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**Some experimental results on hydrogen - cladding material interactions**

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## Some experimental results on hydrogen - cladding material interactions

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Separate effect tests have been performed in order to get an overview about the hydrogen transfer during steam oxidation of cladding zirconium alloys and the metal-gas interactions. The investigations were performed at temperatures high enough to get reaction rates producing measurable effects in one day experimental time scale. The processes belonging to this range are those, which have importance mainly at LOCA events. However in some cases the results are relevant for long time scale processes and provide valuable limits for the estimation of different effects.

The aim of the experiments were to get quantitative results regarding the amount of absorbed hydrogen at equilibrium circumstances, the absorption during steam oxidation and the rate of  $H_2$  escape, the rate of hydrogen escape during steam oxidation of cladding alloys with high hydrogen content, the delay of effective absorption from hydrogen gas phase because of surface oxide layer, moreover the embrittlement.

### 1. Equilibrium solubility of hydrogen in cladding alloys with oxygen content

A basic question is to get acceptable assessment about the hydrogen source term during high temperature processes to know the solubility of hydrogen in cladding materials containing substantial amount of oxygen. The pure zirconium is thoroughly studied and the data are acceptable up to atmospheric pressure. The low extent alloying of zirconium for cladding does not affect substantially the solubility of hydrogen in these materials. Some data regarding these materials with low oxygen content and at low  $H_2$  pressures are also acceptable. However data for high oxygen content and near to atmospheric pressure hydrogen were not available. Our effort aimed to clear up the solubility of hydrogen in this range. We have performed the relevant determinations both for Zr1%Nb and Zircaloy-4.

In closed system we measured the amount of absorbed  $H_2$  by samples with O/Zr ratio up to 0.15 at different pressures and at temperatures of 900, 1000 and 1100°C. The samples were 5 mm long pieces from original cladding material tubes. They were oxidised in 1:4 oxygen - argon mixture at 900 °C and then homogenised in high purity argon at 1150 °C. At the measurements the  $H_2$  pressure was raised step by step, waiting at each point until the pressure was stabilised and then determined the amount of absorbed hydrogen. At the end of each experiment the samples were weighted to control the total absorption data.

The H/Zr equilibrium ratios for the different alloys and temperatures were plotted as function of the hydrogen pressure with different O/Zr values. The plot regarding of the Zr1%Nb at 1000 °C can be seen in Fig. 1.

By evaluation of experimental data the following general formula has been found to describe reasonably well the experimental results:

$$\left(\frac{H}{Zr}\right)_{ox} = \frac{K_s * \sqrt{P_{H_2}}}{1 + \frac{K_s}{M} * \sqrt{P_{H_2}}} * \left[1 - A * \left(\frac{O}{Zr}\right)\right]$$

where  $H/Zr$  is the atomic ratio in the metal phase,  $K_s$  is the Sievert's constants for the given alloys,  $M$  are temperature dependent constant (interstitial absorption places regarding for one Zr atom),  $P_{H_2}$  partial pressure of hydrogen in the gas phase,  $O/Zr$  is the oxygen content of the metal phase in atomic ratio and  $A$  is a factor indicating how many interstitial H absorption place is blocked by one O atom.

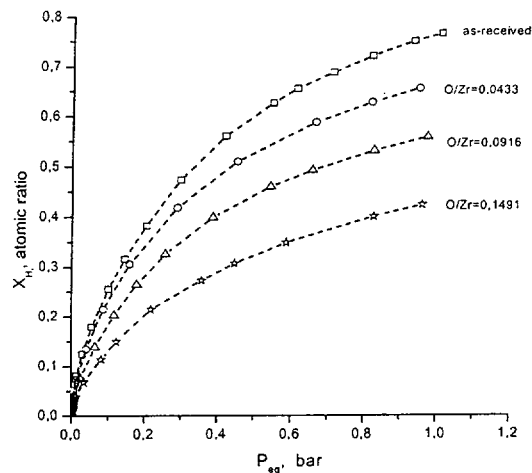


Figure 1. Equilibrium hydrogen concentrations ( $H/Zr$ ) for Zr1%Nb at 1000 °C at different oxygen content ( $O/Zr$ ) as function of the pressure of hydrogen gas.

