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Neutron radiography and tomography investigations of the secondary hydriding of zircaloy-4 during simulated loss of coolant nuclear accidents

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Abstract

In the framework of the post-test examinations of the large-scale LOCA simulation tests at the fuel rod bundle scale, the hydrogen distributions in specimens prepared from the QUENCH-L0 and -L1 tests were studied by means of neutron radiography and tomography. In order to determine quantitative hydrogen concentrations, both, neutron radiography and tomography were calibrated using cladding tube segments with known hydrogen concentrations. The linear dependence of the total macroscopic neutron cross section with the H/Zr atomic ratio was determined for both methods. The hydrogen distributions in samples prepared from the two tests differ significantly as a first glance to the results obtained for the QUENCH-L1 shows. Whereas clearly visible hydrogen bands were found in samples of the QUENCH-L0 test with a time between burst and quenching of more than 70 s; in some specimens prepared from the QUENCH-L1 test only blurred bands could be detected. The reasons for these different behaviors can be the different times between reaching the temperature maxima and the quenching, as well as bending of the QUENCH-L1 bundle. In the QUENCH-L0 test the bundle was quenched immediately after reaching the maximal temperature. In QUENCH-L1 the hydrogen had about 130 s to diffuse and reach more homogeneous distributions without clear contrasts between the hydrogen bands and the neighboring regions in the neutron images.

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**Nomenclature**

| Symbol | Definition |
|--------|------------|
| LOCA  | loss of coolant accident |
| T     | neutron transmission |
| I     | neutron intensity behind the sample |
| I₀    | neutron intensity before the sample |
| x, y  | horizontal and vertical detector pixel position |
| Σₜₜₜₜ | total macroscopic neutron cross section |
| s     | neutron path length through the material |
| ℜ     | real part of the complex term |
| i     | indices of the isotope |
| N     | number density of the isotope |
| σ     | total microscopic neutron cross section |
| L     | aperture to detector distance |
| d     | aperture width |
| t     | time |
| Δₜₜₜₜ | time between burst and quenching |
| l     | diffusion length |
| D     | diffusion coefficient |
1. Introduction

Loss of coolant in nuclear power plants (NPP) can result in ecological and economical disasters as shown in the accidents occurring after the very strong earthquake and tsunami in Japan at 11th March 2011 and thereafter. At the Karlsruhe Institute of Technology (KIT, the former research center Karlsruhe FZK) such accident scenarios were simulated at the fuel rod bundle level in 18 large-scale experiments since 1997 in the framework of the QUENCH program [1]. Safe reactor behavior during loss of coolant accidents (LOCA) is one factor for licensing of a NPP. Criteria for the coolability of the reactor core are (1) that it is ensured that the temperatures do not exceed 1200°C between loss of coolant and start-up of emergency cooling and (2) that the oxidation level ECR (equivalent cladding reacted) of the cladding material is kept below the value of 17% [2, 3]. Various simulation experiments at single rod level have shown that in addition to the existing degradation criteria, hydrogen absorption occurring after the burst of the cladding rods has to be taken into account [4-8]. The phenomenon known as secondary hydriding results in an embrittlement of the cladding material in addition to the embrittlement caused by oxygen uptake and oxide layer formation.

During LOCA the following processes occur: At first the pressure in the reactor vessel decreases to about 3 bar and the coolant is lost. The temperature increases rapidly. Due to pressure within the fuel rod resulting from initial gas filling and gaseous fission products, ballooning occurs at hot spots of the cladding tube. This effect becomes strong when the temperature exceeds about 800°C at which the α to β phase transition in zirconium starts. Simultaneously, the burst pressure of the cladding tube very strongly decreases with increasing temperature [9, 10]. When the rods burst, the fission gases are released from the fuel rods. Steam penetrates through the burst opening into the gap between fuel pellets and inner cladding surface (gap width varies due to ballooning between 0.1 and more than 2 mm). The freshly exposed metallic inner wall of the tube cladding surface reacts strongly with the incoming steam. Very simply, the chemical reaction can be described by:

\[
2 \text{H}_2\text{O} + \text{Zr} \rightarrow \text{ZrO}_2 + 2x \text{H}_2 + 4(1-x) \text{H}_{\text{absorbed}}
\]

The resulting free hydrogen can be released as H₂ gas into the environment or can be absorbed by the remaining metallic zirconium; x is the fraction of released hydrogen. Detailed descriptions of these processes are given for instance in [11]. The release of molecular hydrogen causes the risk of a hydrogen detonation as happened in the Fukushima reactor buildings. The absorbed hydrogen changes the time scale of hydrogen release and embrittles the metallic β-Zr phase with the consequence of reducing the toughness of the cladding and the thermo-shock resistance, which can result in a fragmentation of the cladding tube and a re-arrangement and massive release of nuclear fuel and fission products during quenching.

