MELCOR
further development of the air ingress modelling

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Duration of the Project	1.7.2013 – 30.6.2017

ABSTRACT

Cladding degradation in 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 with less data for cladding oxidation in air. Until recently it was believed that nitrogen did not play a major role as an active chemical species. 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. The consequences of nitriding are two-fold. Firstly, the reaction of Zr with nitrogen in air appears to make the fuel cladding more fragile, i.e., more prone for failure. And secondly, as both the nitriding and the re-oxidation of ZrN are exothermic reactions, they increase the heat generation during the transient, and subsequently, may accelerate the accident progression. The present severe accident codes take the nitriding effect into account only to very limited extend, and consequently, they may predict accident progression which is nonconservative.

In this work, the effect of nitriding was investigated by carrying out a series of separate effect tests under well-controlled conditions in the temperature range 900 – 1200 °C. The cladding samples were first exposed to air for a predetermined time of pre-oxidation. This step was an important preparatory phase because the oxide layer is known to protect the cladding for further oxidation. After the pre-oxidation, the samples were exposed to pure nitrogen for the nitriding reaction to take place, and finally, the nitrided samples were re-oxidized in oxygen. During all the phases, a thermogravimetric device recorded the mass change of the sample. After the tests, metallographic analyses were carried out to determine the composition of the samples after each one of the phases. The composition was then compared with the mass gain from the thermogravimetry to determine the mechanisms of the cladding degradation during the nitriding and re-oxidation. Even though the mass gain of the samples during the nitriding stage was generally small, it had a significant effect on the final cladding degradation due to re-oxidation. A simple model will be postulated based on the experimental results.

Project goals

The aim of the investigation is to understand the mechanisms of the reaction for formation of ZrN compounds in order to develop and validate a model which can be implemented in system analysis codes. In addition, re-oxidation of the formed ZrN compounds is investigated, and their effect on the cladding degradation determined.

Simplistically, the nitriding can be represented by an overall reaction:

$2Zr + N_2 = 2ZrN$ (1)

Experiments have shown that the pure Zr metal is not prone for nitriding reaction, however, oxygen-stabilized α-Zr(O) reacts readily with nitrogen [Steinbrück, 2014]. This oxygen-stabilized α-Zr(O) is formed along with the protective Zr-oxide scale in the nuclear reactor fuel cladding during oxidation in the reactor under operation conditions and also as the temperature rises during a transient. In this work, the oxygen-stabilized α-Zr(O) layer was formed during the pre-oxidation phase of each experiment underneath the oxide scale. After pre-oxidation, the sample was exposed to pure nitrogen for the nitriding to take place.

Further cladding degradation takes place once the nitrided sample is re-exposed to oxygen:

$2ZrN + 2O2 \rightarrow 2ZrO2 + N2$ (2)

The re-oxidation reaction is exothermic potentially accelerating the cladding degradation and accident progression considerably [Steinbrück et al., 2006]. In this work, the mechanisms of the above described processes were investigated, and the damage to the cladding was analysed after the different process steps. Extensive sample analyses were carried out to indentify the different phases which were formed in order to link their formation on the cladding degradation mechanisms, and to include all the important reactions on the overall description of the nitriding process.

Work carried out and results obtained

Methods

The main part of the work has been devoted to experiments with two different thermogravimetric instruments. The first series of experiments was carried out using a Netzsch STA-409 system with which tests were conducted in the temperature range 900 – 1200 °C. The instrument allows the use of different reacting gases (Ar, O2, N2) with well-controlled flow rates, Figure 1. The gas is supplied via Bronkhorst® flow controllers, and injected into the lower part of the vertical tube furnace. Argon used as a carrier and reference gas for mass spectroscopy entered into the furnace through the balance containment. The reaction gases were directly injected to the reaction tube to avoid contamination of the balance containment. Tests were carried out at four temperatures, and at each temperature, two different pre-oxidation times, two different nitriding times, and two different re-oxidation times were used. 48 tests were carried out with the STA device.

