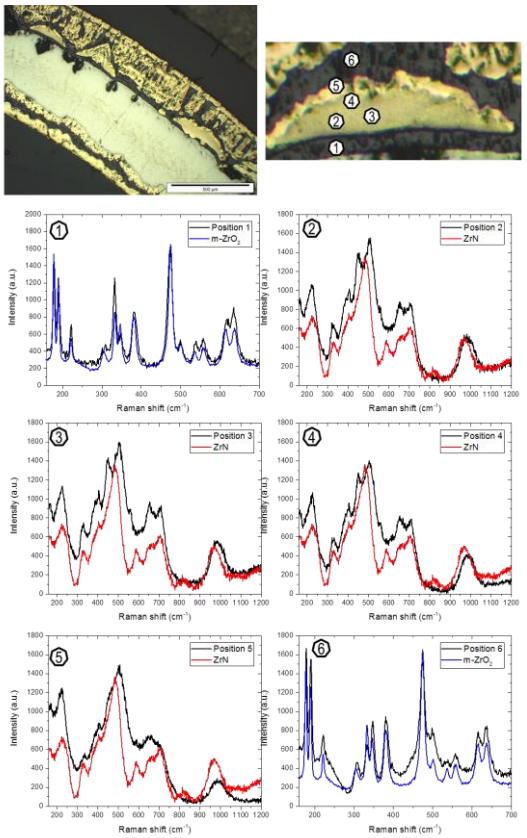


Fig. 2 Raman spectra of the island-shaped region

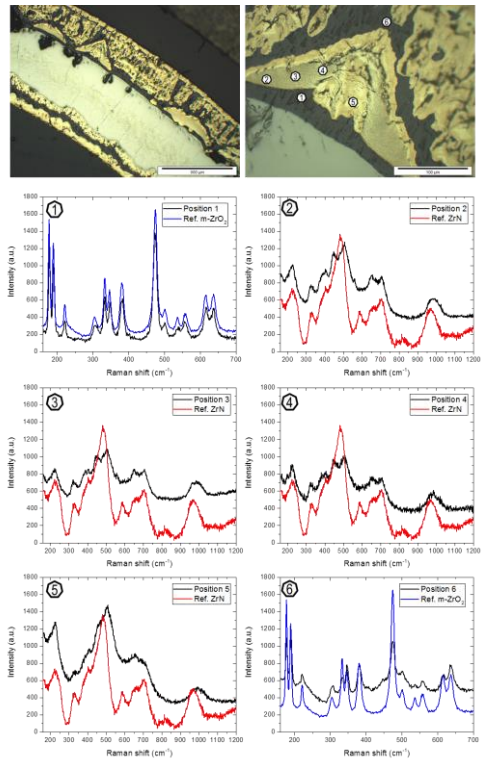


Fig. 3 Raman spectra of the triangular-shaped region

As shown in Fig. 1 and 2, each six position was measured in both the island-shape region and the triangular-shaped region. Findings from each position were summarized in Table 1.

Table 1. Summary of Raman spectra for the regions of interest

Position	Island-shaped region	Triangular-shaped region
1	$m\text{-}ZrO_2$ Raman spectrum	
2	Similar with ZrN Raman spectrum, but no characteristic peak of ZrN at 485 cm^{-1} and unknown twin peaks at 452 cm^{-1} and 502 cm^{-1}	
3		
4		
5	ZrN Raman spectrum with a peak broadening and a peak shift	
6	$m\text{-}ZrO_2$ Raman spectrum	

From the summary in Table 1, it was found that as follows:

○ Common features of ZrN Raman specturm (one dominant peak at 492 cm^{-1}):

- Bright golden-yellow colored region
- One dominant peak (492 cm^{-1}) seems the shifted characteristic peak of ZrN (485 cm^{-1})

○ Common features of unknown twin peaks (452 cm^{-1} and 502 cm^{-1}):

- Dark golden-yellow colored region
- Two dominant peaks (452 cm^{-1} and 502 cm^{-1}) were apparently showed instead of the characteristic peak of ZrN (485 cm^{-1})

In order to identify the origin of the unknown twin peaks (452 cm^{-1} and 502 cm^{-1}), theoretical values Raman spectra of oxide and nitride are investigated in the following.

Only particular lattice vibrations having specified symmetry are Raman active modes, and infrared (IR) active modes cannot be assigned with the symmetry that are Raman active modes by the rule of mutual exclusion [5]. Therefore there is no overlap between Raman and IR spectra [6]. The symmetry that has Raman active modes can be determined by factor group analysis. Factor group analysis is a method to predict the number of expected Raman and IR peaks based on the symmetry properties. From factor group analysis, Raman peaks are calculated upon the rule of mutual exclusion for the crystal vibrational modes with known structure. Based on factor group analysis and the rule of mutual exclusion, the Raman active modes of oxide and nitride are summarized in the following.