The absorbed hydrogen is concentrated in axial regions close to the burst opening. Fig. 1 gives an example for the hydrogen distribution dependence on the distance to the burst opening centre [7, 8]. The data are determined by the hot extraction method usually applied for quantitative measurements of hydrogen uptake by zirconium alloys[7]. In the burst opening region none or little hydrogen is absorbed, whereas wide hydrogen containing bands are found some millimetres distant from the burst opening.
In order to prove the safety of fuel rod bundles during LOCA scenarios valid for German NPP, a series of large-scale bundle simulation experiments has been launched at KIT. In contrast to single-rod experiments already performed, the interaction between the rods is also simulated. As a first experiment the commissioning test QUENCH-L0 [12] of this series was performed in 2010. For this test, as well as for the following test QUENCH-L1 (performed in February 2012), fuel rod bundles with Zircaloy-4 cladding tubes were studied. The QUENCH-L1 test will be the reference for subsequent series of four tests employing different cladding materials and bundle geometries.

Neutron radiography is used to determine the hydrogen concentration and distribution in zirconium alloys [13-23]. In [13, 17] the hydrogen concentration is correlated with the CT number (voxel value of the 3D computer reconstruction on the basis of neutron tomography) or neutron transmission, respectively. Own investigations used the dependence of the total macroscopic neutron cross section on the atomic ratio between hydrogen and zirconium [18, 19, 21] which should be linear given by the theoretical view below.

From the measurements the transmission $T$ can be calculated for each pixel $(x,y)$:

$$ T(x, y) = \frac{I(x, y) - \frac{D_0}{D_B} I_B(x, y)}{I_0(x, y) - \frac{D_0}{D_B} I_B(x, y)} $$

$I, I_0$ and $I_B$ are the intensities behind and in front of the sample and the background intensity and $D_0$ and $D_B$ the neutron dose of the actual measurement and the background measurement, respectively. From the neutron transmission the total macroscopic neutron cross section $\Sigma_{\text{total}}$ can be calculated:

$$ \Sigma_{\text{total}}(x, y) = -\frac{\ln(T(x, y))}{s(x, y)} $$

$s$ is the neutron path length through the material. For a vertical oriented tube-shaped specimen it can be calculated by:

$$ s = \Re\left(\sqrt{d_0^2 - (x - x_0)^2} - \sqrt{d_i^2 - (x - x_0)^2}\right) $$
\( \Re \) represents the real part of the complex term, \( x \) and \( x_0 \) are the actual horizontal position and the middle position of the sample and \( d_o \) and \( d_i \) the outer and inner diameter of the tube, respectively. At radial middle position \( s \) equals two times of the tube wall thickness (1.45 mm for the conventional Zircaloy-4 claddings).

The total macroscopic neutron cross section is the sum of the total microscopic cross section \( \sigma \) of the isotopes \( i \) multiplied by their number density \( N \):

\[
\Sigma_{total}(x, y) = \sum_i N_i \cdot \sigma_i = N_{\text{Zr}}(x, y) \sigma_{\text{Zr}} + N_{\text{O}}(x, y) \sigma_{\text{O}} + N_{\text{H}}(x, y) \sigma_{\text{H}} \tag{5}
\]

In the case of steam oxidation of zirconium-based cladding materials, it can be assumed that only the number densities of oxygen and hydrogen are changed whereas the number densities of zirconium and the alloying elements are not influenced significantly.

A detailed description of the method including the calibration of the dependence of the total macroscopic neutron cross section on the H/Zr atomic ratio is given in [18].

The post-test analysis of the QUENCH-L1 test is still ongoing. Neutron imaging investigations were performed in May 2012. A first glance on these investigations will be given. Very first results of this test are compared with the results of the neutron imaging investigations of the QUENCH-L0 rods. The main focus of this paper is on the calibration of the dependence of the total neutron cross section and with it the CT number on the hydrogen concentration and the hydrogen distribution in cladding specimens of the two QUENCH-LOCA tests.

