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REPORT**

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**EXPERIMENTAL RESULTS ON THE INTERACTIONS  
BETWEEN HYDROGEN AND ZIRCONIUM CLADDINGS**

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**B U D A P E S T**

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Abstract

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**EXPERIMENTAL RESULTS ON THE INTERACTIONS BETWEEN  
HYDROGEN AND ZIRCONIUM CLADDINGS**

Experiments were performed with Zr1%Nb and Zircaloy-4 alloys to study the interaction between hydrogen and Zr containing cladding materials. Four main activities are summarised in the report:

- equilibrium solubility of hydrogen in cladding with oxygen content,
- escape of hydrogen during steam oxidation,
- escape of hydrogen during steam oxidation of cladding alloys with H-content,
- delaying effect of surface oxide layer on the hydrogen absorption from gas phase by the Zr alloys.

Kivonat

**Matus L., Vasáros L., Hózer Z.:**

**KÍSÉRLETI EREDMÉNYEK A CIRKÓNÍUM BURKOLATANYAGOK ÉS A  
HIDROGÉN KÖZÖTTI KÖLCSÖNHATÁSOKRÓL**

Kísérleteket hajtottunk végre Zr1%Nb és Zircaloy-4 ötvözetekkel a Zr tartalmú burkolatanyagok és a hidrogén kölcsönhatásának vizsgálatára. A kísérleti tevékenység négy fő területét foglalja össze a riport:

- a hidrogén egyensúlyi oldhatósága oxigén tartalmú burkolatokban,
- hidrogén felszabadulás a burkolat vízgőzös oxidációja során
- hidrogén felszabadulás H-tartalmú burkolat vízgőzös oxidációja során,
- a külső oxidréteg késleltető hatása a Zr ötvözetek gázfázisból történő hidrogén felvételére.

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## 1. INTRODUCTION

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 in Loss-of-Coolant-Accidents (LOCAs). 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<sub>2</sub> 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.

## 2. EQUILIBRIUM SOLUBILITY OF HYDROGEN IN CLADDING ALLOYS WITH OXYGEN CONTENT

The solubility of hydrogen in cladding materials containing substantial amount of oxygen must be known in order to get acceptable assessment regarding the hydrogen source term during high temperature processes.

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<sub>2</sub> pressures are also acceptable. However data for high oxygen content of cladding and near to atmospheric pressure of 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<sub>2</sub> 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 the oxygen concentration was homogenised during 3 hours at 1150 °C in high purity argon. At the measurements the H<sub>2</sub> pressure was raised step by step, waiting at each point until the pressure was stabilised, the equilibrium has been accomplished, then determined the amount of absorbed hydrogen volumetrically. At the end of each experiment the samples were weighted to control the highest 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 the experimental results reasonably well:

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

where H/Zr is the atomic ratio in the metal phase, K<sub>S</sub> is the Sievert's constants for the given alloys, M is a temperature dependent constant (interstitial absorption places regarding for one Zr atom), P<sub>H<sub>2</sub></sub> 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.

Sievert's constants for the cladding materials do not agree exactly with that of the pure zirconium, even not exactly of the two cladding material of as received form. Using these data the fitting by equation (1) resulted in better agreement at the high O content and pressure range. The fitted values of  $K_s$  and M to experimental results are given in Table 1. The mean value of A has been found to be 2.7 for both of the Zr1%Nb and Zircaloy-4.

	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

Table 1 Fitted  $K_s$  and M values for Zircaloy-4 and Zr1%Nb



### 3. 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 outer 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<sub>2</sub>. A thermal conductivity detector (TCD) of a gas chromatograph was applied for recording of H<sub>2</sub> 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<sub>2</sub> before and after the oxidation of every sample. The total H<sub>2</sub> escape was determined by integrating the thermal conductivity detector (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 H<sub>2</sub> escape rates (TCD signal vs. time) are shown in Fig. 2-5 for Zr1%Nb and in Fig. 6-9 for Zircaloy-4.

The escape of hydrogen - at temperatures when no break up effect appeared - proved the square root time dependence of oxidation rate. For example the steam oxidation of Zircaloy-4 at 900 °C is presented in Fig. 6. Similar results were for Zircaloy-4 at 1100 (Fig. 8) and 1200 °C (Fig. 9), for Zr1%Nb at 1100 (Fig. 4) and 1200 °C (Fig. 5).

Break up effect appeared for Zircaloy-4 at 1000 °C (Fig. 7), for Zr1%Nb at 900 (Fig. 2) and 1000 °C (Fig. 3). 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.

From the amount of hydrogen the oxide layer thickness 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

Table 2 Thickness of peeled off  $ZrO_2$  layers

According to the data above the peeling off of the oxide layers took 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 Table 2.

The hydrogen content of metal phases 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. Fig. 10 shows the absorbed ratio of formed hydrogen in case of Zr1%Nb, on Fig. 11 the H/Zr ratio in the metal phase at the end of oxidation processes can be seen.

