

Hydrogen absorption by zirconium alloys at high temperatures

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Abstract

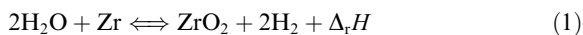
At high temperatures, e.g. during a hypothetical severe accident, zirconium and its alloys are not stable to other materials and to oxidising atmospheres. Exothermic reactions with steam cause the production of hydrogen which will be released to the atmosphere and, thus, endanger the containment or may be absorbed by the remaining metal. The hydrogen solubility in Zircaloy-4 and Zr–1Nb was measured in the temperature range of 1230–1730 K and at hydrogen partial pressures between 10 and 100 kPa. The parameters of the Sieverts constant were determined. No significant differences between the two alloys were observed. The hydrogen solubility of oxygen containing Zircaloy-4 decreases with increasing oxygen content.

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1. Introduction

Zirconium and its alloys are widely used in nuclear and chemical industries because of their low neutron absorption and their excellent mechanical and corrosion properties. In today's nuclear reactors, optimised Zircaloy and zirconium–niobium alloys are used for structural components like fuel claddings, guide tubes, and grid spacers.

At Forschungszentrum Karlsruhe (FZK), the hydrogen source term during a hypothetical severe nuclear accident, especially during the reflood phase, is being investigated within the QUENCH program [1–3]. Hydrogen is produced by the strongly exothermic zirconium–steam reaction (Eq. (1)). It is either released as a gas into the atmosphere or may be absorbed by the remaining zirconium metal (Eq. (2)):



where $\Delta_r H$ and $\Delta_s H$ are the enthalpies of reaction and solution, respectively. The latter reaction which is subject of this paper may considerably affect the course of events during and after quenching of an overheated, partially degraded core. The zirconium alloy may act as a sink or source of hydrogen, depending on the conditions prevailing (temperature, pressure). In this way, the hydrogen solubility of the cladding material may alter the time of hydrogen release from the core. Furthermore, the heat of solution of hydrogen in zirconium relative to 1 mol H_2 is about half the enthalpy of the strongly exothermic oxidation reaction by steam and may therefore influence the energy balance during severe accident transients at least temporarily.

The hydrogen absorption by zirconium alloys was studied extensively in the past, in particular with regard to the embrittlement of cladding material during long-term operation, which is beyond the scope of this work. Some publications also deal with higher temperatures [4–8], but actually only Moalem and Olander [9] published data for the temperature region above 1270 K which is considered in this paper.

It is well known that the hydrogen solubility in zirconium follows the Sieverts law (Eq. (3)), according to which the amount of hydrogen absorbed in a diluted solution is a function of the hydrogen partial pressure:

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$$\left(\frac{H}{Zr}\right)_{\text{at}} = K_S \cdot \sqrt{p_{\text{H}_2}}, \quad (3)$$

where $(H/Zr)_{\text{at}}$ is the atom ratio of both components, K_S the Sieverts constant, and p_{H_2} the hydrogen partial pressure in Pa. The temperature dependence of the Sieverts constant is described by an Arrhenius-type equation:

$$K_S = \exp\left(\frac{\Delta_s S}{R} - \frac{\Delta_s H}{RT}\right), \quad (4)$$

where $\Delta_s S$ is the entropy of solution in $\text{JK}^{-1} \text{mol}^{-1}$, $\Delta_s H$ the enthalpy of solution in J mol^{-1} , T the temperature in K, and R the molar gas constant ($8.314 \text{JK}^{-1} \text{mol}^{-1}$).

The Zr–H phase diagram [10] shows that hydrogen stabilises the cubic (bcc) β -phase of zirconium, in which more than 50 at% hydrogen can be dissolved above the eutectoid temperature of about 820 K. This means that the density of hydrogen dissolved in the β -phase of zirconium may be of the same order of magnitude or even higher than the density of liquid hydrogen at 15 K. The hydrogen solubility in the hexagonal (hcp) α -phase is limited to maximum values of about 6 at%.