The second series of tests was conducted at a thermo-balance Setaram TAG. Compared to the STA instrument, the TAG offers improved leak tightness and a more accurate measurement of mass change due to the use of a reference sample in an identical geometry, Figure 2. The tests were carried out at 1000 and 1100 °C. Altogether 32 tests were carried out with the TAG system.

In both systems, Zry-4 samples were tube segments of 1 cm height, 10.75 mm outer diameter, and 0.725 mm wall thickness. Samples were cut and ground at both ends, and finally they were cleaned in an ultrasonic bath in acetone. The samples were open at both ends allowing both external and internal oxidation, Fig. 3. For the samples for Setaram TAG instrument, two holes were made for mounting the samples in the reaction chamber.

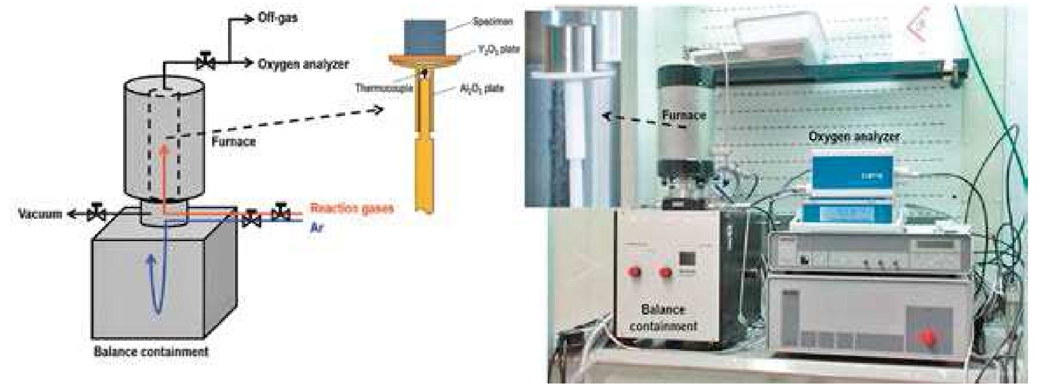


Figure 1: *Thermo-balance Netzsch STA-409*

Figure 2 (left): *Thermo-balance Setaram TAG.*

Figure 3 (right): *Fresh Zry-4 samples used in the thermogravimetric tests.*

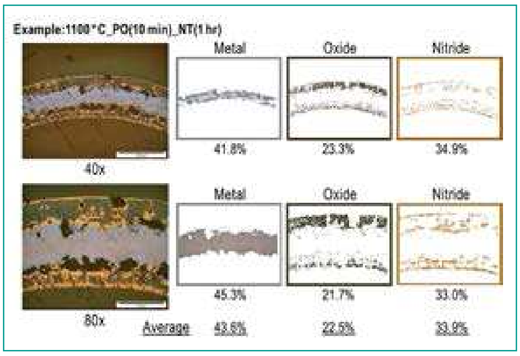


Figure 4: *Image analysis for determination of the different phases in the optical micrographs*

Each test included a heating period, and the main reaction period, or reaction periods at a given temperature. The mass gain of the sample was recorded continuously. The exhaust gas composition was measured in most of the tests.

Sample analysis

After the tests, the samples were embedded in an epoxy resin, cut, ground, and polished. Analysis was carried out with an optical microscope using magnifications of 40 × and larger. The morphology and surface structure as well as the elemental composition of some of the samples was determined with a scanning electron microscope (SEM) combined with a wave-length dispersive spectroscopy (WDS). The different Zr-O-N phases were analysed with Raman spectroscopy to identify chemical speciation of the samples, and to evaluate the possibility of formation of mixed Zr-O-N phases. Crystalline phases were analysed with X-ray diffraction (XDR), and attempts were made to identify Zr-O-N mixed phases using X-ray photoelectron spectroscopy (XPS).