## 4. 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, otherwise 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 in Fig. 12.

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 in case of as received samples. It indicates a lower oxidation rate for the hydrogenated alloys compared to the as received ones. The emission of hydrogen during the late steam oxidation phase did 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 Fig. 13.

## 5. DELAYING EFFECT OF SURFACE OXIDE LAYER ON THE HYDROGEN ABSORPTION BY THE ZR ALLOYS FROM GAS PHASE

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<sub>2</sub>. The hydrogen content of the outlet gas was continuously monitored. In case of as received samples the H<sub>2</sub> concentration in the argon dropped suddenly and grow back slowly as the equilibrium partial pressure growth because of the increasing H/Zr ratio in the sample. For samples with oxide layers the fall back of H<sub>2</sub> concentration in the argon delayed. The delay times were dependent on the temperatures and oxide thicknesses. At the evaluation we compared the actual H<sub>2</sub> 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 values became the same was accepted as delay time. The results are shown in Fig. 14.

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

$$\text{Zr1\%Nb:} \quad dt = d(\text{ox}) \cdot (48 - 1.3 \cdot 10^5/T + 0.95 \cdot 10^8/T^2) \quad (2)$$

$$\text{Zircaloy-4:} \quad dt = d(\text{ox}) \cdot (93 - 2.6 \cdot 10^5/T + 1.8 \cdot 10^8/T^2) \quad (3)$$

where **dt** in minute, **d(ox)** in µm and **T** in Kelvin has to be given.

Interesting to note, that after break-through time equilibrium took place entirely in the range of time resolution of experimental device. The O content of metal phase did not reduce the absorption rate.

## **6. CONCLUSIONS**

The work summarized in this paper was a several-year effort to clear up the hydrogen behaviour in high temperature core conditions. We suppose that the presented results gave some valuable contribution to the modeling of the high temperature processes in the core regarding of the cladding material and hydrogen interactions.

## **ACKNOWLEDGMENTS**

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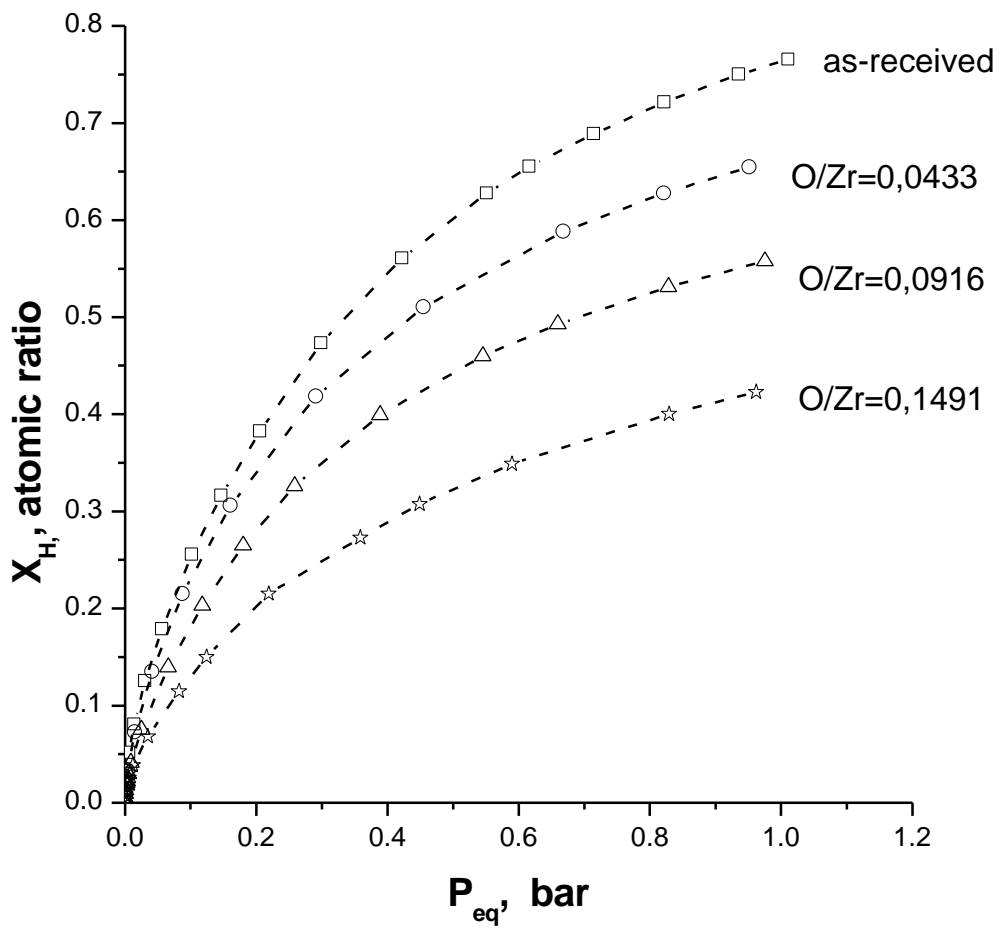