○ Oxide: monoclinic-, tetragonal- and cubic-ZrO_2

Monoclinic ZrO_2 belongs to the space group C2h5 ($P2_{1/c}$) and a unit cell includes four molecules. From the

factor group analysis, there are 36 lattice vibration modes in m-ZrO_2: $G_{mono} = 9A_g + 9A_u + 9B_g + 9B_u$. Out of 36 vibration modes, only 18 (9 A_g and 9 B_g) lattice vibration modes are Raman active. Among 18 Raman active modes of m-ZrO_2, peak of 502 cm^{-1} is assigned to O-O bonding. The others are IR active ($8A_u$ and $7B_u$) and acoustic modes ($1A_u$ and $2B_u$) [7].

Tetragonal ZrO_2 belongs to space group C_{4h}^{15} ($P4_2/nmc$), we expect six vibrational Raman active modes, with symmetries $A1_g + 2B1_g + 3E_g$ and located at 150 ($B1_g$), 260 (E_g), 320 ($B1_g$), 480 (E_g), 602 ($A1_g$) and 650 (E_g) cm^{-1} [8].

Cubic ZrO_2 presents Oh^5 space group (Fm3m, Fluorite type structure) with four molecules per unit cell. There is one single Raman active mode of cubic ZrO2 which appears at 600 cm^{-1} ($F2_g$ band) [6] and [9].

○ Nitride

There are two types of nitride phase: orthorombic Zr_3N_4 and cubic rock-salt ZrN. The Zr_3N_4 phase is a metastable state and hence it might be decomposed to ZrN at high temperatures and also during post-test investigation work.

ZrN is a metallic nitride phase that has a cubic rock-salt structure (Fm-3m, NaCl structure). For stoichiometric ZrN which has a rock salt structure first order Raman peaks are forbidden by symmetry of O_h. The second order Raman peaks are dominated by an asymmetric band centered at around 485 cm^{-1}.

The ionic-covalent metastable nitride phase, Zr_3N_4, belongs to the Th_3P_4-type structure (space group I-43d or T_d^6) with the following symmetry species of vibrational modes: $A_1 + 2A_2 + 3E + 5T_1 + 5T_2$. Nine of them ($A_1 + 3E + 5T_2$) are Raman-active and five ($5T_2$) are also IR-active. The Raman peaks are located at 142 (T_2), 165 (E), 282 (T_2), 336 (A_1), 368 (T_2), 423 (T_2), 506 (T_2), 609 (E) and 670 (E) [10].

From the investigation of Raman active modes of oxide and nitride, one of the unknown twin peaks at 502 cm^{-1} might be assigned to an O-O bonding of m-ZrO_2. However, the other of unknown twin peaks at 452 cm^{-1} was not found from the investigation of Raman active modes of oxide and nitride. This peak of 452 cm^{-1} might be a peak of Zr-O-N phase.

During a phase transformation from m-ZrO_2 to ZrN, nitrogen is incorporated into oxide and produce oxygen vacancies. Due to a formation of oxygen vacancies by incorporating nitrogen into oxide, original m-ZrO2 structure (e.g. O-O bonding) would be distorted and gradually transformed to oxyntride/nitride. This phase of unknown twin peaks may be an intermediate phase during a phase transformation from m-ZrO_2 to ZrN.

For the past researches performed at KIT [1] and IRSN [2], the golden-yellow inclusion was considered only ZrN. They performed no structural analysis like XRD to determine the crystal structure of the golden-yellow inclusion in the oxide scale. However, both ZrN and Zr_2ON_2 are optically golden-yellow color. For this reason, the golden-yellow inclusion could be a mixture of ZrN and Zr_2ON_2. A ZrN reference Raman spectrum was measured but no Zr_2ON_2 reference Raman spectrum was prepared. Furthermore, No Zr_2ON_2 Raman spectrum was available in literature, but Carvalho [141] synthesized Zr-O-N samples and measured a Raman spectrum as shown in Fig 4.

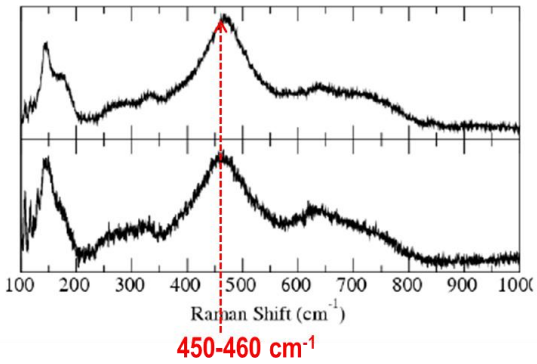
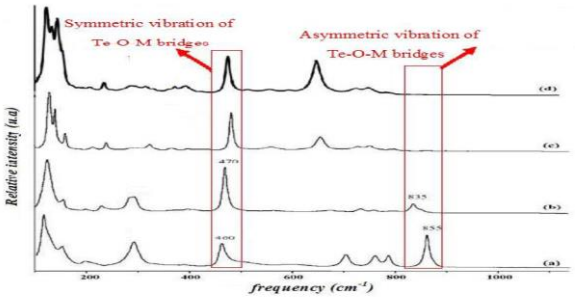