1. Material and Measurements

As mentioned before, the cladding tubes for the QUENCH-L0 and -L1 simulation tests were made of Zircaloy-4 (Sn-1.5, Fe-0.23, Cr-0.11 and O-0.14 wt.%, Zr balance). Fig. 2 shows schemes of the bundle cross sections of both tests. In QUENCH-L0, it was found that the initial inner tube pressure has only a minor effect on burst time and burst opening dimensions, therefore, in QUENCH-L1 the same initial inner pressure was applied to all rods. The temperature scenarios of both tests are given in Fig. 3. The QUENCH-L1 test differs from the commissioning test QUENCH-L0 mainly in a larger heating rate and a cooling phase before quenching. The QUENCH-L1 scenario corresponds with the LOCA scenarios determined for German nuclear power reactors. Detailed information about the QUENCH-L0 test is given in [12].

After the test the bundle was dismounted, the heaters (tungsten or tantalum) and pellets were removed from the rods and the cladding tubes were investigated separately.

For the calibration measurements, segments of a length of 20 mm were cut from original cladding tubes. They were cleaned and hydrogen loaded by annealing in Ar/H\(_2\) atmosphere at various temperatures in the range between 1073 and 1373 K. In agreement with Sieverts’ law [24] different amounts of hydrogen were absorbed. The mass of the absorbed hydrogen was determined by measuring the weight gain.
The investigations were performed using the ICON neutron imaging facility at the Swiss neutron source SINQ (Paul Scherrer Institut Villigen, Switzerland) [25]. The micro-tomography setup was used as characterized by L/d = 343, a field of view 28 mm x 28 mm and a pixel pitch of 13.5 μm. The real spatial resolution determined by measuring a Siemens star was about 25 μm. The illumination time of the radiography measurements was 300 s. The data were analysed using image analysis software “ImageJ”. The tomography projections were measured using the same setup. Illumination times between 30 and 90 s per frame were applied. According to the sampling theorem, 625 radiography images detected from different orientations were illuminated to reconstruct the 3D image without loss of information. The software MuhRec2 [26] was applied for the reconstruction.
2. Results and Discussion

2.1. Calibration

The correlation between total macroscopic neutron cross section and H/Zr atomic ratio was determined according to [18]. Radiographs of the calibration specimens are given in Fig. 4. The different neutron attenuations are obvious. The gray value distribution along the horizontal direction corresponds with the neutron path lengths through the tubular specimens with 0.725 mm wall thickness and 10.75 mm outer diameter.

![Radiographs of calibration specimens](image)

Fig. 4 Neutron radiographs of the calibration specimens. H/Zr = 0.990 is equivalent to 10940 wppm.

Four specimens were chosen for the calibration of the neutron tomography. Fig. 5 gives a slice of the 3D reconstruction of the samples. Clear differences in the gray scale can be seen here too. Even the samples with H/Zr = 0.23 and 0.28, respectively can be clearly distinguished.

![Tomography reconstruction](image)

Fig. 5 Slice of the tomography reconstruction of the calibration specimens

In Fig. 6 the total macroscopic neutron cross section determined from the radiograph and calculated for the reconstructed voxels, respectively, are plotted versus the H/Zr atomic ratio. According to Eq. (5), linear correlations were found. The cross section values determined by neutron tomography are a little bit below the values determined from the neutron radiographs. The reason can be that for the analysis of the radiography data the sample middle positions were used. At these positions the path length of the neutron through the materials equals two times of the wall thickness (1.45 mm for the as received state).
The slight swelling of the samples during hydrogen uptake as well as the curvature of the tube segments were not taken into account in the analysis of the radiography data. Therefore, a little bit smaller neutron path length was used for the analysis resulting in a slightly higher total macroscopic neutron cross section. However, both methods provide the possibility for the quantitative determination of the absolute hydrogen concentrations in the cladding tube specimens from the data.

2.2. Results of the post-test examination of QUENCH-L0

The cladding tubes of the QUENCH-L0 bundle can be divided into two groups; claddings showing clear hydrogen bands (mainly the inner rods of the bundle) and tubes without these bands (mainly the outer rods). Fig. 7 gives typical radiographs of both groups. In Fig. 7 a) dark bands in the near of the burst opening are visible. The bands are bended and oriented non-symmetrically relative to the tube axis. It was the first time known that those bands were imaged.

The parameters controlling the formation of the hydrogen band and the amount of absorbed hydrogen seem to be (1) the time between burst and quenching $\Delta t_{b,q}$ and (2) the temperatures during this time. These times varies between 49 and 112 s in the QUENCH-L0 test. Because of the uncertainty of the wall
thickness and of the contribution of front and back side of the tube, the hydrogen concentrations cannot be determined exactly from the neutron radiographs. Neutron tomography is needed to measure the correct concentrations. In Fig. 8 the maximal hydrogen concentrations determined from tomography investigations is plotted versus $\Delta t_{b-q}$. The shortest time after which hydrogen bands are visible is 70 s. More detailed results and discussions of the neutron imaging investigations of samples prepared from the QUENCH-L0 test are given in [27].