Fig. 1 Equilibrium hydrogen concentrations (H/Zr) for Zr1%Nb at 1000 °C at different oxygen content (O/Zr) as function of the pressure of hydrogen gas

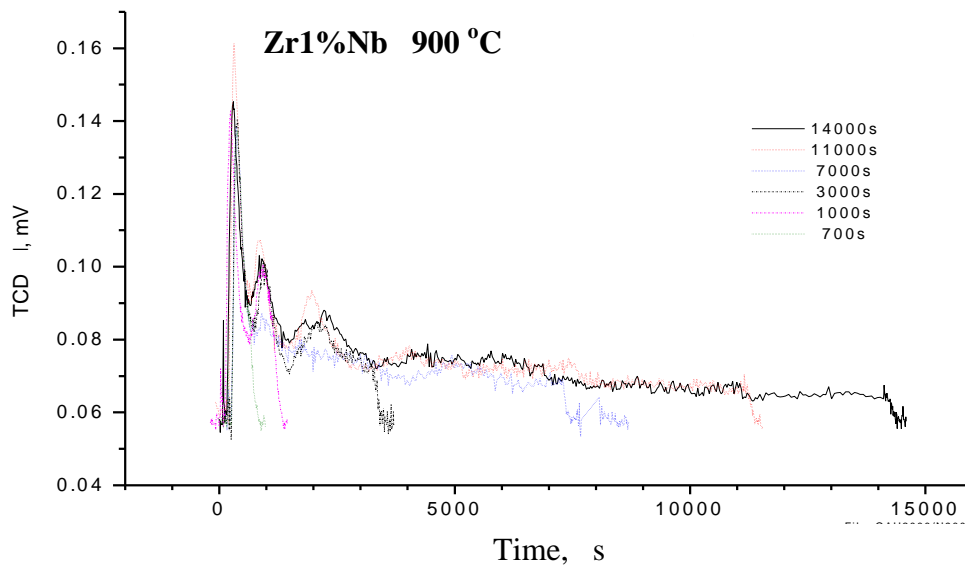


Fig. 2 H<sub>2</sub> escape rate at steam oxidation of Zr1%Nb at 900 °C

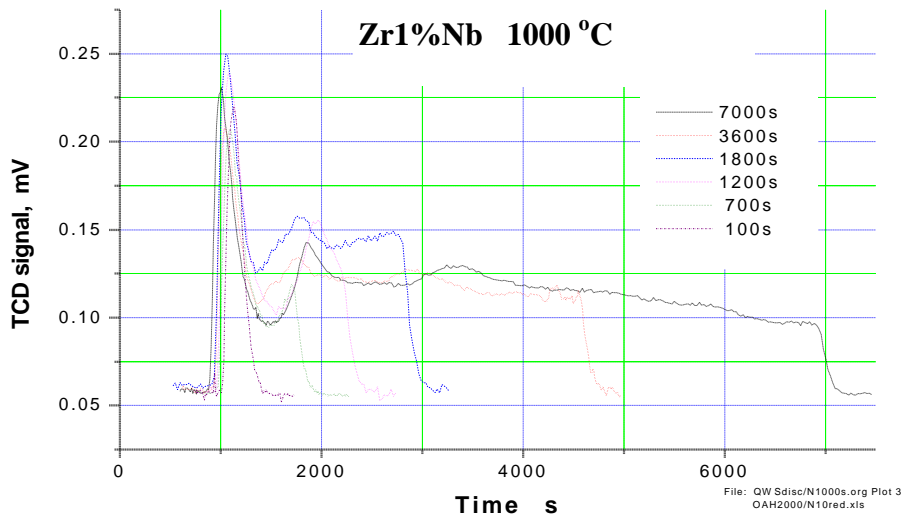