Sievert's constants for the cladding materials are not exactly agree with that of the pure zirconium, even not exactly of the two cladding material of as received form. The fitting process resulted better agreement at the high O content and pressure range using these data. The fitted values of  $K_s$  and  $M$  to experimental results are the followings:

	T(°C)	$K_s$	$M$
Zircaloy-4	900	1.9	2.0
	1000	0.85	5.0
	1100	0.52	5.5
Zr1%Nb	900	2.1	1.92
	1000	0.85	5.0
	1100	0.052	7.0

The mean value of  $A$  has been found to be 2.7 for both of the Zr1%Nb and Zircaloy-4.

## 2. Escape of hydrogen during steam oxidation

Main aims of the work were to study the

- hydrogen release kinetics during steam oxidation,
- extent of hydrogen absorption.

The experimental device was a vertical resistance heated furnace equipped with a sample lifting device. The samples were prepared also from original cladding materials in as received form. Their length were 8 mm and diameter of Zr1%Nb was 9.15 mm and of Zircaloy-4 was 10.75 mm, like at many standard fuels.

The oxidation was performed in atmospheric pressure steam with 12 % argon as carrier gas for the  $H_2$ . A thermal conductivity detector like in gas chromatography made continuous recording of  $H_2$  content of argon. The steam was condensed at the outlet of system by water and an ice bad stabilised the water concentration of the argon stream. Calibration of detector sensitivity was made by injecting  $H_2$  before and after the oxidation of every sample. The total  $H_2$  escape was determined by integrating the TCD signal. Moreover the samples were weighted for checking the mass increase and their hydrogen content was determined later through high temperature desorption in argon stream. Temperatures used for the oxidation experiments were 900, 1000, 1100 and 1200 °C. At every temperature and of both materials about 5-6 samples were oxidised through different times to get results about the absorbed hydrogen in function of the extent of oxidation.

The escape of hydrogen at temperatures when no break up effect appeared in the oxidation rate proved the square root time dependence of oxidation rate. An example can be seen on Figure 2, the steam oxidation of Zircaloy-4 at 900 °C. Similar results were for Zircaloy-4 at 1100 and 1200 °C, for Zr1%Nb at 1100 and 1200 °C.

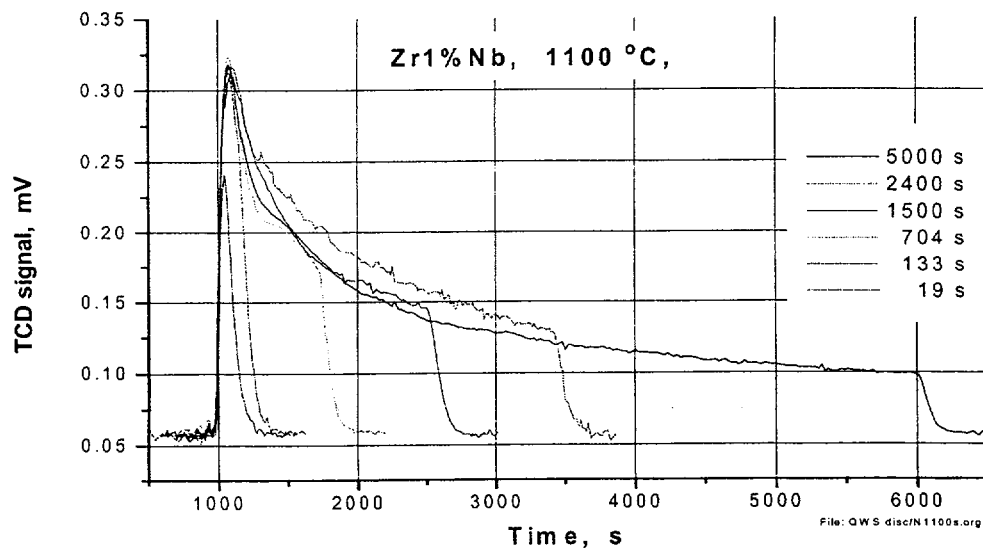


Figure 2. The  $H_2$  escape rate at steam oxidation of Zircaloy-4 at 900 °C.