The experiments described here covered the temperature range from 1230 to 1730 K with hydrogen partial pressures between 10 and 100 kPa, which resulted in maximum H/Zr ratios of about 0.9. The tests were performed in dry Ar/H₂ mixtures. Therefore, the effect of an oxide scale suppressing hydrogen absorption was not covered by this study. Nevertheless, the influence of oxygen dissolved in the α - and β -phase was investigated extensively. The main objective of the work presented here was to provide Sieverts' constants for the cladding materials Zircaloy-4 and Zr–1Nb at high temperatures that are of relevance when modelling severe accident transients.

2. Experimental set-up and procedure

Generally, two different devices were used by the various experimental groups to determine the hydrogen solubility in zirconium alloys: firstly, a modified Sieverts apparatus based on the measurement of the hydrogen partial pressure in a known volume and secondly, a thermobalance that continuously recorded the specimen mass. The latter method was used in the experiments presented here.

For the present study, a commercial thermoanalysis apparatus (NETZSCH STA 409) was coupled with a mass spectrometer (Fig. 1). This set-up allows for the continuous registration of mass change and simultaneous control of the gaseous environment during interaction between the specimen and the hydrogen containing atmosphere. The resistance furnace of the thermobalance is designed for maximum temperatures of 1870 K, the accuracy of the analytical balance is better than 0.2 mg, and the mass spectrometer (BALZERS Prisma) used for process control measures hydrogen concentrations down to about 100 yppm. The whole system is vacuum-tight. The specimen is located in an alumina reaction tube in the hot zone of the furnace. A gas supply system, consisting of two BRONKHORST gas mass flow controllers for argon and hydrogen (1–30 l/h (NTP) each), a mixing device and a vacuum pump, supplies any argon/hydrogen mixture needed with high accuracy and long-term stability. Argon and hydrogen are 99.9999% pure gases which were used without any further purification. The total system pressure was about 100 kPa; the total gas flow usually amounted to 20 l/h.

The specimens were approx. 20 mm long segments of reactor-grade cladding material used in western-type pressurised water reactors (Zircaloy-4) and Russian nuclear reactors (Zr–1Nb). The compositions and geometrical parameters of the specimens are compiled in Table 1. Prior to the test, the samples were cleaned and

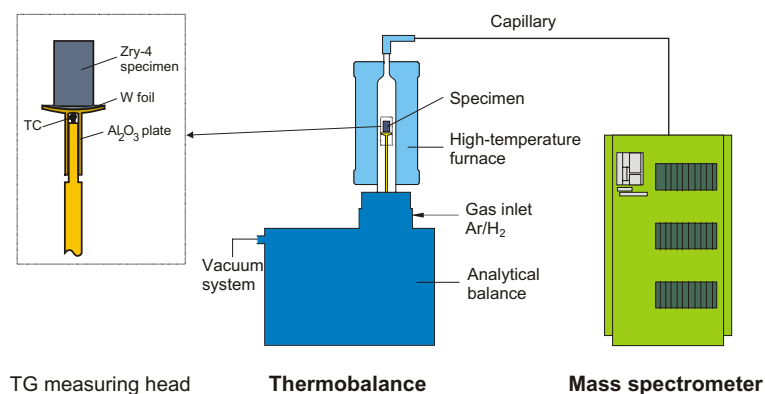


Fig. 1. Schematic view of the test set-up and sample holder with specimen.

Table 1
Specification of the zirconium alloys used for the tests

<i>Zircaloy-4</i>	
Chemical composition (≥ 0.01 wt%)	
Sn	1.52 wt%
Fe	0.22 wt%
Cr	0.11 wt%
O	0.13 wt%
Zr	Bal.
Cladding tube segment	
Mass	≈ 2.7 g
Height	≈ 20 mm
Outer diameter	10.75 mm
Thickness	0.725 mm
<i>Zr-Nb</i>	
Chemical composition (≥ 0.01 wt%)	
Nb	0.97 wt%
Hf	0.03 wt%
Fe	0.01 wt%
O	0.05 wt%
Zr	Bal.
Cladding tube segment	
Mass	≈ 2.2 g
Height	≈ 20 mm
Outer diameter	9.13 mm
Thickness	0.705 mm

decreased in an ultrasonic bath of acetone. A tungsten foil (in inert and reducing atmospheres) or hafnia plate (in oxidising atmosphere) was used to prevent chemical interactions between the zirconium alloy specimens and the alumina sample holder.

