MELCOR further development in the area of air ingress and the effect of nitriding

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ABSTRACT

Cladding degradation of an overheated core during a hypothetical accident in a nuclear power plant has been extensively studied in the past. Most of the knowledge has concentrated to the exposure of cladding to steam. In this situation the cladding undergoes exothermic oxidation. Under such circumstances the oxidation rate would typically be limited by the oxygen diffusion through the oxide layer which builds up on the cladding surface. In recent years the possibility of oxidation with air has been brought into attention, of special concern are the spent fuel ponds. Exposure to air leads to accelerated degradation since the nitrogen present in the air may degrade the oxide layer which hence becomes a less effective barrier, resulting in faster oxidation kinetics. The oxide layer typically becomes porous and can break away, a process known as breakaway oxidation. As well as faster oxidation, the nitrogen also promotes faster and more complete mechanical degradation of the cladding, leading to more widespread destruction of the fuel rods and exposure of the fuel itself.

Until recently it was believed that nitrogen did not play a major role as an active chemical species, instead its main effect was considered to be the accelerated oxidation. Recent experiments have shown that the reaction with nitrogen can result in extensive formation of zirconium nitride (ZrN) which contributes very significantly to both the heat generation and fuel rod degradation. Furthermore, if the cladding is further exposed to oxygen, the degradation is significantly enhanced during re-oxidation of the nitride layer.

The current project addresses the active role of nitrogen and ZrN formation in the air oxidation process by means of a coupled analytical and experimental investigation. A nitriding model will be developed and formulated to be implementable into the severe accident analysis codes such as MELCOR and SCDAP.

Project goals

The goal of the project is an oxidation/nitriding model development which can be implemented into severe accident analysis codes (e.g. MELCOR or SCDAP). In order to understand the nitriding process the study was performed at two different scales: the small scale experiments and the microscale analyses.

The small scale experiments will serve to quantify the key parameters that are relevant for the model development. This part of the work includes:

- **Study of the kinetic behaviour**. Identify data available in the literature as well as missing data. The gaps in knowledge will be investigated by performing Separate Effect Tests (SET's) with Zircaloy-4 cladding samples by using a Thermo-Gravimetric (TG) device.

The micro-scale study serves to identify the phases that may intervene during the nitriding-re-oxidation process and that contribute to the degradation of the Zr cladding in this type of scenario. Therefore, the following substudies were performed:

- **Thermodynamic analysis:** This area focuses on understanding the nitriding process at the micro-scale. This is supported by analyses of the phase compositions within the zirconium-oxygen-nitrogen ternary system, based on available literature and thermodynamic data.
- **Chemical composition of nitrided samples:** analytical methods like Raman spectroscopy and X-ray diffraction analysis were used to analyse the phases, elemental composition and crystal structure of the formed compounds during the nitriding and re-oxidation process.

The integration of the observations obtained with the SET's and the micro-scale analysis would set the basis to develop a nitriding model.

The present project is a coupled analytical and experimental work in the frame of a PhD thesis work by Mr. Sanggil Park. The analytical work is performed at PSI under the supervision of Dr. Leticia Fernandez-Moguel and the experimental work is conducted at Karlsruhe Institute of Technology (KIT) being supervised by Dr. Martin Steinbrück. During the present period, the efforts were concentrated in performing several separate effect tests at KIT as well as analyses to identify the product phases of the nitriding process.

Work carried out and results obtained

1. Introduction

Air ingress scenarios are a concern for the nuclear industry. There are situations where air ingress may occur: during a severe accident the reactor pressure vessel could fail and air could ingress [1–2], during mid loop operation when the reactor coolant system is usually open to the containment [3], or in spent fuel facilities such as pools and dry casks in either the event of loss of coolant or handling and transport accidents [4–6].

Many separate effect tests have been performed in the past to study the influence of the effect of nitrogen during air oxidation. The studies have mainly been performed with fresh Zircaloy-4 cladding samples, but also M5®, Zirlo™ and E-110 have been used [7–15]. These tests have helped to reach a macroscopic understanding of the process.