Fig. 3 H<sub>2</sub> escape rate at steam oxidation of Zr1%Nb at 1000 °C

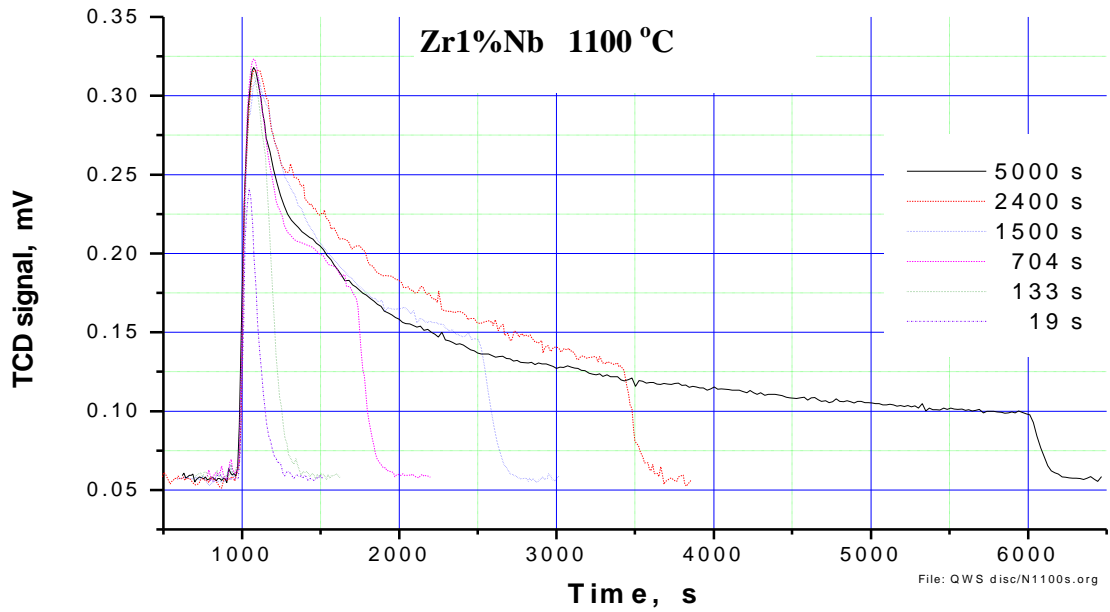


Fig. 4 H<sub>2</sub> escape rate at steam oxidation of Zr1%Nb at 1100 °C

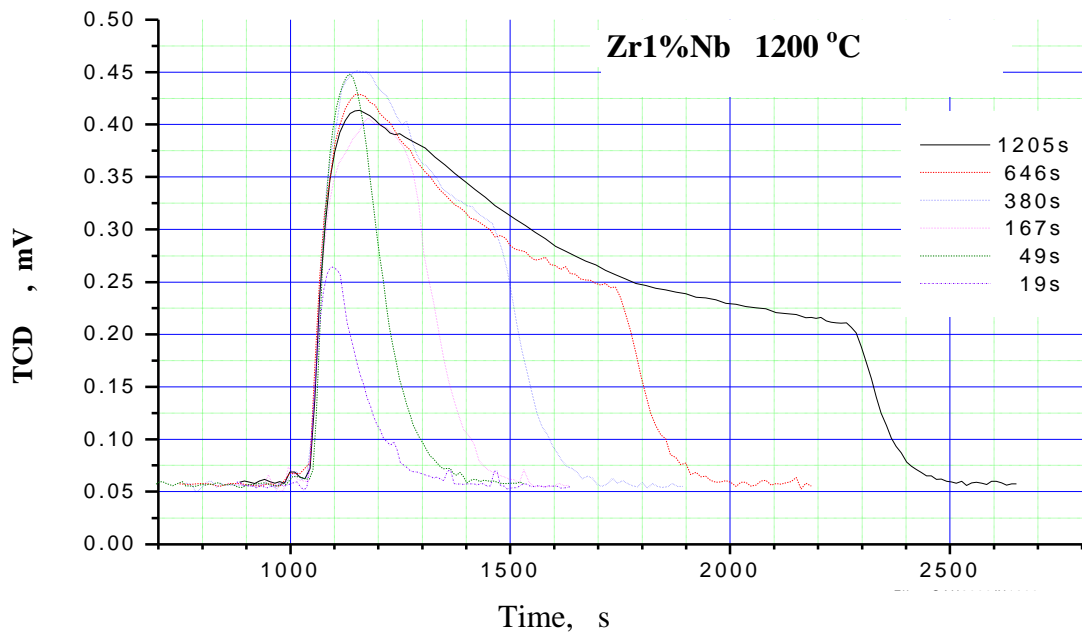


Fig. 5 H<sub>2</sub> escape rate at steam oxidation of Zr1%Nb at 1200 °C