Fig. 4 Suspected Zr-O-N Raman spectrum by (Carvalho, 2008) [11]

Carvalho [11] observed a new peak around 450-460 cm^{-1} and he assumed that the appearance of this new peak in the spectra indicated the local structural change with the formation of orth-Zr_3N_4(O) and Zr_2ON_2 by showing a XRD pattern of Zr_2ON_2. It is highly probable that the Zr_2ON_2 Raman spectrum may contain the peak of 450-460 cm^{-1}.

Hagemann and Bill [12] and Chaix-Pluchery and Kreisel [13] reported similar Raman spectra were observed in the same crystal structure. Like their observations, one possibility to expect a Raman spectrum of Zr_2ON_2 might be an investigation of same structure of Zr_2ON_2. The space group of Zr_2ON_2 is Ia-3 and the Raman active mode of Zr_2ON_2 is $4A_g + 4^1E_g + 4^2E_g + 14T_g$ (calculated from [14]). One of the ternary compounds that has the same crystal structure (Ia-3) of Zr_2ON_2 is MTe_3O_8 (M = Ti, Zr, Sn), and their Raman active modes are $5A_g + 5^1E_g + 5^2E_g + 17T_g$ (calculated from [14]). The difference between Raman active modes of Zr_2ON_2 and MTe_3O_8 (M = Ti, Zr, Sn) is $1A_g + 1^1E_g + 1^2E_g$. This difference is caused by 16c Wyckoff position. Wyckoff position indicates a point belonging to a particular symmetry in crystal structure. For this reason, the Raman spectra of MTe_3O_8 (M = Ti, Zr, Sn) and Zr_2ON_2 cannot be totally identical but their characteristic peak may be located at same position.



(a) Raman Spectrum of crystalline phase $ZrTe_3O_8$.
(b) Raman Spectrum of crystalline phase $SnTe_3O_8$.
(c) Raman Spectrum of crystalline phase $TiTe_3O_8$.
(d) Raman Spectrum of crystalline phase $Ce_{0.07}Ti_{0.93}Te_3O_8$.

Fig. 5 Examples of Ia-3 space group Raman spectra (excerpted from [15])

As shown in Fig. 5, Ia-3 space group phases have a Raman peak around 460 cm^{-1}. In addition, the lattice parameters of MTe_3O_8 (M = Zr (11.308 Å), Sn (11.144 Å), Ti (10.963 Å)) and $Ce_{0.07}Ti_{0.93}Te_3O_8$ (10.985 Å) are very similar with lattice parameter of γ-Zr_2ON_2 (10.430Å) [16].

Crystal structures of MTe_3O_8 (M = Zr, Sn, Ti) are quite similar and their Raman spectra are also very comparable as shown in Fig. 5. Although Zr_2ON_2 and MTe_3O_8 (M = Zr, Sn, Ti) belong to the same crystal structure (Ia-3 space group), configurations of atomic coordination are different. However they share some of common vibrational Raman active modes. This may weakly support to expect the characteristic Raman peaks of Zr_2ON_2 from the Raman spectra of MTe_3O_8 (M = Zr, Sn, Ti).

Based on literature finding regarding the characteristic Raman peak of Zr_2ON_2 and the same crystal structure (MTe_3O_8 (M = Zr, Sn, Ti)), Raman spectra of Zr_2ON_2 may have a characteristic peak around 450-460 cm^{-1}. This might be the Raman band observed from a golden-yellow inclusion in the sample.

In summary, two hints may support an existence of Zr_2ON_2 in the nitrided sample:

1) Zr_2ON_2 is optically golden-yellow colored
2) the Raman spectrum of Zr_2ON_2 may have a characteristic peak of 450-460 cm^{-1}.
It seems that Zr_2ON_2 might be formed from a reaction between ZrO_2 and N_2 as follows:
$2ZrO_2 + N_2 \rightarrow Zr_2ON_2 + 3O$.

Complementary measurements to investigate the existence of Zr-O-N phase (e.g. Zr_2ON_2 phase) in the same sample were performed by SEM/EDS, XPS, XRD, etc.

3. Conclusion

In summary, the possibility of existence of Zr-O-N phase in the sample (pre-oxidation for 10 sec and then nitriding for 30 min at 1200°C) were investigated by Raman spectroscopy analysis. From the Raman spectrum, one of the unknown peaks in the dark golden-yellow colored region was suspected as an indication of Zr_2ON_2 peak based on the theoretical work and other complementary analyses also supported the findings from the Raman investigation.

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