Optical micrographs were used for semi-quantitative analysis to determine the relative amounts of different phases in the samples based on image analysis, Figure 4. In the analysis, the colours of different phases were detected and separated, and fractions of metal, oxide, and nitride were determined based on the area of each phase in the micrographs. The phase compositions were then used for comparison with the mass gain data from the thermo-balance to assess the possible reaction mechanisms during the different steps in the nitriding process.

Results – pre-oxidation

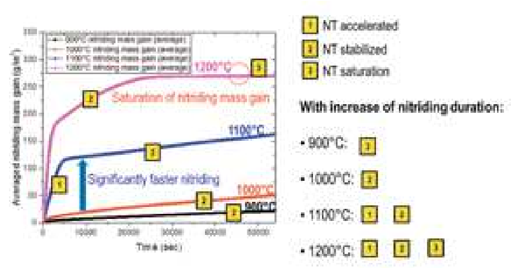
Pre-oxidation was carried out in oxygen atmosphere with argon used as a carrier and reference gas. In the Netzsch STA system, the oxygen flow was 10 l/h and Ar flow 3 l/h. Table 1 shows the mass gain during pre-oxidation at four temperatures and two pre-oxidation durations for each temperature. Mass gain for temperatures 1100 °C and 1200 °C shows only minor differences between the two pre-oxidation times. This is presumably due to the relatively long residence time of the reagent gases in the thermo-balance system, and subsequently inaccurate time resolution in the tests with very short exposure. For this reason, the pre-oxidation times 30 s at 1100 °C and 10 s at 1200 °C are preliminarily excluded from further quantitative analysis.

During oxidation of the Zr cladding, metallic Zr reacts with oxygen forming Zr-oxides. Separate effect tests have shown that during oxidation, also oxidized metal, i.e. oxygen stabilized α-Zr(O), is formed. The amount of oxidised metal depends on the temperature, gas atmosphere and the exposure time. α-Zr(O) is known to react readily with nitrogen in oxygen-poor atmospheres, therefore, the

Temperature (°C)	Duration of the pre-oxidation	Pre-oxidation mass gain [g / m²]
900	2 hr	61.7
900	6 hr	102
1000	20 min	91.2
1000	40 min	171
1100	30 sec	134
1100	10 min	215
1200	10 sec	162
1200	1 min	167

Table 1: *Mass gain during pre-oxidation*

Figure 5:
Typical nitriding mass gain at different temperatures.



formation of this phase is critical for the further nitriding reaction kinetics. The amount of α-Zr(O) which is formed during the pre-oxidation phase in these tests could not be determined based on the thermogravimetric data which only gives the total mass gain of the sample (oxide and α-Zr(O)). However, the formation rate for α-Zr(O) can be estimated based on the literature [Steinbrück, 2014].

Another important process to consider in the pre-oxidation step is the potential for breakaway oxidation. Break-away oxidation means that the oxide layer degrades during oxidation, and mechanically breaks forming cracks. The cracks allow fast access for the reacting gases to the metal surface this way accelerating the reaction between the metal surface and the gas. Break-away oxidation is known to occur at temperatures below 1050 °C when the metal is fragile and the exposure to oxygen is long enough for a critical oxide thickness to be formed [Birchley and Fernandez, 2012]. The critical thickness depends on the oxidation history of the sample and the temperature. It can be postulated that if breakaway oxidation occurs, it would also accelerate the nitriding reaction because nitrogen would have faster access through the oxide layer. In this work, comparison tests were carried out to investigate this effect.