The knowledge collected in the cited studies has helped to identify two major roles of nitrogen during air oxidation:

- Cladding degradation by forming a micro porous and macro cracked oxide due to the volume changes.
- Exothermic heat release from the nitride formation and re-oxidation.

A PhD work started in September 2013 in order to address the lack of knowledge on the nitriding effects. The goal of the thesis is to develop a nitriding model which could be implemented in severe accident analysis codes such as MELCOR.

After reviewing the available data it was judged that additional separate effect tests were needed in order to further understand the mechanics of the degradation by nitrogen. Therefore, several SET's have been performed in the present period. The studied parameters included a variation of pre-oxidation time (in oxygen), nitriding time, and temperature. The analysis of the results is still on going, a preliminary summary of the main results is provided in section 2.

On the other hand, the outcome of the thermodynamic analysis pointed out the possibility of oxy-nitride phases forming during the nitriding process [16]. The theoretical study suggests that the presence of an oxy-nitride phase may contribute to further degradation of the cladding by forming a more porous oxide/nitride layer by having higher volume mismatch in the ternary system compared to the binary system. Therefore, one of the main tasks of the present period was to prove the existence of such phases by performing various analytical measures. The outcome of the main results is described in section 3.

2. Separate Effect Tests

The SET's were performed in a commercial thermobalance coupled with a mass spectrometer. The gases (Ar, O_2, N_2, synthetic air) were injected into the lower part of the vertical tube furnace. The experiments consisted of three phases: pre-oxidation phase, nitriding and re-oxidation.

Zircaloy-4 tube segments (1 cm height, 10.75 mm outer diameter, 0.725 mm wall thickness) were cut from the long tubes, ground at both ends, and cleaned in an ultrasonic bath of acetone. The specimens were open at both ends, allowing external and internal oxidation.

Argon was used in all tests as a carrier gas in the furnace and as a reference gas for mass spectroscopy. Therefore, «tests in pure oxygen and nitrogen atmosphere» were performed in oxygen-argon and nitrogen-argon mixtures, respectively. The pre-oxidation phase was performed in oxygen environment since the thermobalance was not designed for operation under steam-containing atmospheres (i.e. more prototypical of an accident scenario). The oxide scale developed by oxygen simulated the pre-oxidation in steam. The oxide scale developed by reaction with oxygen is known to be very comparable to that developed under steam [8]. In all the tests, the flow rate of argon was 3 l/h, and the flow rates of reaction gases (oxygen, nitrogen) were 10 l/h.

After each test, the samples were embedded in an epoxy resin and the embedded specimens were cut, ground and polished. Metallographic examination by optical microscope was performed for all specimens. The metal-lographic investigations were mainly focused on the external oxide scale of the specimens to concentrate on the external surface oxidation which is prototypic in reactors.

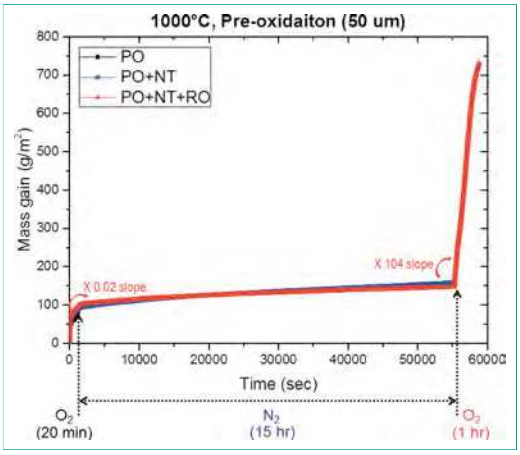

Figure 1:
Re-oxidation with a long nitriding phase.