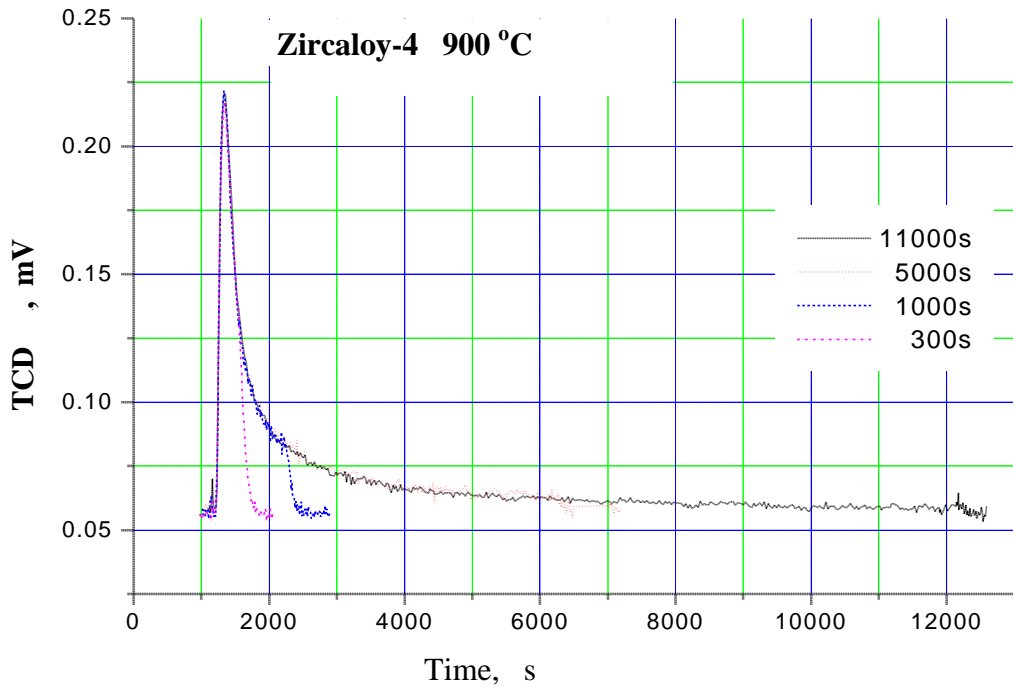


Fig. 6 H<sub>2</sub> escape rate at steam oxidation of Zircaloy-4 at 900 °C

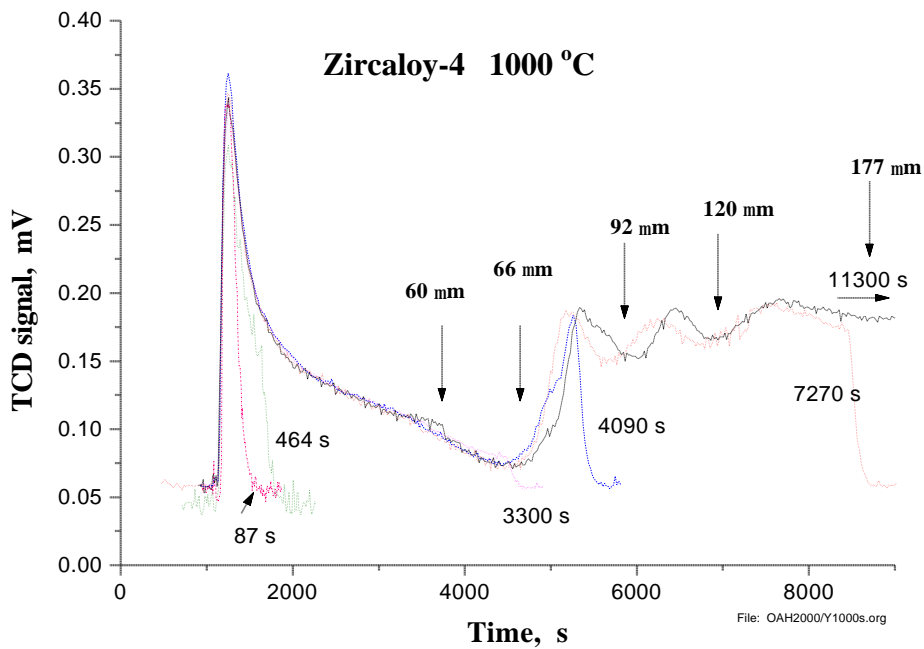


Fig. 7 H<sub>2</sub> escape rate at steam oxidation of Zircaloy-4 at 1000 °C

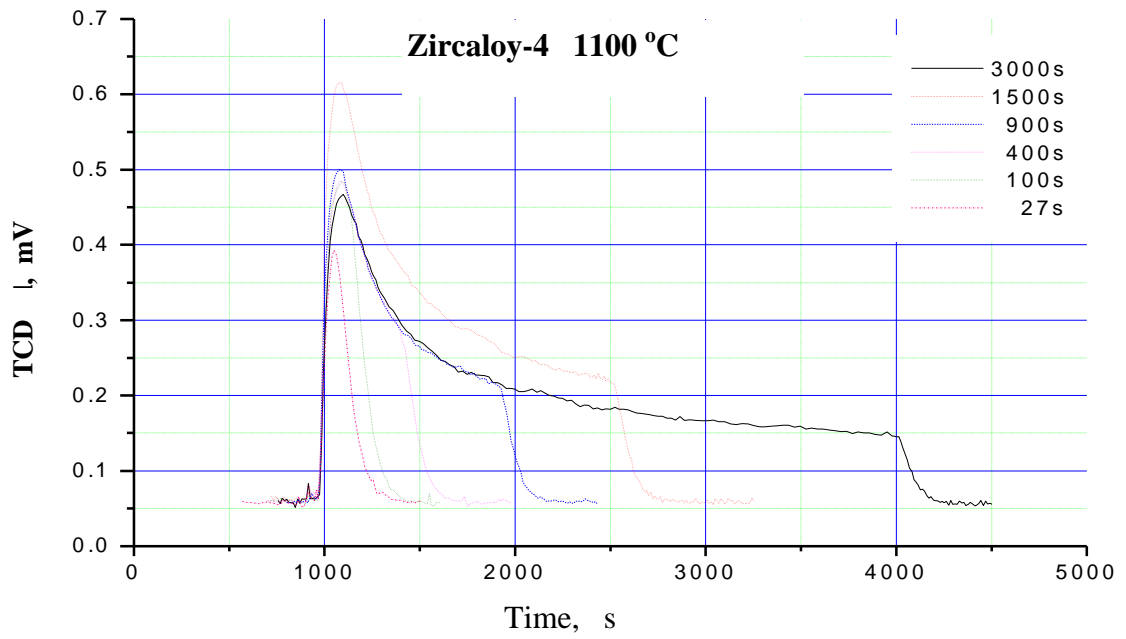