Fig. 8 Dependence of the maximum hydrogen concentrations determined from the 3D tomography reconstructions on the time between burst and quenching.

2.3. Very first results of the post-test examination of QUENCH-L1

The times between burst and quenching were more homogeneous and significantly larger in the QUENCH-L1 test than in QUENCH-L0. The minimal and maximal times were 192 and 225 s, respectively. However, no clear hydrogen bands as found in samples of the QUENCH-L0 test could be detected in the QUENCH-L1 cladding tubes. As an example, radiographs of the rods #06 ($\Delta t_{b-q} = 225$ s) and #08 ($\Delta t_{b-q} = 221$ s) are given in Fig. 9.

Whereas weak hydrogen bands without sharp contrasts to the neighborhood and larger distances to the burst opening compared to the findings obtained at samples from the QUENCH-L0 test were found in rod #06, an increased hydrogen concentration in the upper part of the burst region was detected in rod #08. Fig. 10 gives the axial distributions of the neutron transmission and the calculated total macroscopic neutron cross sections (calculated on the basis of the initial tube wall thickness). Here the hydrogen bands become visible more clearly.
A possible explanation of the difference in the hydrogen bands between the two tests is the difference in the temperature scenarios. In QUENCH-L0 directly after reaching the maximal temperature the bundle was quenched. In QUENCH-L1 the temperature increase was much faster. After reaching the maximum a slower cooling phase followed. The duration of this phase was about 130 s. Additionally, the temperature increase due to switch-off of the cooling steam was registered on the beginning of the quench initiation. All together the $z = 950$ mm axial position had a temperature above 800 K for nearly 200 s. During this time, hydrogen diffuses rapidly in the metallic zirconium. On the basis of the results in [27] the diffusion length $l = \sqrt{D \cdot t}$ during 100 s is in the order of magnitude of 1 mm (0.8 mm and 1.6 mm for 1000 K and 1300K, respectively). It means that the diffusion is fast enough to significantly equalize the hydrogen concentration in the cool down phase. The gradients in the hydrogen distribution become less and the hydrogen bands lose the contrast with respect to the neighboring regions of the tube.

A second difference between the two tests was the heater material. Whereas in the QUENCH-L0 tungsten heaters were used, tantalum heaters were used in the QUENCH-L1 test in order to reach a higher heating rate. The mechanical strength of tantalum at high temperatures is much less than the strength of tungsten. As a consequence, we observed a more pronounced bending of the rod simulators in the QUENCH-L1 test due to interaction with spacer grids. This bending results in 1) a direct mechanical contact between neighbor rods with blockage of the opening, and 2) a less well defined gap between pellets and inner cladding surface.
3. Summary and Conclusions

The secondary hydrogenation of the cladding tubes under LOCA conditions were studied by means of neutron imaging methods. The data were analyzed quantitatively to determine absolute hydrogen concentration distributions.

The dependence of the total macroscopic neutron cross section on the hydrogen concentration was determined using calibration specimens with known hydrogen content. For both neutron radiography and tomography, a linear dependence of $\Sigma_{\text{total}}$ on the H/Zr atomic ratio was determined experimentally. The results show that the two methods, radiography as well as tomography, can be used to extract quantitative values of the hydrogen concentration.

Neutron radiography and tomography were applied for the post-test examination of the hydrogen distribution in samples from the large-scale QUENCH-LOCA simulation tests. The hydrogen distributions differ significantly between both tests. Whereas in the QUENCH-L0 test for the inner rods, clearly visible hydrogen bands were found, the maxima of the hydrogen distributions in samples prepared from the QUENCH-L1 test bundle has no clear contrast with respect to neighboring tube regions. As a first hypothesis explaining these different behaviors, the differences in the temperature scenarios are proposed. The longer and slower cooling phase between reaching maximal temperatures and quenching results in lower gradients in the hydrogen distribution in rod #06 of the QUENCH-L1 test.

Additionally, it is proposed that the more pronounced bending of the QUENCH-L1 rods can result in 1) closing the gap between inner cladding surface and pellets; 2) closing of some burst openings by neighbor rods and with that closure, a blockage of the steam and hydrogen transport as seen in rod #08.

The analysis of the radiography and tomography data is still in process. Further results will be given elsewhere.
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