In-situ investigation of hydrogen diffusion in Zircaloy-4 by means of neutron radiography

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Abstract. The hydrogen diffusion from the gas phase into Zircaloy-4 solid cylinders was investigated at various temperatures between 823 and 1473 K. Diffusion coefficients were fitted using axial hydrogen distributions for all temperatures investigated. The activation energy of the hydrogen diffusion was calculated for temperatures at which the bcc β-phase is stable. The determined value of 48.3 kJ mol⁻¹ K⁻¹ is significantly higher than values published by other authors. At lower temperatures the hydrogen uptake is connected with a phase transformation from the hcp α- to the bcc β-phase. The spatial phase distribution and the hydrogen concentrations in the two phases were analysed.

1. Introduction

The progression of accidents in nuclear power reactors are studied experimentally at the Karlsruhe Institute of Technology (KIT, the former Research Centre Karlsruhe - FZK) in the framework of the QUENCH program. The investigations comprise loss of coolant accidents (LOCA) and severe accidents (accidents beyond LOCA). The processes occurring during such accidents are simulated on fuel rod bundle scale in the large scale QUENCH tests. The very expensive tests were supplemented by separate-effect tests on laboratory scale. In the framework of this program, the hydrogen diffusion in the β-phase of the classic nuclear fuel rod cladding material Zircaloy-4 (Zry-4) was studied in-situ by means of neutron radiography.

During loss of coolant accidents, free hydrogen is produced by the reaction between the hot zirconium alloy cladding material covering the fuel rods and steam. Very simplified the reaction can be described by:

\[ \text{Zr} + 2 \text{H}_2\text{O} = \text{ZrO}_2 + 4\text{H} \]  \hspace{1cm} (1)

Part of the produced hydrogen is released as gaseous H₂ into the reactor environment. The release can result in hydrogen detonations as happened in the Fukushima accident. The other part of the produced hydrogen is absorbed by the remaining metallic zirconium alloy. It degrades the mechanical properties and in particular the thermo-shock stability. An emergency cooling to terminate the accident can then result in a destruction of the cladding tube connected with release and redistribution of fuel and fission products.

Fig. 1 gives the zirconium-hydrogen binary phase diagram together with hydrogen partial pressure isobars according to Sieverts’ law [1]. In [1] the temperature correlations of the Sieverts’ coefficients were determined. For a given temperature and hydrogen partial pressure in the environment, the
hydrogen concentration in the metallic zirconium and the stable crystallographic phase can be examined. However, in order to understand the transient processes occurring during nuclear accidents, it is not sufficient to only know the thermodynamic equilibrium conditions. Kinetic parameters like the hydrogen transport have to be quantified as well.

Hydrogen diffusion in zirconium was studied in various works [2-8]. The published diffusion coefficients differ for some temperatures by more than two orders of magnitude. Fig. 2 shows the temperature correlations given in [2-4, 6] in an Arrhenius plot. The phase transformation between the hexagonal closest packed \( \alpha \)- and the body centred cubic \( \beta \)-structure at about 1100 K \((10^4/T \approx 9 \text{ K}^{-1})\) cannot explain the discrepancy in these values completely.

The aim of this work is the determination of the hydrogen diffusion coefficient in the \( \beta \)-phase of Zry-4 and the investigation of the diffusion processes in the two phase region between 800 and 1100 K. The investigations were performed by means of in-situ neutron radiography experiments. The advantage of neutron radiography in comparison to other methods like inelastic neutron scattering are the short
measurement times, the high spatial resolution and the determination of macroscopic diffusion coefficients needed for nuclear engineering applications.

2. Material and Measurements

The investigations were performed with Zry-4 cylinders (1.5 % Sn, 0.21 % Fe, 0.10 % Cr, balance: Zr) having a length of 20 mm and a diameter of 12 mm. The cylinders were oxidized ex-situ for 2 h at 1473 K in Ar/O₂ atmosphere to produce a dense oxide layer of about 300 µm. The oxide layer suppresses the hydrogen uptake in significant manner. The oxide layer was removed at one base plane of the cylinder by mechanical grinding and polishing. Through this plane hydrogen can be absorbed.

The neutron radiography experiments were performed at the ICON beamline [9] at the Swiss neutron source SINQ (Paul Scherrer Institute Villigen, Switzerland). Experimental details are given in [10]. For the in-situ measurements a special reaction furnace, the INRRO furnace (see scheme in Fig. 3), with neutron transparent windows was constructed by the XERION company. A Bronkhorst system controls the gas flow through the furnace and allows establishing a well defined atmosphere in the furnace.