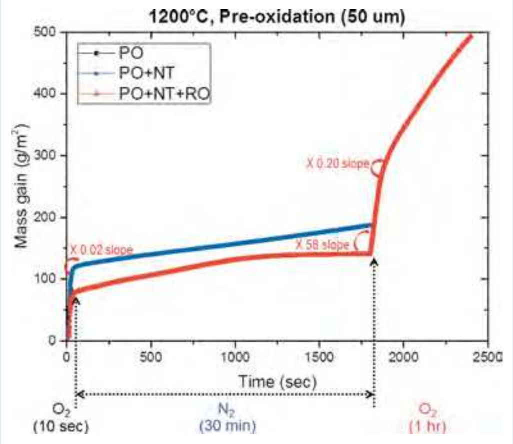

Figure 2:
Re-oxidation with a short nitriding phase

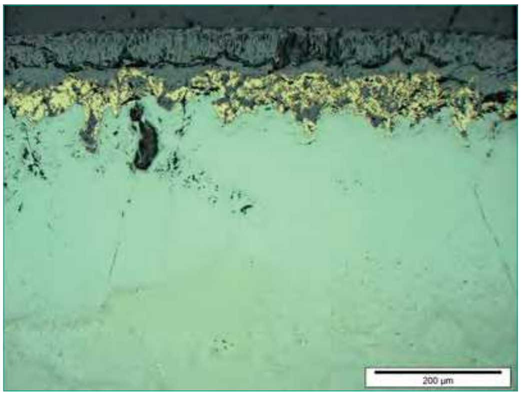

Figure 3:
Nitride layer with long nitriding

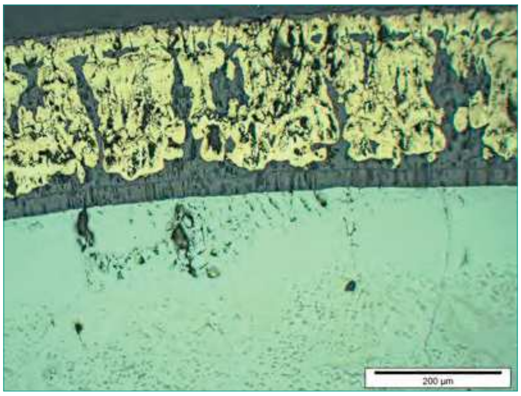

Figure 4:
Nitride layer with short nitriding

The first series of separate effect tests was performed at KIT during November to December 2014. These tests were exploratory and served to identify possible conditions that can contribute to the nitride formation and the subsequent re-oxidation of the nitrides. The results pointed out that the longer nitriding process under oxygen starved conditions (i.e. pure nitrogen environment) lead to a faster cladding degradation during the re-oxidation phase (figures 1 and 2). The sample with a long nitriding period (figure1) shows that during re-oxidation the slope of the mass gain was more accelerated than with the sample with a short period of nitriding (figure 2). In the latter case, the re-oxidation seems to be very fast at first, followed by a slower oxidation phase.

Figures 3 and 4 show the nitride layers formed during long and short duration nitriding, respectively. The sample with a long nitriding period formed an internal nitride layer, whereas the test with a short nitriding period formed only an external nitride layer. One possible explanation for the different behaviour is that the nitrogen reacts first with the oxide layer that has been formed during pre-oxidation, hence the very fast kinetics observed right after re-exposure to oxygen. In the case of a short nitriding period, the kinetics slows down after all the nitrogen from the external layer has been consumed.

In the case of a long time nitriding period, nitrogen was transported through the oxide, possibly by diffusion or gas phase transport through the porosity in the oxide, leading to formation of an internal nitride layer. Another possibility would be the occurrence of macro cladding degradation, i.e., cracks in the oxide layer, potentially following prior breakaway oxidation. In this case nitrogen could access easily the oxide-metal interface, causing the kinetics during re-oxidation to be very fast. However, no breakaway was observed from the optical micrographs, and therefore, the results of the first test series supported the theory of nitrogen diffusion through the oxide layer. Other causes for the observed behaviour could be, e.g., possible formation of an alpha-Zr(O) layer during pre-oxidation and nitriding. This mechanism will be carefully analysed in the next period.

To extend the database for the analysis, a second series of tests was designed with different temperatures, pre-oxidation history, annealing times in nitrogen, and better defined boundary conditions (i.e. reducing the oxygen impurities in the thermobalance device). The experiments were performed at KIT during August to September 2015. A total of 72 experiments were performed during the second series of tests. The detailed analysis of the experiments is still ongoing and will be presented during the next period.