For the test, the specimens were heated up to the specified temperature usually in pure argon. Then, the gas composition was switched to the desired argon–hydrogen mixture and a pre-defined temperature program was run. For analysis, the mass signals recorded were corrected for buoyancy and drag as well as for a small continuous mass increase (<1 mg/h) that was observed during hydrogen flow only. It was probably caused by impurities in the gas or by gas-phase diffusion from the reaction tube to the sample.

Oxygenated species were prepared in situ in the thermobalance in an argon–5% oxygen mixture at 1470 K. After the weight gain specified was reached due to specimen oxidation, the samples were homogenised at 1770 K for 2 h in pure argon.

3. Results and discussion

3.1. Hydrogen solubility in Zircaloy-4

In total, eight tests were performed to determine the temperature dependence of the Sieverts constant of

Zircaloy-4 cladding material in the temperature range of 1230–1730 K at hydrogen partial pressures between 10 and 100 kPa. A typical test conduct and the results of three experiments at different hydrogen partial pressures are shown in Fig. 2.

The specimens were heated up to 1730 K and thermally equilibrated at this temperature under pure argon. Change to the hydrogen partial pressure specified caused the specimen mass to increase instantaneously due to the fast uptake of hydrogen at this temperature until the equilibrium was established. In the course of the test, the temperature was decreased by 100 K in a stepwise manner. The three curves qualitatively exhibit the Sieverts law behaviour: the amount of dissolved hydrogen rises with decreasing temperature and increasing hydrogen partial pressure.

The Sieverts constants were determined by least-square fitting of the data of all tests. The results are summarised in Figs. 3, 4 and Table 2. In the domain investigated, hydrogen uptake by Zircaloy-4 follows the Sieverts law (Fig. 3) and the dependence on temperature of the Sieverts constant is represented well by an Arrhenius-type equation (Fig. 4). Only for high hydrogen contents is the hydrogen solubility no longer linearly dependent on the square root of the hydrogen partial pressure which is probably due to saturation effects. To check this, a test was conducted at constant temperature of 1238 K. Hydrogen partial pressures were varied from 0 to 100 kPa in a stepwise manner. Indeed, the slope of the curve in the Sieverts diagram was found to change at a hydrogen/zirconium ratio of about 0.65 (Fig. 5). This indicates that the assumption of a diluted solution is no longer valid and interactions between hydrogen atoms at the interstitial sites play a role. It is obvious from Fig. 5, however, that the deviation of the experimental data from the correlation given in Table 2 is less than 10% even at the highest hydrogen concentrations. Consequently, the general equation with the parameters given in Table 2 can be used for modelling purposes in severe accident codes.

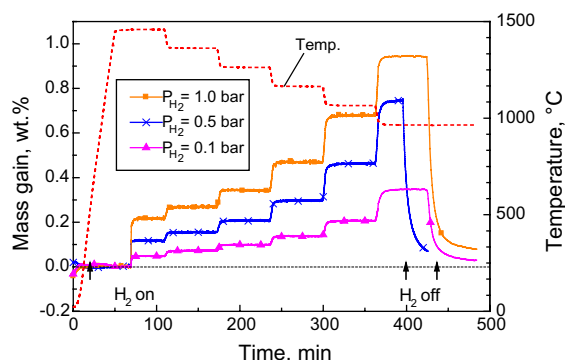


Fig. 2. Hydrogen uptake of Zircaloy-4 as a function of temperature and hydrogen partial pressure.