Break up effect appeared for Zircaloy-4 at 1000 °C (Figure 3), at Zr1%Nb at 900 and 1000 °C (Figure 4). In these cases second and further maximums were found in the hydrogen escape rates. After peeling off the oxide scale new more or less clean metal surfaces were formed resulting higher oxidation rate, enhanced hydrogen formation.

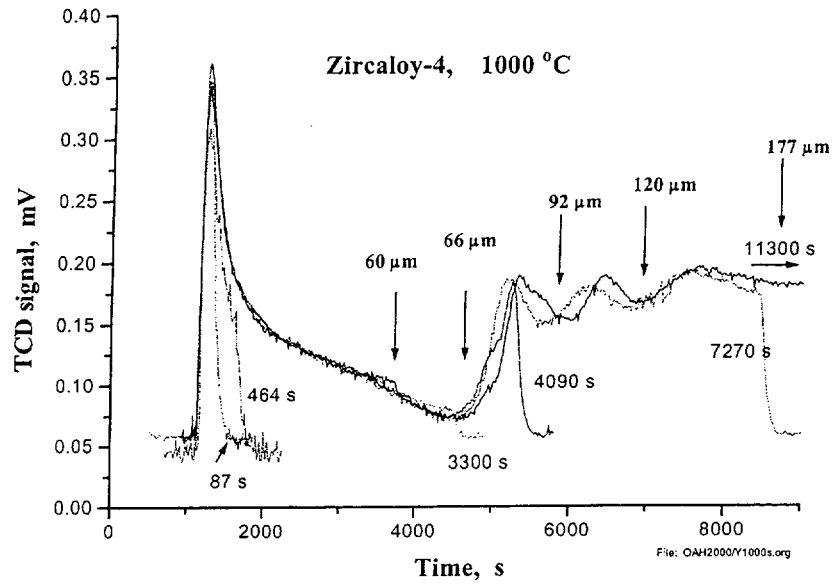


Figure 3. The  $H_2$  escape rate at steam oxidation of Zircaloy-4 at 1000 °C.

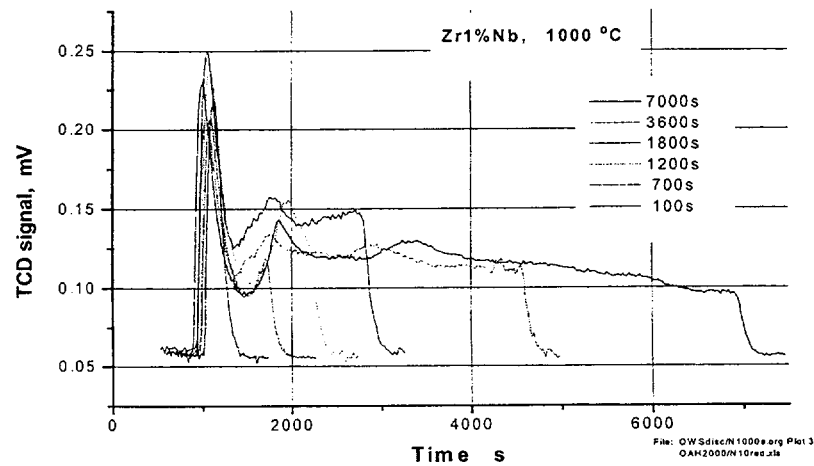


Figure 4. The  $H_2$  escape rate at steam oxidation of Zr1%Nb at 1000 °C

From the amount of hydrogen the oxide layer thicknesses were calculated. About three break up step could be recognised, later the poorly reproduced peeling processes smoothed the escape rates. Thickness of peeled off  $ZrO_2$  layers calculated from the amount of escaped hydrogen at steam oxidation of cladding alloys is given in the next table.