3. Sample analysis

As mentioned in section 1, the thermodynamic study points out the possibility of oxy-nitrides being present during the nitriding process, as well as their possible contribution to further degradation of the cladding. The following characteristics of the oxy-nitrides were found in the literature:

- Both γ-Zr_2ON_2 and ZrN are **optically golden-yellow colour** [17].
- Due to the different molar volumes between γ-Zr_2ON_2 and ZrN, the mixture of γ-Zr_2ON_2/ZrN layer could be **more porous than the pure ZrN layer**.
- The mixture of γ-Zr_2ON_2/ZrN may contribute to more **mechanical degradation and heat release** than the pure ZrN layer.

Therefore, one of the main tasks during this period was to find out if oxy-nitrides were present in the samples generated in the thermobalance. Several measurement techniques were used:

A. Raman spectroscopy

The Raman spectroscopy provided the possibility to study the phase compositions. A test where an external nitride layer was formed was chosen for the analysis. The sample was created at 1200 °C, had a pre-oxidation phase of 10 s, and a short nitriding phase of 30 minutes. After performing metallography and optical analyses, the sample was prepared for the Raman analysis. The studied region is presented in figure 5 where 7 positions are identified.

The analysis started with the reference spectra preparation for which m-ZrO_2 and ZrN powders were used. The m-ZrO_2 reference sample was prepared by steam oxidation of Zry-4 at 1200 °C for 15 minutes whereas the ZrN powder sample was purchased. Unfortunately, it was not possible to obtain a reference spectrum for the oxy-nitrides. (One sample of potential oxy-nitride was obtained from TU-Berlin, but in reality the sample was found to be m-ZrO_2 based on the analysis by Raman). The Raman analysis consisted of per-

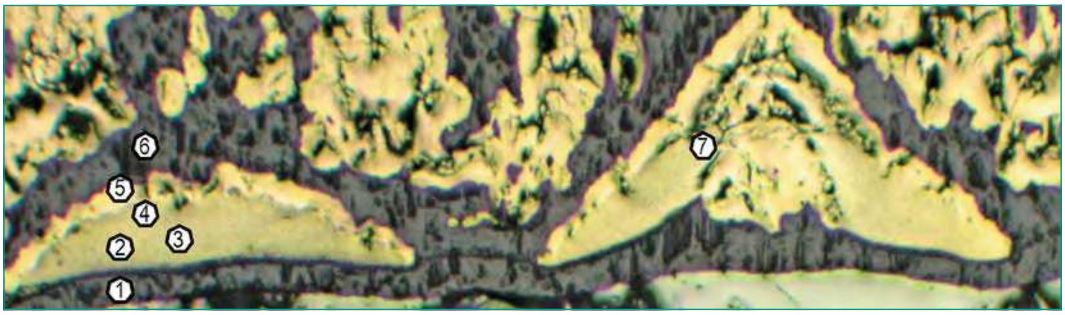

Figure 5:
Sample used for the Raman analysis: Pre-oxidation 10s, nitriding 30 min at 1200 °C

forming Raman scattering in the positions shown in figure 5.

The analysis was carried out to answer the following questions:

a) Is the spectrum comparable to the reference spectra of m-ZrO_2 and/or ZrN?

The positions 1 and 6 were comparable to m-ZrO_2 whereas position 5 was comparable to the ZrN spectrum. Figures 6 and 7 present the spectra for positions 5 (ZrN), and 1 and 6 (m-ZrO_2), respectively.

b) Is the sample a mixture of m-ZrO_2 and ZrN?

If there is a mixture of phases, the Raman spectrum will contain peaks representing all of the different phases. Fitted Raman spectra of mixtures of m-ZrO_2 and ZrN were generated (figure 8). The analysed spectra of the points that didn't correspond to the spectra of m-ZrO_2 and/or ZrN were compared with the mixtures. According to the analysis, the position 7 seems to be a mixture of m-ZrO_2 and ZrN. Figure 9 shows an example of a mixed spectrum in position 7.

c) Is the analysed sample an oxy-nitride?