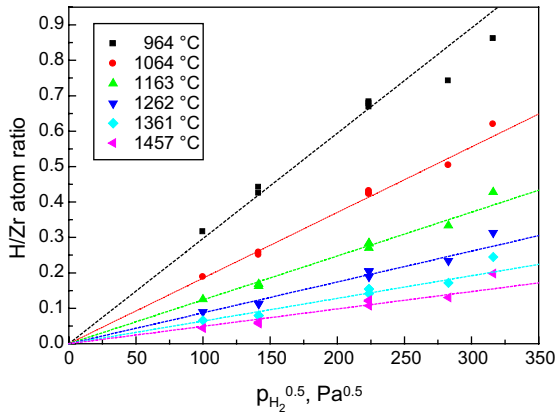


Fig. 3. Verification of the Sieverts law for Zircaloy-4 cladding material. The dashed lines correspond to the Sieverts constants given in Table 2.

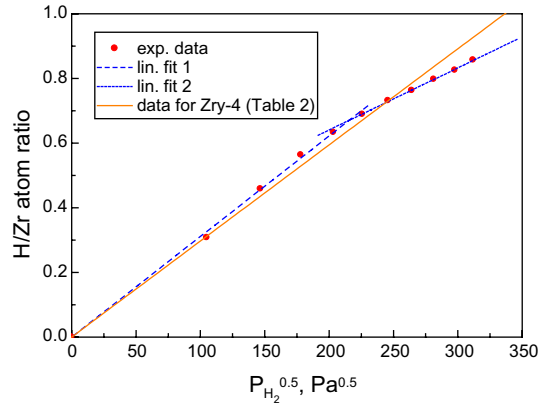


Fig. 5. Sieverts law verification for Zircaloy-4 at 1238 K and hydrogen partial pressures ranging between 0 and 100 kPa.

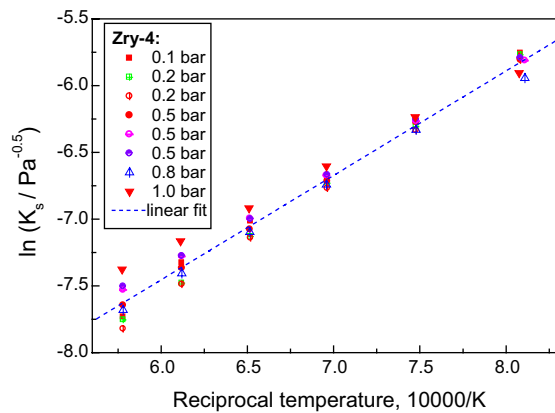


Fig. 4. Arrhenius plot of the Sieverts constant for Zircaloy-4 cladding material.

Table 2
Sieverts constant parameters according to (Eq. (4)) (entropies and enthalpies of solution of hydrogen in zirconium alloys)

Specimen	$\Delta_s H$, J mol ⁻¹	$\Delta_s S$, J K ⁻¹ mol ⁻¹
Zry-4 (mean of 8 tests)	-65015 ± 1393	-101.0 ± 1.0
Zr-1Nb (mean of 3 tests)	-67908 ± 1931	-102.8 ± 1.3
Zry-4+0.31 wt% O	-63737 ± 1106	-100.4 ± 0.7
Zry-4+0.48 wt% O	-64157 ± 1345	-100.6 ± 0.9
Zry-4+0.73 wt% O	-63096 ± 744	-100.4 ± 0.5
Zry-4+1.02 wt% O	-60915 ± 958	-99.0 ± 0.7
Zry-4+3.27 wt% O	-51017 ± 652	-97.0 ± 0.4
Zry-4+3.88 wt% O	-47531 ± 672	-95.3 ± 0.5
Zry-4+4.75 wt% O	-44802 ± 1024	-94.8 ± 0.7
Zry-4+5.48 wt% O	-45243 ± 1505	-96.2 ± 1.0
Zry-4+6.15 wt% O	-40290 ± 1124	-94.7 ± 0.7

3.2. Hydrogen solubility in Zr-1Nb

Zirconium–niobium alloys are used as cladding and structure materials in Russian RBMK and VVER and Canadian CANDU reactors. More recently, they have also been tested and used in US and West European light water reactors [11]. For this reason, three experiments were performed with Russian Zr-1Nb cladding material (E110) to investigate the influence of alloying elements on the hydrogen absorption behaviour.