The specimen was put in the INRRO furnace at room temperature. It was heated up to test temperature in flowing argon (50 l/h under normal pressure) with a rate of 10 K/min. Recording of the radiograph was started when the test temperature was reached. A frame repetition rate of 0.05 Hz was applied. The first radiographs were used as reference. After about 180 s, in addition to the argon flow, the hydrogen flow (8 l/h under normal pressure) was switched on. After a predefined time the hydrogen was switched off and the release of hydrogen was measured. Finally, the specimen was cooled down in the furnace to room temperature.

The contrast of the radiography image is caused by differences in the neutron transmissions. Provided that scattered intensity does not contribute to the intensity measured at the detector (multiple scattering can be ignored), the neutron transmission of the specimen \( T(x,y) \) at the point \( x,y \) of the radiograph is given by the ratio of the intensity behind and in front of the sample, \( I(x,y) \) and \( I_0(x,y) \), respectively, corrected by the background intensity \( I_B(x,y) \).

\[
T(x,y) = \frac{I(x,y) - I_B(x,y)}{I_0(x,y) - I_B(x,y)} = \exp(-\Sigma_{\text{total}}(x,y) + s(x,y))
\]  

Fig. 3. Scheme of the INRRO furnace.
The transmission depends exponentially on the total macroscopic neutron cross section of the specimen $\Sigma_{\text{total}}(x,y)$ and on the path length of the neutron through the specimen $s(x,y)$. The total macroscopic neutron cross section can be described by the sum over all total microscopic neutron cross sections $\sigma$ of the isotopes $i$ in the specimens multiplied by their number density $N$:

$$\Sigma_{\text{total}} = \sum_i N_i \sigma_i$$  \hspace{1cm} (3)

For hydrogen diffusion in zirconium alloys Eq. (3) can be described by:

$$\Sigma_{\text{total}} = N_{Zr} \sigma_{Zr} + N_{Sn} \sigma_{Sn} + \ldots + N_{H} \sigma_{H}$$  \hspace{1cm} (3b)

The radiographs were referenced by images taken at test temperature but without hydrogen flow. The resulting image can be described by

$$T_R(x, y) = \frac{T(x, y)}{T_{\text{ref}}(x, y)} = \frac{\exp(-\Sigma_{\text{total}}(x, y) \cdot s(x, y))}{\exp(-\Sigma_{\text{total}_{\text{ref}}}(x, y) \cdot s(x, y))} = \exp(-N_{H} \sigma_{H} \cdot s(x, y))$$  \hspace{1cm} (4)

Eq. (4) demonstrates that after the described referencing only the hydrogen containing parts are visible.

3. Results and Discussion

3.1. Hydrogen diffusion in single phase $\beta$-Zr

As an example, parts of the radiography images sequence obtained at 1273 K are given in Fig. 4. According to Eq. (4), the hydrogen containing parts appear darker. The propagation of the diffusion front is clearly visible. No significant hydrogen penetration through the oxide layer was observed.

From each of the images the axial distribution of the total macroscopic neutron cross section and with it the hydrogen distribution in the specimen can be obtained by quantitative image analysis. Fig. 5 gives as example of the axial distribution of the total macroscopic neutron cross section.

The diffusion can be described by the second Fick’s law:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right)$$  \hspace{1cm} (5)

The following boundary conditions were realized in the experiment:

1. The hydrogen concentration at the entrance plane is constant ($c(x=0,t) = c_0$)
2. The hydrogen concentration at the opposite side of the specimen is zero
3. The hydrogen diffusion coefficient $D$ does not depend on the hydrogen concentration

Fig. 4. Radiography image sequence of the hydrogen diffusion at 1273 K (hydrogen dark).
Boundary condition 1 is fulfilled because the experiments were performed in flowing gas atmosphere. Boundary condition 2 is fulfilled at the beginning of the experiment as long as the diffusion front has not reached the opposite side. On this basis Eq. (5) can be solved by:

\[ c(x,t) = c_0 \left( 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right) \]  

where \( \text{erf} \) is the Gaussian error function. Fig. 6 compares the fit according to Eq. (6) with the experimental data. The good agreement indicates that all three boundary conditions are fulfilled.

For each temperature investigated the diffusion coefficients were determined at different radiographs representing four to six different times. The temperature dependence of the diffusion coefficients determined is shown as an Arrhenius plot in Fig. 7. The temperature correlations given in [2-4] are compared. Whereas the data obtained for 1123 K and partially at 1173 K agree well with the correlation given in [4] and be not far away from [2], the slope of the curve and with it the activation energy determined is higher than the values given in [2, 3].