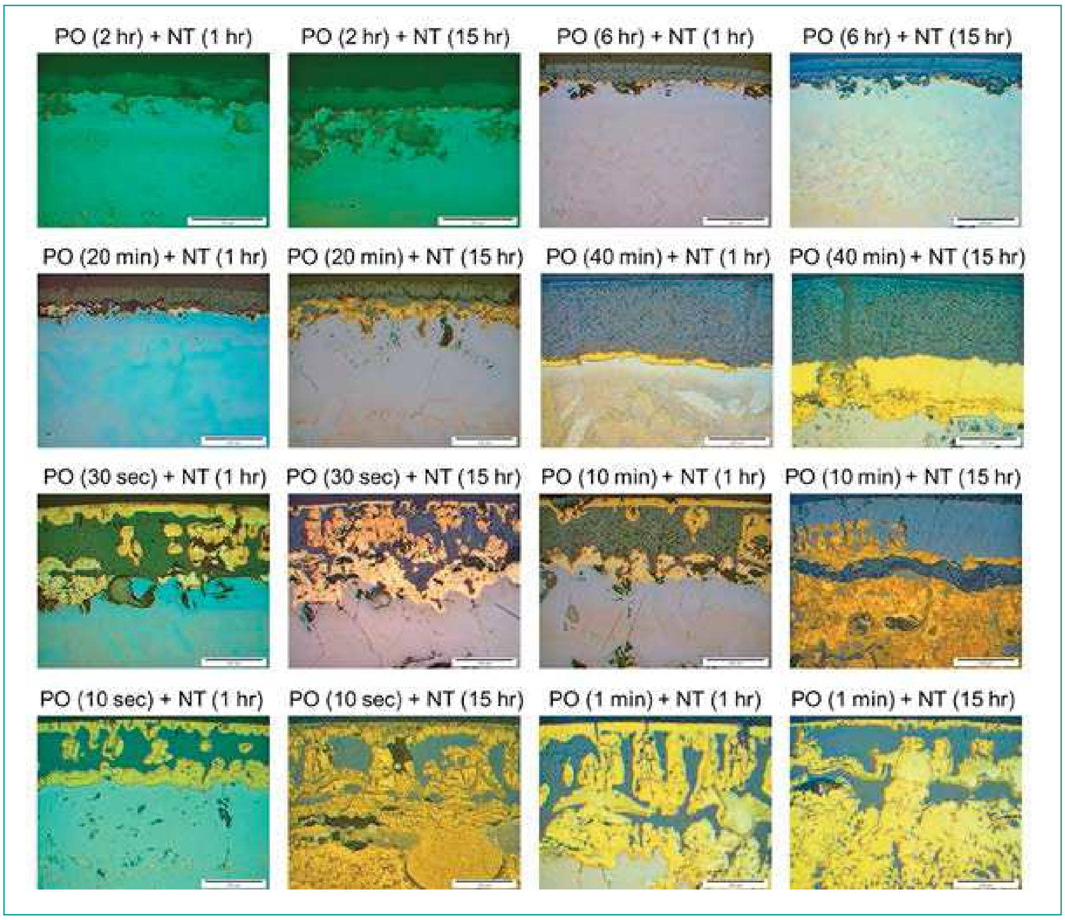
Results – nitriding

Nitriding is a reaction between Zr-containing species and nitrogen. As mentioned above, nitrogen does not react with Zr metal, but it reacts readily with oxygen stabilized α-Zr(O), as well as with sub-stoichiometric Zr-oxides [Steinbrück, 2014].

In our tests, nitriding was carried out in the absence of oxygen with pure nitrogen and carrier Ar gas with the pre-oxidized samples which contained a Zr-oxide scale, and an oxygen stabilized α-Zr(O) layer underneath. The flow rates were similar to the ones used in the pre-oxidation tests, i.e., 10 l/h nitrogen and 3 l/h argon.

In the results, two temperature regions were clearly distinguished. At 900 °C and 1000 °C, parabolic kinetic behavior was observed for the whole duration of the nitriding, Figure 5, leading to the formation of a nitride layer in the oxide-metal interface,

Figure 6:
Micrographs showing the nitride formation at different temperatures. Note the different pre-oxidation and nitriding times in the different samples.