Fig. 6 shows that hydrogen absorption values of the two cladding materials do not differ within the range of experimental scatter. The Sieverts parameters for Zr-1Nb are also given in Table 2.

3.3. Hydrogen solubility in the Zircaloy-4–oxygen system

It is well known that the hydrogen solubility in zirconium oxide ZrO₂ is very low (10⁻⁵ to 10⁻⁴ mol H per

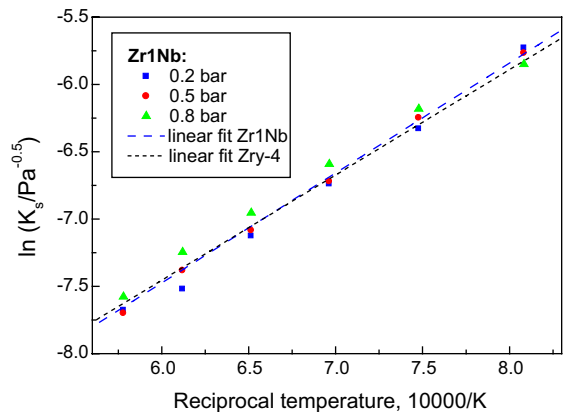


Fig. 6. Arrhenius plot of the Sieverts constant for Zr-1Nb cladding material.

mole oxide) compared to that in the metal [8,12]. Consequently, an intact oxide scale on the Zircaloy surface significantly impedes hydrogen uptake by the metal phase, as was also confirmed by some pre-tests [13]. However, the oxide layer may be dissolved by the metal at high temperatures under oxygen starvation conditions. Therefore, it is of interest to know the influence of dissolved oxygen on the solubility of hydrogen in the metal phases.

Nine tests were performed with Zircaloy-4 specimens loaded with 0.31–6.15 wt% oxygen at 50 kPa hydrogen partial pressure. The results are summarised in Fig. 7 and Table 2. Generally, it was found that the hydrogen solubility in the metal decreases with increasing oxygen content. At high oxygen contents near the solubility limit of the α -phase (about 7 wt%, see [14] for the phase diagram), the hydrogen uptake is smaller than that of the as-received material by factors of 3–6, with the differences being higher at lower temperatures. The hydrogen solubility in the β -phase changes only slightly with the oxygen content increasing up to about 1 wt%, but it is always smaller than for pure Zircaloy. This contradicts the results obtained partly by other groups at lower temperatures [8,9]. They found a slight increase of hydrogen solubility with rising oxygen content in the β -phase before higher oxygen concentrations caused a reduction of the hydrogen solubility. However, by extrapolating the data obtained between 1170 and 1320 K, Miyake [8] estimated a decreasing positive effect of small amounts of oxygen on the hydrogen solubility at higher temperatures, which is in accordance with the results obtained here.

The parameters of the Sieverts constant $\Delta_s H$ and $\Delta_s S$ are plotted vs. oxygen concentration in Fig. 8. Both parameters exhibit a linear dependence on the oxygen dissolved in the metal. Hence, the following relations result:

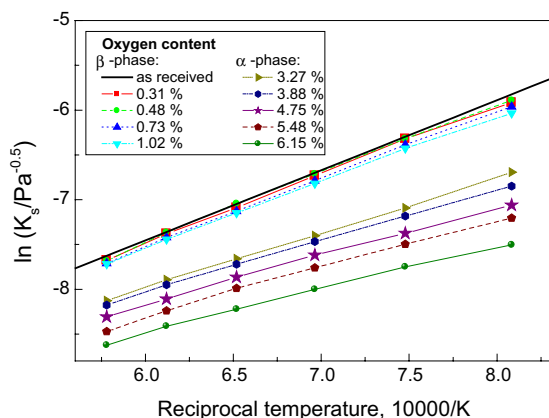


Fig. 7. Temperature dependence of the Sieverts constant for Zry(O) solid solutions.