Fig. 8 H<sub>2</sub> escape rate at steam oxidation of Zircaloy-4 at 1100 °C

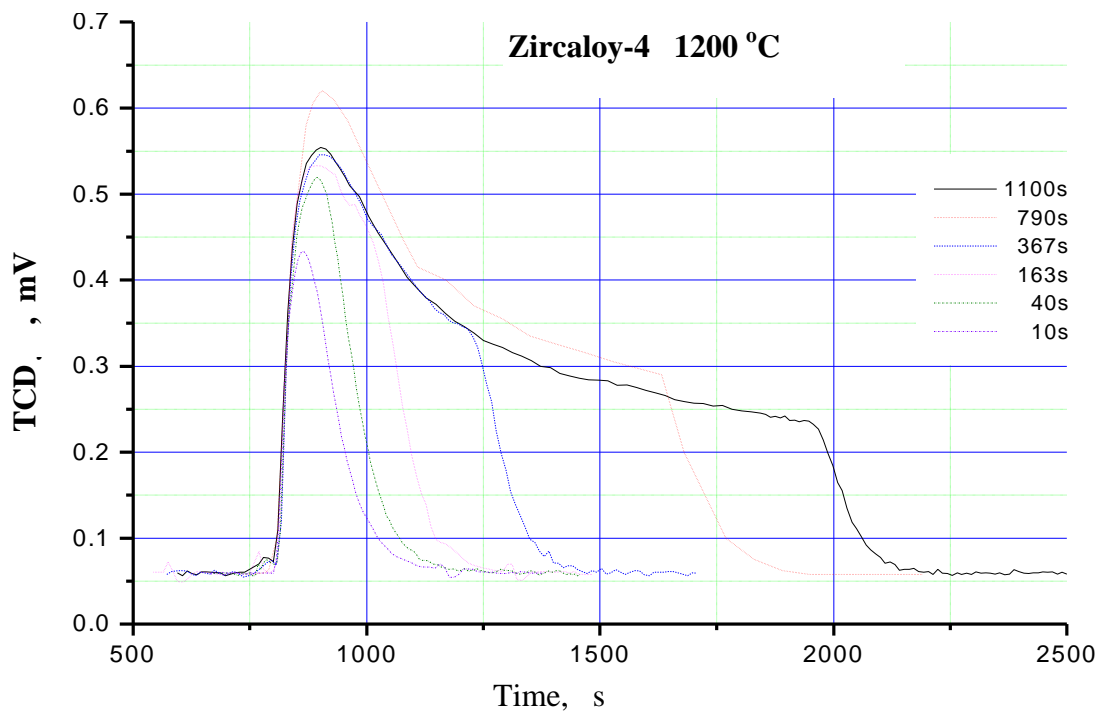


Fig. 9 H<sub>2</sub> escape rate at steam oxidation of Zircaloy-4 at 1200 °C

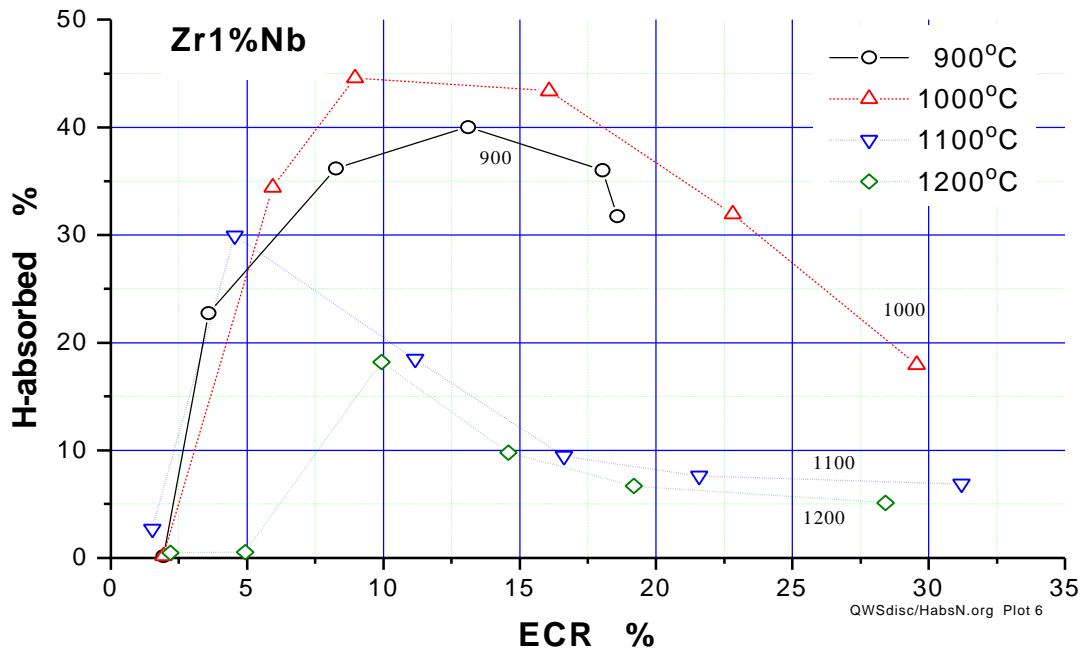


Fig. 10 Absorbed part of hydrogen at steam oxidation of Zr1%Nb as function of equivalent cladding reacted (ECR)