Fig. 6. Comparison between fit and experimental data of the hydrogen distribution after 900 s annealing in Ar/H₂ atmosphere at 1373 K.
The data obtained for 1273 and 1373 K and partially for 900 K agree better with the correlation given in [3]. At 1473 K the experimental data are significantly higher than the values expected from [3, 4]. The following correlation was determined from the experimental data:

\[
D_H = 0.023 \ cm^2 \ s \ \exp \left( \frac{48.3 \ kJ \ mol \ K}{R \ T} \right)
\] (7)

![Graph showing comparison of results with temperature correlations from literature.](image)

Fig. 7. Comparison of the results with temperature correlations from literature.

The strong texture of the applied specimens can be assumed as reason for the discrepancy between the data determined in this work and the correlations given in the references. The texture at high temperature was not yet measured. According to [11] a strong texture of the rod material at room temperature can be expected also for the \( \beta \) phase.

3.2. Hydrogen diffusion in the \( \alpha-\beta \) two-phase range

The absorption of hydrogen extends the temperature range at which the bcc \( \beta \) phase is stable to lower temperatures (see Fig. 1). Therefore, the hydrogen diffusion at temperatures between 823 and 1123 K is connected with \( \alpha \)- to \( \beta \)-phase transition.

Examples of the neutron radiograph sequence measured at 823 K are given in Fig. 8. The sample starts with hcp structure (\( \alpha \)-phase). At the beginning, represented by the radiograph taken after 120 s, only a small region containing hydrogen is visible at the surface through which hydrogen can penetrate. The amount of hydrogen is low because the \( \alpha \)-phase can absorb less hydrogen than the \( \beta \)-phase. The hydrogen is distributed more or less homogeneously over the whole sample cross section. After short time, represented by the radiograph taken at 1200 s, a local transformation to the \( \beta \)-phase starts at the upper left edge of the specimen. Because the \( \beta \)-region can absorb much more hydrogen than the former \( \alpha \)-phase, it seems that the location transformed take hydrogen not only from the gas phase but also from the neighbouring \( \alpha \) locations. This hinders reaching critical hydrogen concentration for the phase transformation at these locations. The further hydrogen uptake results only in a growth of the \( \beta \)-phase region. In no other region, the phase transformation occurs until the end of the experiment.
Fig. 8. Radiography image sequence of the hydrogen diffusion at 823 K (hydrogen dark).

Fig. 9 shows the hydrogen distribution perpendicular to the cylinder axis close to the surface through which the hydrogen penetrates. The different hydrogen concentrations in the two phases are clearly visible. Whereas in the \( \beta \)-region maximal concentrations of about 21.4 at.% were measured (corresponds with \( H/Zr = 27.4 \% \) marked as solid green line in Fig. 9), a constant hydrogen concentration of 1.72 at.% was found in the \( \alpha \)-region at the opposite side (\( H/Zr = 1.75 \% \), dotted blue line in Fig. 9). A monotonic decrease of the hydrogen concentration was observed between the two regions. At the left side of the diagram, the concentration is lower than found for the regions of the \( \beta \)-phase. It can be assumed that the pre-oxidation leads to a stabilization of the \( \alpha \)-phase because of the oxygen absorption in the first 0.5 mm. According to the phase diagram given in Fig. 1, the maximal \( H/Zr \) atomic ratio in the \( \alpha \)-phase at 823 K is about 7.5 %. The hydrogen concentration at the lower edge of the sample where the \( \alpha \)-phase remains is significantly lower than this value marked by the black dashed line in Fig. 9. A slight kink in the hydrogen distribution gradient was found at this concentration value.

![Graph showing hydrogen distribution](image)

Fig. 9. Hydrogen distribution perpendicular to the cylinder axis close to the surface.

4. Summary and Conclusions
The hydrogen diffusion in Zry-4 was investigated by means of in-situ neutron radiography experiments.

At temperatures at which the bcc \( \beta \)-phase is stable, an activation energy of 48.3 kJ mol\(^{-1}\) K\(^{-1}\) was determined. It is significantly higher than formerly published data. However, the data presented here agree well with the temperature correlations published for various temperature ranges.

At temperatures between 823 and 1123 K the hydrogen uptake is connected with a stabilization of the \( \beta \)-phase to lower temperatures. The uptake starts homogeneously in the hcp \( \alpha \)-phase. When a certain concentration level is reached, the phase transition occurs. Because the \( \beta \)-phase can absorb much more hydrogen than the \( \alpha \)-phase, hydrogen diffuses from the \( \alpha \)-region into the \( \beta \)-phase. The hydrogen
depletion of the α-phase hinders further phase transitions at a second location. Hence, the further hydrogen uptake is connected with a growth of the location with bcc structure.

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