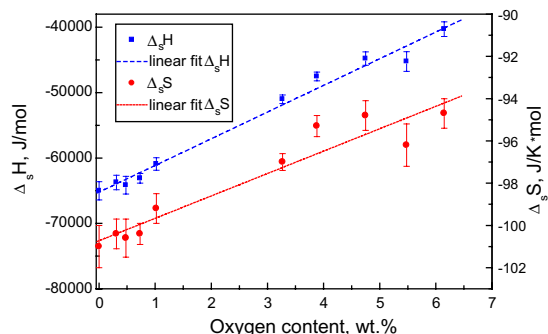


Fig. 8. Enthalpy and entropy of solution for hydrogen in Zry(O) solid solutions.

$$\Delta_s H = -65216(\pm 610) + 4080(\pm 177) \cdot C_O, \quad (5a)$$

$$\Delta_s S = -100.7(\pm 0.4) + 1.06(\pm 0.11) \cdot C_O, \quad (5b)$$

with $\Delta_s H$ given in J mol^{-1} , $\Delta_s S$ in $\text{J K}^{-1} \text{mol}^{-1}$, and C_O in wt%.

It is known from literature [7,8] that oxygen atoms occupy the octahedral interstitial sites in the zirconium lattice, whereas the smaller hydrogen atoms are preferably located on the tetrahedral sites. Obviously, the presence of oxygen on the octahedral sites affects the state and configuration of the neighbouring hydrogen atoms. Oxygen is known to stabilise the hexagonal α -phase. The higher melting point of this phase compared to that of pure metal indicates strong chemical interactions between zirconium and oxygen in the solid solution. These may affect the Zr–H interaction and lead to a decrease of the enthalpy of solution. Furthermore, it can be expected that the presence of oxygen decreases the randomness of the distribution of hydrogen atoms at the tetrahedral sites due to repulsion. This effect explains the change of the (configurational) entropy of solution found in the experiments.

3.4. Transient hydrogen uptake and release

So far, equilibrium properties of the zirconium alloy–hydrogen system have been described. Although it was not the main aim of the present study to investigate kinetic parameters, the results of one transient experiment shall be presented now. During this test, the hydrogen flow which resulted in a partial pressure of 50 kPa H_2 was switched off during each isothermal plateau. According to Fig. 9, the equilibrium establishes within a few minutes depending on temperature. In the time scale of a severe accident scenario, this is a relatively short time. Secondly, hydrogen uptake and release are reversible processes, but non-symmetric in time. Hydrogen uptake is a rather rapid process, especially at higher temperatures where the mass increase follows the

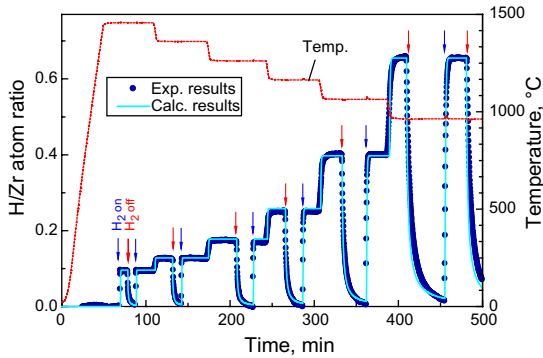


Fig. 9. Transient behaviour of hydrogen uptake/release when switching between 0 and 100 kPa hydrogen partial pressure. Comparison between experimental results and calculation with the IBRAE model [15,16].

growth of hydrogen partial pressure in the system. Hydrogen release, however, takes much more time before equilibrium is attained.

A kinetic model which describes this behaviour was developed by Veshchunov and co-workers [15,16]. To quantitatively describe hydrogen uptake and release by Zircaloy, mass transfer in the gas phase and in the metal phase is considered. The model is based on the hydrogen diffusion equation of the Zircaloy-4 specimen under non-linear boundary conditions determined by the Sieverts law. In the gas phase, the standard approach of modelling multi-component transport through the diffusion boundary layer is complemented by the consideration of additional convective fluxes due to hydrogen absorption (Stefan's flow). As obvious from Fig. 9, the model with the effective mass transfer coefficient of hydrogen in the gas phase as the only fitting parameter corresponds very well with the experimental results. The model also predicts a more symmetric behaviour between uptake and release of hydrogen when switching between two finite (non-zero) hydrogen partial pressures, which was confirmed by the corresponding experiments.