Nr.	t (s)	d ( $\mu\text{m}$ )
Zr1%Nb, 900 °C		
1	502	6.8
2	1360	13.6
3	2650	22.6
4	5080	31
5	7300	40
Zr1%Nb, 1000 °C		
1	520	13.4
2	1230	27.5
3	1840	38
4	2810	57.4
Zircaloy-4, 1000 °C		
1/a	2360	58
1/b	3390	65
1/c	4730	89
2	5800	117
3	7600	172

According to the data above the peeling off of the oxide layers take place at definite thickness, depending on the temperature and alloy type. The post test microscopic investigation of the samples resulted the same values for peeled off layers as given in the Table above.

The hydrogen content of samples after the oxidation has been determined. The Zr1%Nb took up hydrogen in all cases, even if the break up effect did not appear. However the Zircaloy-4 alloy absorbed hydrogen only at the 1000 °C oxidation, where break up effect was found and only about 1/5 of the value of Zr1%Nb. Figure 5 shows the absorbed ratio of formed hydrogen in case of Zr1%Nb, on Figure 6 the H/Zr ratio in the metal phase at the end of oxidation processes can be seen.

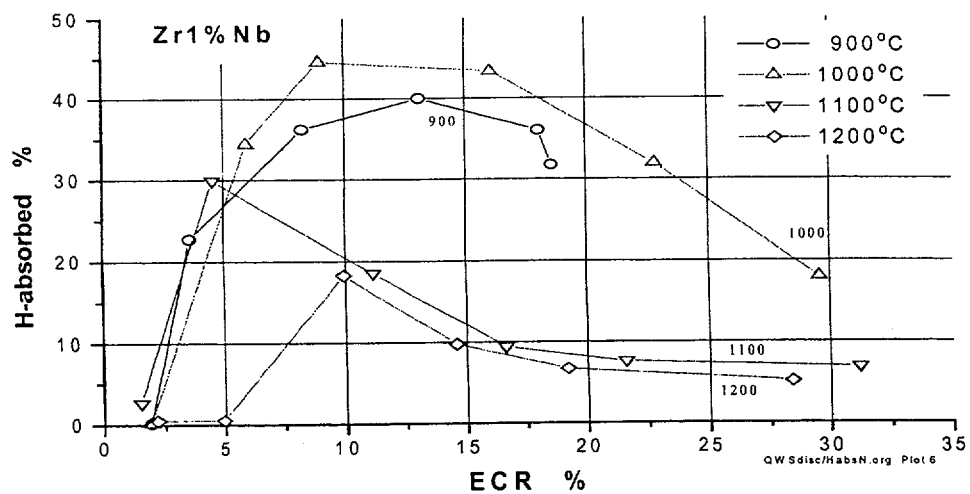


Figure 5. The absorbed part of hydrogen at steam oxidation of Zr1%Nb

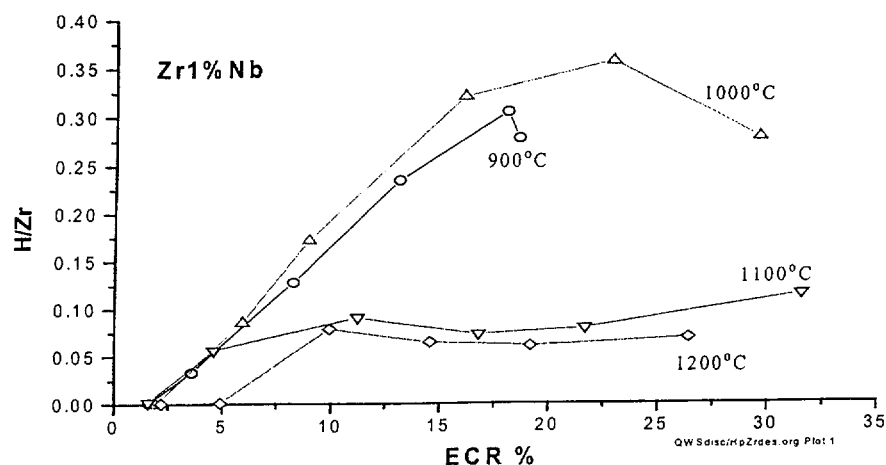


Figure 6. The concentration of hydrogen in the metal phase at the end of steam oxidation of Zr1%Nb

### 3. Escape of hydrogen during steam oxidation of cladding alloys with high H-content.

During a steam starvation period the cladding material can be filled up with hydrogen according to equilibrium concentration depending on the temperature and  $H_2$  partial pressure. This process can take place only if the steam concentration is very low, other case the formation of new oxide layers prevents the absorption process.