The positions 2, 3 and 4 showed additional two unidentified peaks at 452 and 502 cm^{-1} when compared to the ZrN spectra (figure 10). The peak 502 cm^{-1} corresponds to m-ZrO_2. The unknown peak at 452 cm^{-1} may indicate the existence of oxy-nitrides (Zr2ON2). In addition, Raman indicates that the bright golden-yellow coloured regions are ZrN, and the dark golden-yellow coloured region is the phase that may contain oxy-nitrides. However, it is not possible with the Raman data alone to conclude that the observed peaks are indicative of oxy-nitrides, since there is neither Zr-O-N spectrum available in the literature nor a suitable Zr-O-N reference sample to prepare a reference Raman spectrum. Additional analytical techniques are needed to confirm the composition of the different regions.

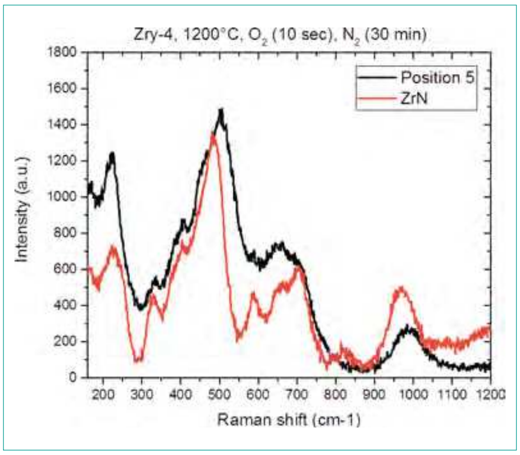

Figure 6:
Raman spectrum position 5

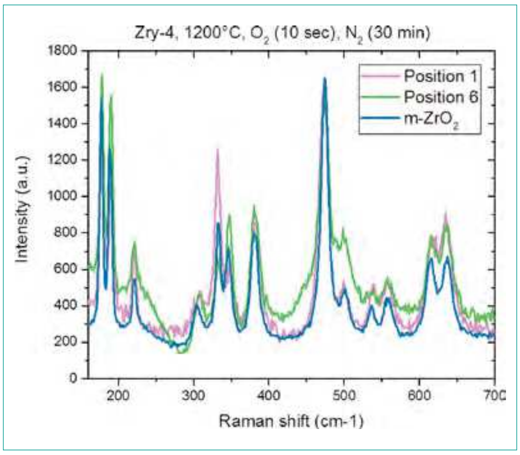

Figure 7:
Raman spectra positions 1 and 6

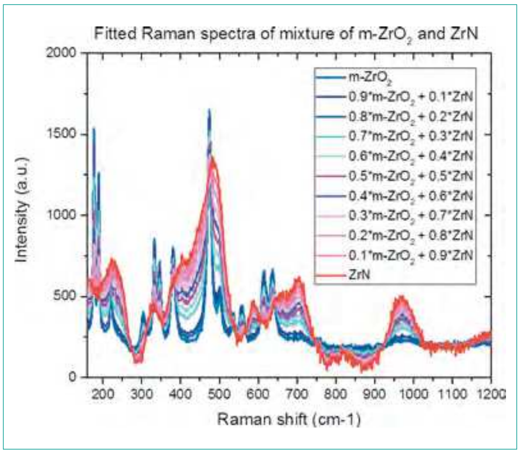

Figure 8:
Fitted Raman spectra of mixture

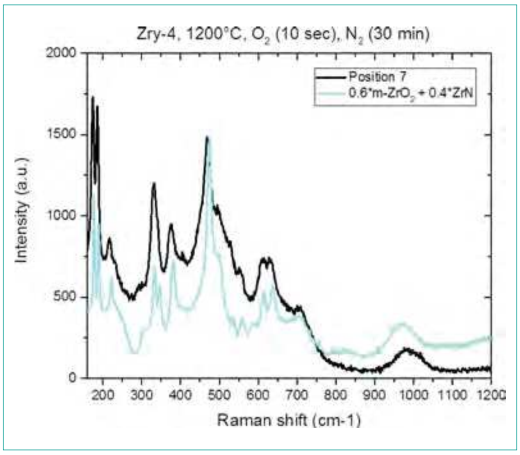

Figure 9:
Raman spectra position 7

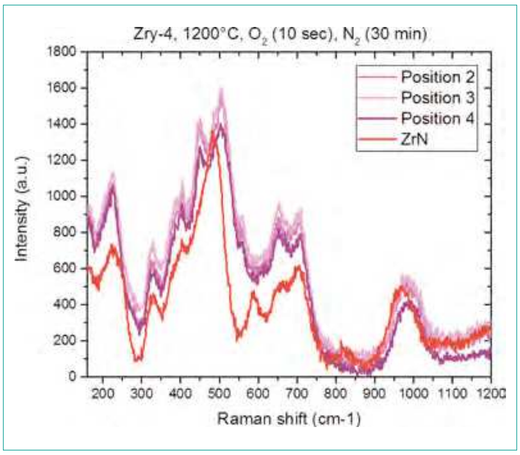

Figure 10:
Raman scattering in position 2

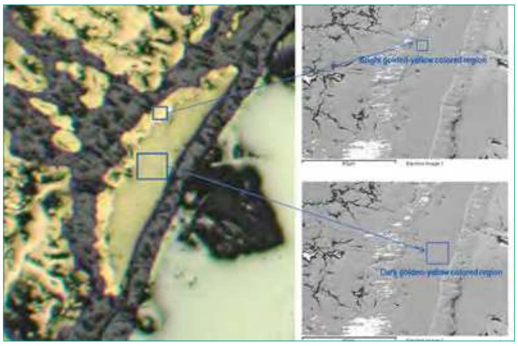