The diffusion coefficient of hydrogen in Zircaloy-4 was estimated with Eq. (6) being assumed to be applicable to a metal plate of 2 h in thickness [17]:

$$\frac{D_{\text{H}} \cdot t}{h^2} \cong 1 \quad (93\% \text{ of hydrogen saturation}). \quad (6)$$

The diffusion coefficients estimated on the basis of the experimental results presented here are lower than the literature data [18,19] by a factor of 10 (for the lowest temperature: $3 \times 10^{-5} \text{ cm}^2/\text{s}$) to 2 (for the highest temperature: $2 \times 10^{-4} \text{ cm}^2/\text{s}$). This indicates that apart from the diffusion in the metal, gas-phase diffusion plays an important role in these tests.

4. Summary

Experimental results with respect to the hydrogen solubility in zirconium alloys used as cladding materials in light water reactors were presented. The experiments were carried out at temperatures ranging from 1230 to 1730 K and hydrogen partial pressures between 10 and 100 kPa. It was shown that zirconium alloys have a considerable hydrogen storage capacity even at temperatures beyond 1270 K. Maximum hydrogen contents of $\text{H/Zr} = 0.9$ (which is still in the single-phase $\beta\text{-Zr}$ region) were obtained for the lowest temperatures and highest partial pressures investigated.

The hydrogen solubility of zirconium-rich alloys is well described by the Sieverts law up to an atom ratio of $\text{H/Zr} = 0.7$. At higher hydrogen contents, interactions between the hydrogen atoms on the interstitial sites lead to a slight deviation from Sieverts' law towards lower solubilities.

The hydrogen absorption of the two studied alloys Zircaloy-4 and Zr-1Nb is comparable within the experimental scatter. Obviously, the influence of alloying elements is negligible at these high temperatures.

The effect of oxygen dissolved in the metal is important. It considerably decreases the hydrogen absorption capacity of zirconium. Correlations for the parameters of the Sieverts constants $\Delta_s H$ and $\Delta_s S$ were given as a function of the oxygen content. In addition, data on the pure alloys Zircaloy-4 and Zr-1Nb were provided.

Transient tests revealed a non-symmetric behaviour of hydrogen uptake and release vs. time following changes of the hydrogen partial pressure. This behaviour could be described well by a kinetic model developed by IBRAE (Moscow).

The experimental results of the present study are in good agreement with literature data, except for the influence of dissolved oxygen in the β -phase on hydrogen

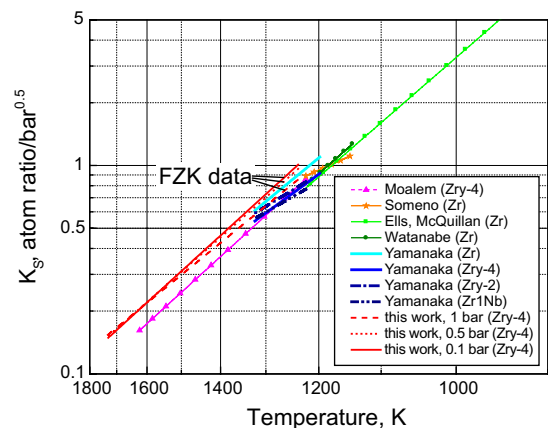


Fig. 10. Comparison of Sieverts constants determined with literature data.

solubility, which was discussed above. Fig. 10 shows the Sieverts constants obtained in comparison with literature data. The FZK data determined at high temperatures are within the scatter band of extrapolated data obtained at lower temperatures and are about 25% higher than the data given by Moalem and Olander [9]. They confirm the Arrhenius-type behaviour also at temperatures above 1273 K and show the slight influence of saturation effects at higher hydrogen partial pressures.

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