We performed steam oxidation experiments on Zr1%Nb and Zircaloy-4 with as received samples and those with high hydrogen content ( $H/Zr \sim 1$ ) at different temperatures. The experimental set up was the same as before, steam with argon for the oxidation and the escape of hydrogen was continuously recorded by TCD. Typical results can be seen on Figure 7.

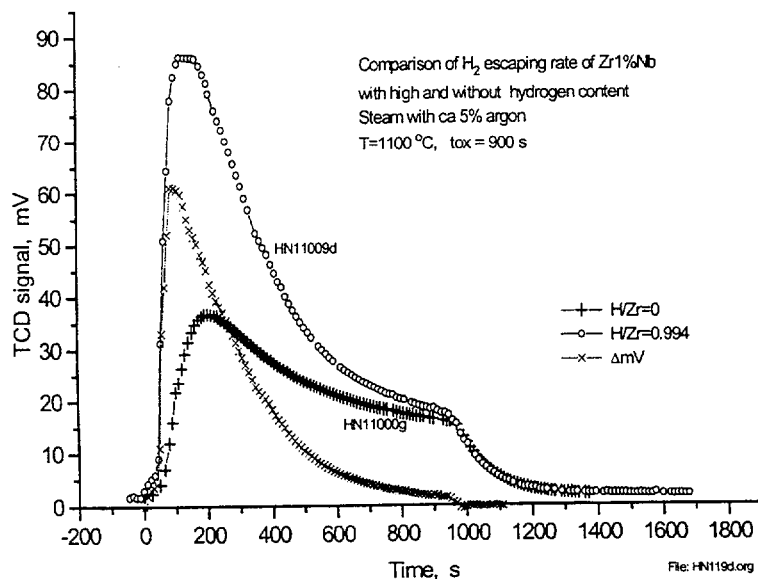


Figure 7. The escape rate of hydrogen during steam oxidation of Zr1%Nb as received and hydrogenated ( $H/Zr \sim 1$ ) samples at 1100 °C.

Substantial part of dissolved H escaped at the beginning of oxidation. After a while the  $H_2$  escape rate usually diminished to a lower level as at the as received sample. It indicates a lower oxidation rate for the hydrogenated alloys compared to the as received ones. Anyhow the emission of hydrogen during the late steam oxidation phase does not differ substantially from the value of as received samples. We have to take into account, that the amount of absorbed hydrogen at  $H/Zr=1$  is only one fourth of that to be formed until the Zr metal is fully oxidised. The ratio of escaped hydrogen in the first oxidation phase compared to the solved quantity is depending on the temperature as shown in Figure 8.

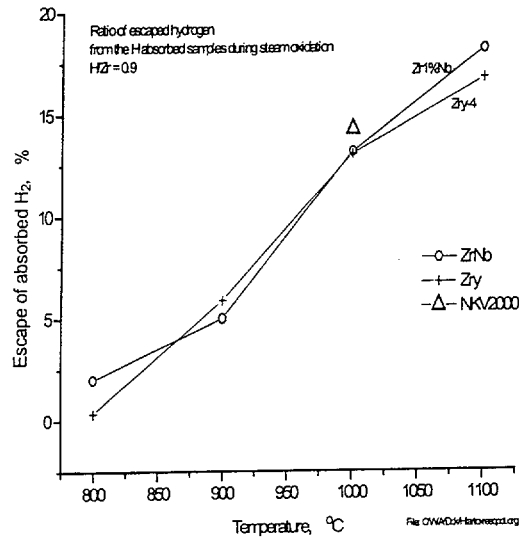


Figure 8. The escaped part of dissolved hydrogen during the first phase of steam oxidation of cladding alloys hydrogenated up to  $H/Zr \sim 1$

#### 4. Delay of hydrogen absorption by the Zr alloys from gas phase because of surface oxide layer

The surface oxide scale on cladding materials shows a barrier effect on the absorption of hydrogen from gas phase. Similar investigations have been performed at temperatures usual in the normal working stage of nuclear power plants. Data for higher temperature conditions arise for instance at a LOCA event were not at our disposal. To get information about these process we performed investigations from 800 to 1100 °C temperatures in 100 °C steps, using both Zr1%Nb and Zircaloy-4 samples in as received form and oxidised to 5 and 10 µm oxide layer thicknesses.