Figure 11: *Area where EDS was performed*

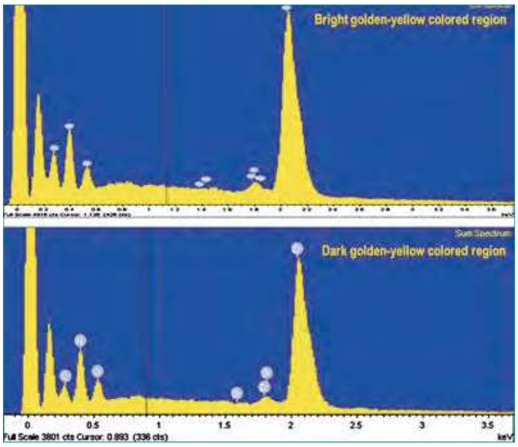

Figure 12: *Spectra obtained by EDS*

B. Energy Dispersive X-ray spectroscopy (EDS)

In order to study the elemental composition of the sample, an Energy Dispersive X-ray Spectroscopy (EDS) was performed concentrating in the region where the nitrides (bright golden-yellow coloured region) and Zr_2ON_2 (dark golden-yellow coloured region) are postulated to be found (Figure 11). Figure 12 shows the spectra obtained by EDS. No distinct difference was observed in the sum spectra of both bright and dark golden-yellow coloured regions. Both regions contained nitrogen and oxygen, and the nitrogen content is higher than the oxygen content. The oxygen content is not negligible and it may indicate the existence of Zr-O-N phase in both regions.

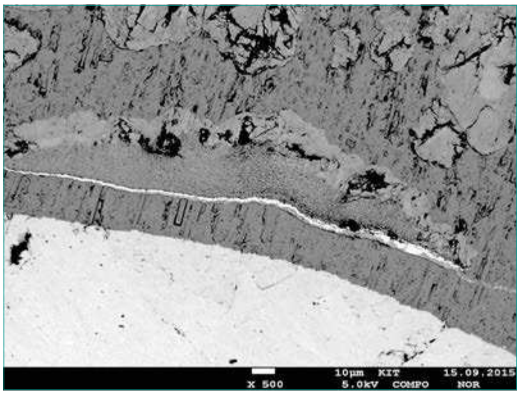

Figure 13: *Scanning Electron Micrograph (SEM)*

C. Wavelength Dispersive Spectroscopy (WDX)

The Scanning Electron Microscope (SEM) image showed that the dark gold region showed more pores than the bright gold region (Figure 13). However, the semi-quantitative study shows no significant difference in the compositions in the different gold coloured regions, Figure 12.