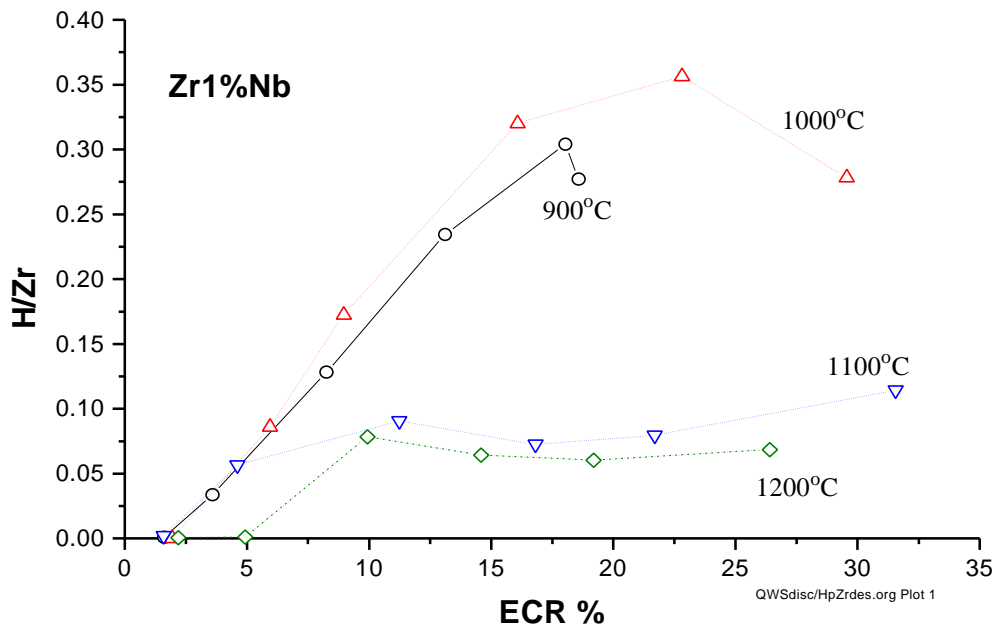


Fig. 11 Hydrogen concentration in the metal phase at the end of steam oxidation of Zr1%Nb

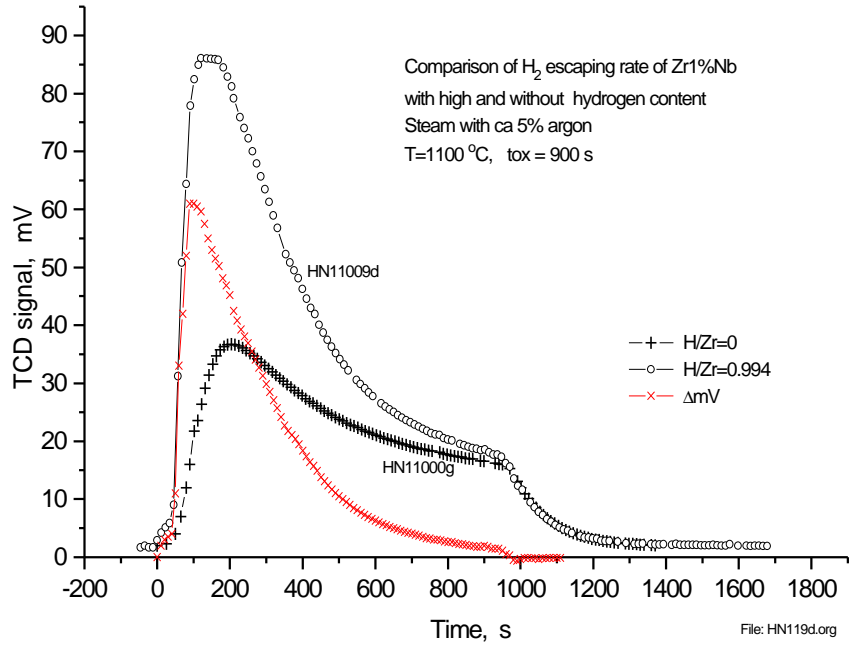


Fig. 12 Escape rate of hydrogen during steam oxidation of Zr1%Nb as received and hydrogenated (H/Zr~1) samples at 1100 °C