PO (2 hr) + NT (1 hr)
PO (2 hr) + NT (15 hr)
PO (6 hr) + NT (1 hr)
PO (6 hr) + NT (15 hr)
PO (20 min) + NT (1 hr)
PO (20 min) + NT (15 hr)
PO (40 min) + NT (1 hr)
PO (40 min) + NT (15 hr)
PO (30 sec) + NT (1 hr)
PO (30 sec) + NT (15 hr)
PO (10 min) + NT (1 hr)
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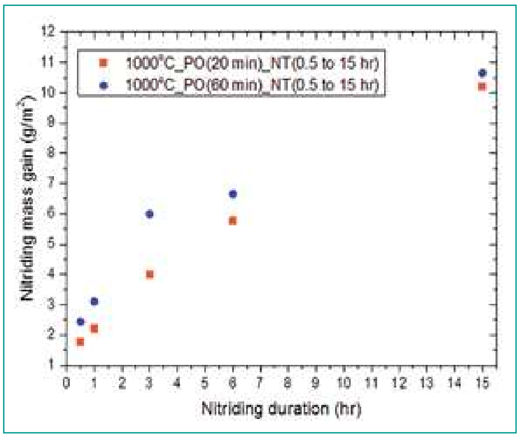

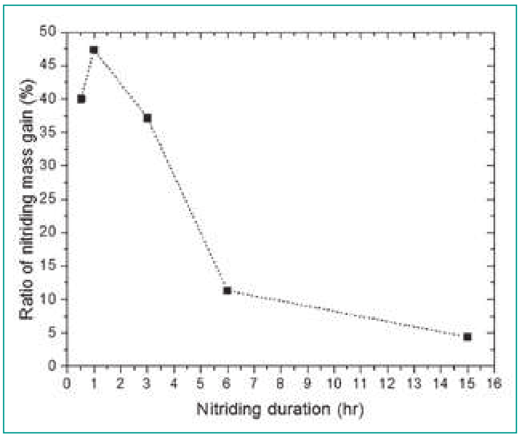

Figure 7 (left): *Nitriding mass gain in the comparison tests with and without breakaway.*

Figure 8 (right): *Relative mass gain in the tests with and without breakaway.*

i.e., between the oxide layer and the cladding metal, Figure 6. At these temperatures, the nitriding mass gain was relatively small even at long nitriding times. The parabolic kinetics imply that the reaction rate was controlled by the diffusion of nitrogen through the oxide scale, and the reaction of nitrogen with the α-Zr(O) was fast compared to the diffusion. It should be noted that no oxygen was measured to be released during nitriding which means that the oxygen which was liberated by nitriding reaction reacted further with the Zr metal forming new α-Zr(O) in the oxide-metal interface. This way, the reaction front moved towards the center of the metal even in the absence of oxygen in the reagent gas.

At the temperatures 900 °C and 1000 °C, breakaway oxidation is expected to take place once the oxide layer reaches a critical thickness. This effect will be described in the next section.

At 1100 °C and 1200 °C, the nitriding kinetics showed three different steps: first very fast reaction, followed by decrease in the reaction rate, and finally almost saturation with close to zero reaction rate, Figure 5. It is proposed that the initial fast kinetics is due to the nitriding of sub-stoichiometric oxide on the outer surface of the oxide scale which is formed in the absense of oxygen. The decrease in the kinetics follows once the sub-stoichiometric oxide on the surface is consumed, and the diffusion through the oxide-nitride scale is limiting further nitride formation. In this phase, α-Zr(O) close to the oxide scale-metal interface is nitrided. The reaction is fast compared to the diffusion. Due to these two mechanisms, nitride layer is formed both on the oxide surface, and in the oxide-metal interface, Figure 6. Whereas earlier investigations have shown formation of nitride layers on the oxide surface, no published investigations have shown the formation of nitride layer both on the oxide surface and in the interface between the oxide and the metal. The final decrease in the reaction rate is presumably caused when practically all the oxygen has been consumed, and no further reaction with nitrogen is possible.