In order to complement the analysis performed by EDS, a Wavelength Dispersive Spectroscopy (WDX) analysis was performed. The elemental mapping for the chosen region is presented in figure 14. Table 1 shows the semi-quantitative elemental analysis results performed in the area in Fig. 14. As for the EDS, the analysis focuses on the bright and dark golden-coloured regions, believed to be ZrN and Zr_2ON_2, respectively. However, no significant difference in the elemental compositions of the two areas can be found.

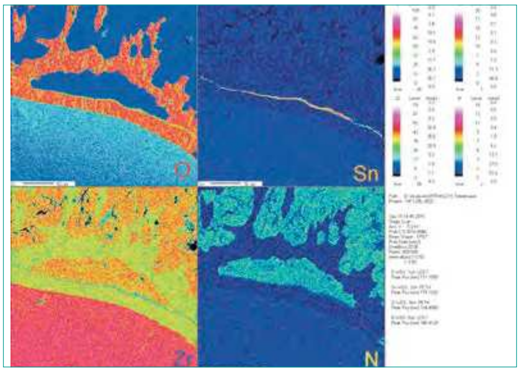

Figure 14: *Elemental mapping*

D. Further analyses

In order to complement the Raman analysis, X-Ray Photoelectric Spectroscopy (XPS) analysis is ongoing. In addition, X-Ray Powder Diffraction (XRD) and Electron Backscatter Diffraction (EBSD) are being performed in order to study the crystal structure of the different phases in the samples. Com-

Table 1: *Quantitative atomic (AT) elemental analysis %*

	At%				
	O	N	Sn	Zr	Total
Dark gold	5.58	47.13	0.18	47.11	100.00
Bright gold	5.04	47.13	0.18	47.64	100.00
Zr-O	65.91	0.00	0.28	33.81	100.00

bined elemental and crystal structure analysis may prove (or discard) the existence of Zr-O-N in the regions of interest.

The integration of the small scale experiments and the micro-scale analysis will serve to understand the complex process of nitriding and re-oxidation and will set the basis to develop a model which could be implemented in a system analysis code.

National Cooperation

The student is enrolled at ETHZ and is supervised by Prof. Prasser/ETHZ.

International Cooperation

The PhD work is performed in collaboration with KIT. The PhD candidate had a first stay at KIT where he learned to perform thermodynamic calculations for the materials (Thermo-Calc. software) with the support of the KIT researchers. The first year of PhD work has been performed with frequent meetings and email communications. For the second year of PhD work, experimental work was carried out at KIT since November until December 2014. The experimental work at KIT is supervised by Dr. Martin Steinbrück. In addition, the second supervising professor of the thesis work is Prof. Seifert from KIT.

To further the understanding of the air oxidation phenomena, an air oxidation research community has been formed by PSI, EDF, GRS, IRSN, KIT and IBRAE. The partners participate actively in seminars and workshops in order to share the state of the art of the air oxidation experimental studies and modelling.

Assessment 2015 and Perspectives for 2016

Several sets of separate effect tests were performed at KIT during November to December 2014 and during August to September 2015 to support the model development. The outcome of the series performed in 2014 was presented in this report. The results of the second series are currently being analysed in detail and the outcome will be presented in 2016. With these results, it is expected to be able to identify the main parameters that contribute to cladding degradation during nitriding and its impact during re-oxidation of the nitrides.

In addition, sample analyses were performed in order to investigate the composition of the samples, the different phases, and the crystalline structure of the compounds formed during the nitriding process. However, the study is not yet conclusive and further analyses are planned to be performed until the end of 2015. It is foreseen that with the conclusion of the sample analysis, sufficient database will be available to formulate a model for the effect of nitrogen in air oxidation.

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