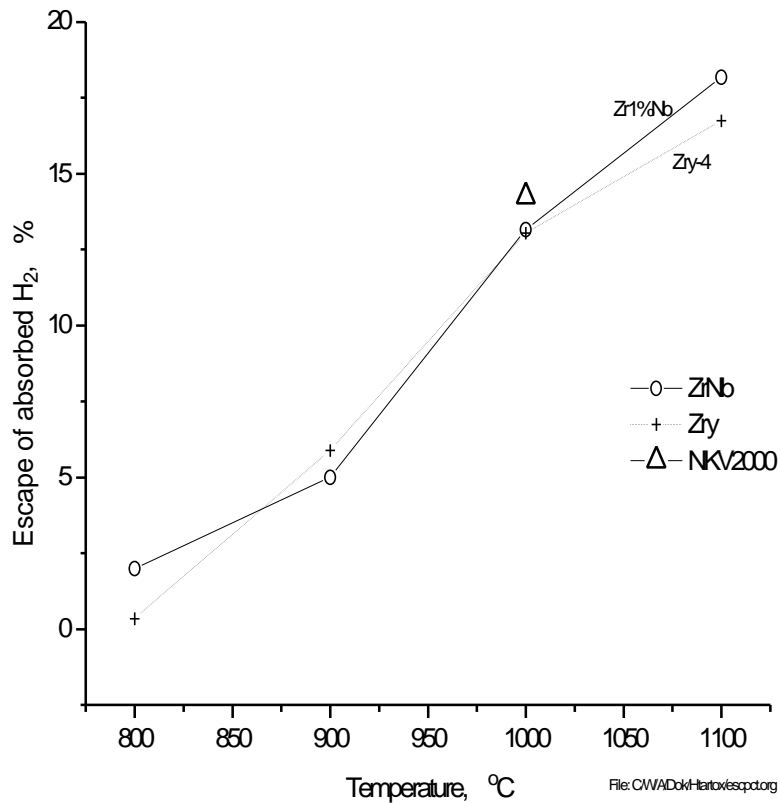


Fig. 13 Escaped part of dissolved hydrogen during the first phase of steam oxidation of cladding alloys hydrogenated up to H/Zr~1

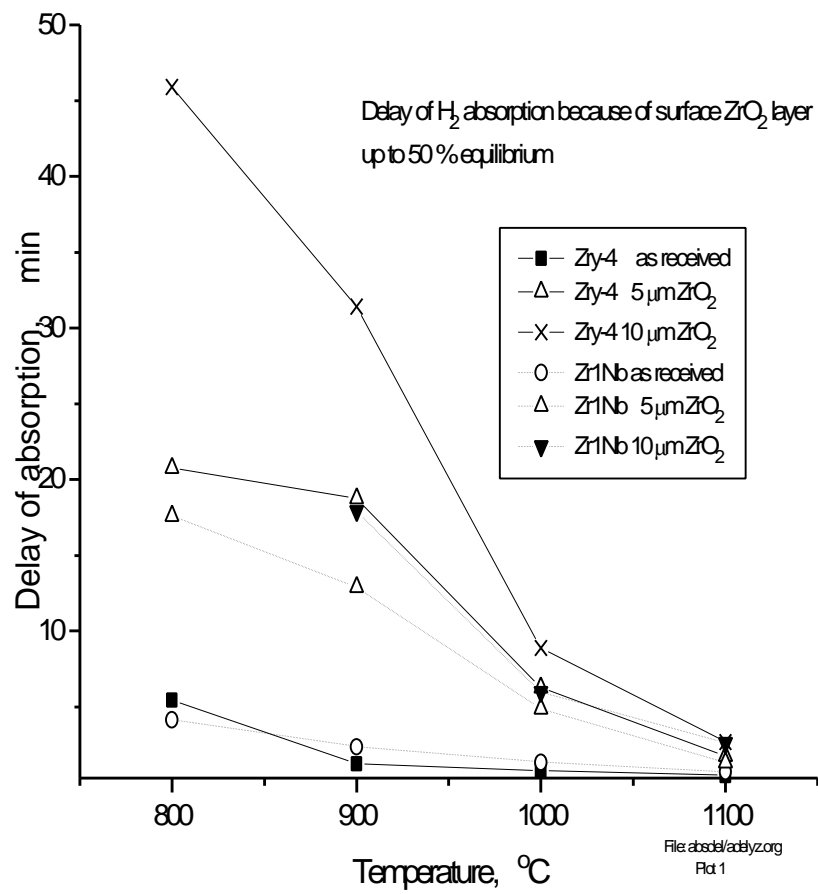


Fig. 14 Delay of H<sub>2</sub> absorption from gas phase by cladding Zr-alloys as function of the surface oxide layer thickness and temperature

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