Results – effect of breakaway oxidation on nitriding

Two sets of tests were carried out to investigate the effect of breakaway during pre-oxidation on the nitriding behavior. In one of the tests, pre-oxidation was carried out without breakaway (20 min oxidation at 1000 °C) and in the other test, with the breakaway (60 min oxidation at 1000 °C). Figure 7 shows the nitriding mass gain of both non-breakaway (red) and breakaway (blue) tests at 1000 °C. It can be seen that while mass gain during nitriding is generally small, the mass gain in the breakaway tests is consistently higher than in the tests without breakaway oxidation during pre-oxidation. Comparing the relative mass gain in the breakaway and non-breakaway tests, Figure 8, it is seen that the breakaway during pre-oxidation increases the nitriding mass gain by up to almost 50 %, and that the effect is strongest with the shortest nitriding times. This is understandable considering that breakaway oxidation allows for the nitrogen to be transported to the metal surface fast through the cracks this way accelerating the reaction at relatively short exposure times.

Results – Re-oxidation

When the nitrided cladding is re-exposed to oxygen, Zr-nitrides oxidize readily forming again Zr-oxides. The reaction is exothermic, and results in significant degradation of the cladding integrity, Figure 9. In addition, due to a molar volume difference between oxide (21.7 cm^3/mol Zr) and nitride (14.8 cm^3/mol Zr), a significant molar volume expansion occurs during a transformation from nitride to oxide causing further degradation. In general, higher temperature and higher degree of nitriding leads to

Figure 9: *Nitrided (left) and nitrided and re-oxidised (right) cladding samples (1000 °C, 15 h nitriding, 1 h re-oxidation)*

accelerated re-oxidation kinetics, and almost complete re-oxidation of the nitrides is reached at long re-oxidation times. The data analysis for the re-oxidation tests is being reviewed, and further results of the experiments will be reported later.

National Cooperation

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

International Cooperation

- The PhD work is performed in collaboration with Karlsruhe Institute of Technology (KIT). The thermogravimetric tests as well as the metallographic analyses were carried out by the PhD student at KIT. The experimental work at KIT is supervised by Dr. Martin Steinbrück. The second supervising professor of the thesis work is Prof. Seifert from KIT.
- XRD analysis of the samples was carried out at VTT Technical Center of Finland.
- An air oxidation research community has been formed by PSI, EDF, GRS, IRSN, KIT and IBRAE. The mentioned partners participate actively in seminars and workshops in order to share the state of the art of the air oxidation experimental studies and modelling.
- Collaboration has tentatively been started with Handong Global University (Korea) in the area of cladding oxidation in air.

Assessment 2016 and Perspectives for 2017

All the experiments have been conducted and analysed for the nitriding and re-oxidation behaviour. No further experimental work is foreseen in the project. Also the composition analyses have been completed. Data analysis for the re-oxidation phase is being reviewed, and the results of the thermo-balance mass gain and the image analysis will be compared for consistency. Chemical reaction mechanisms and rates have been estimated, and will further be elaborated during the last project year. In addition, the model has been formulated and will be elaborated based on the reaction mechanisms and experimental data from the thermo-balance supported by the image analysis for quantification of the different phases.

Publications

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- *S. Park, L. Fernandez-Moguel, H.-M. Prasser, J. Birchley, M. Steinbrück, M. Rinke, H.-J. Seifert.* Effect of nitriding and re-oxidation of pre-oxidized Zry-4. 21st International QUENCH Workshop, 2015.
- *S. Park,* Parametric investigation of nitriding and re-oxidation behaviors of pre-oxidized Zry-4, Transactions of the Korean Nuclear Society Spring Meeting May 12–13, 2016, Jeju, Korea.

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