The experiments were made in flowing argon with 30 vol%  $H_2$ . The hydrogen content of the outlet gas was continuously monitored. In case of as received samples the  $H_2$  concentration in the argon dropped suddenly and grew back slowly as the equilibrium partial pressure growth because of the increasing  $H/Zr$  ratio in the sample. At samples with oxide layers the fall back of  $H_2$  concentration in the argon delayed. The delay times were dependent on the temperature and oxide thickness. At the evaluation we compared the actual  $H_2$  partial pressure in gas phase with the equilibrium value belonging to the  $H/Zr$  ratio calculated from the integral hydrogen uptake by the metal phase. The time when the two became the same was accepted as delay time. The results are shown in Figure 9.



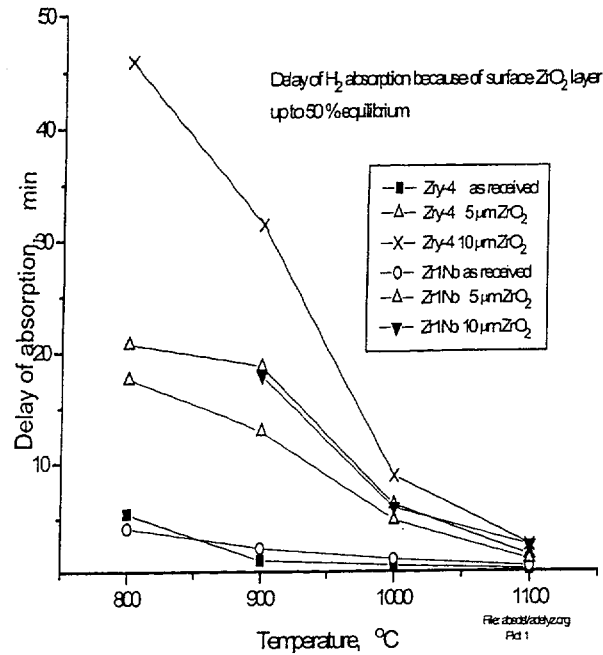


Figure 9. The delay of H<sub>2</sub> absorption from gas phase by cladding Zr-alloys as function of the surface oxide layer thickness and temperature.

The evaluation of experimental data resulted the following formulas for the absorption delay:

For Zr1%Nb:

$$dt = d(ox) \cdot (48 - 1.3 \cdot 10^5/T + 0.95 \cdot 10^8/T^2)$$

For Zircaloy-4:

$$dt = d(ox) \cdot (93 - 2.6 \cdot 10^5/T + 1.8 \cdot 10^8/T^2)$$

where  $dt$  in minute,  $d(ox)$  in  $\mu m$  and  $T$  in Kelvin has to be given.

We suppose the work summarised above gave some valuable contribution to the modelling of the high temperature processes in the core regarding of the cladding material and hydrogen interactions.

### Acknowledgement

The work summarised in this paper was a several-year effort to clear up the hydrogen behaviour in high temperature core conditions. The Atomic Energy Research Institute, Budapest, supported it first of all. Part of the experimental activity was supported by the Hungarian Atomic Energy Authority, the Hungarian National Committee for Technological Developments and the International Atomic Energy Agency. In the frame of co-operation many valuable discussions contributed to the evaluation of results by the experts of FZ Karlsruhe, especially Dr. P. Hofmann, G. Schanz and Dr. M. Steinbrück. We thank Dr. L. Maróti for his critical remarks regarding the selection of the research goals and the presentation of the results.