

# Influence of Simulated LOCA on the Properties of Zircaloy Oxide Layers

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Specimens of Zr1Nb and Zry-4W were pre-oxidized first for 360 days in steam at 425 °C and were then exposed for 3 min to 1200 °C in steam, simulating loss of coolant conditions. In this way, the oxide thickness was more than doubled. The I-V characteristics, measured up to 90 V at temperatures up to 180 °C, revealed the formation of double layers, consisting of dark monoclinic oxide with 1.3 eV activation energy near the metal, and of a whitish surface phase with only 0.5 eV, for both samples. The I-V characteristics of Zr1Nb showed normal behavior, whereas Zry-4W changed from an unusual sub-linear form at low temperatures and voltages to normal space-charge limited currents at higher temperatures and voltages. Observation of the injection and extraction currents in the Zry-4W sample showed abnormally high negative zero voltages produced by extraction after former injection.

**Keywords:** Zirconium alloys, oxide layers, semiconductor doping conduction type, reduction semiconductor, anomalous I-V characteristics, space-charge limited currents, injection and extraction currents, temperature dependence of resistivity, activation energy

## 1 Introduction

In a LOCA-type accident in atomic reactors, the cladding of the fuel cells is exposed to high temperature shock for several minutes, and it is vital to know possible changes in the material properties influencing the safety conduct. The aim of this work is to investigate the oxide layers formed by the thermal shock, and to compare their properties with the original pre-oxidized layers.

## 2 Samples

In order to simulate LOCA conditions, samples of Zr1Nb and of Zry-4W pre-oxidized in steam at 425 °C for 360 days were exposed to 1200 °C in steam for 3 minutes. The oxide layer thickness increased from 33.3 µm to 78.8 µm for Zr1Nb, and from 35.3 µm to 78.7 µm for Zry-4W. On the metallographic section, the additionally grown oxide is of different color, and at the interface a very thin layer of metallic tin could be observed. Oxygen diffused into the underlying zirconium with 30 % at the interface, and structural changes could be asserted down to 100 µm, Table 1.

Tube specimens of 30 mm length and 9 mm outer diameter prepared from zirconium alloys were used. The properties of the pre-oxidized layers have been described in [1].

## 3 Experimental

The oxide at the end faces of the tubes was ground off for good contact. Painted-on contacts of colloidal silver 6.0 mm in diameter were used. The samples were mounted into a mini-thermostat for measurement at temperatures up to 180 °C. Details of the measuring procedure are given in [2]. The relative permittivity of 36 and 31 for the two samples, respectively, was very high, whereas the pre-oxidized forms

Table 1: Characterization of Samples

Sample	material	number	medium	temperature (°C)	time(min.)	thickness (µm)
1a	Zr1Nb	1744332	steam	1200	3	78.79
3a	Zry-4W	3744337	steam	1200	3	78.74

had permittivity of only 20.5 and 17.2, respectively. The I-V characteristics were symmetrical, therefore only the forward voltage branch, with the positive terminal connected to the zirconium metal, was measured in voltage steps of 5 V up to 90 V, and at constant temperatures in steps of 20 °C up to 180 °C.

Sample Zr1Nb had normal I-V characteristics with space-charge limited currents given by

$$I = aU^2 + bU + c, \quad (1)$$

allowing computation of resistivity  $\rho$ , mobility  $\mu$  and carrier concentration  $n$ .

## 4 Results and discussion

Further details concerning the theoretical aspects are given in [3, 4]. As an example the I-V characteristic at room temperature is shown in Fig. 1. At higher temperatures

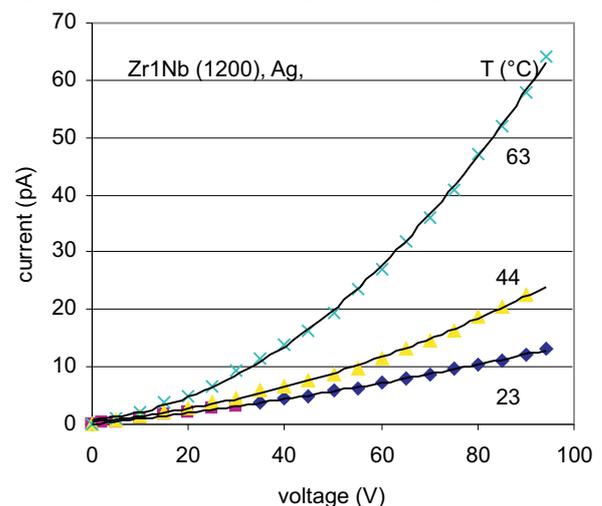


Fig. 1: Zr1Nb, I-V characteristics at 23, 44, 63 °C, respectively

the current values are higher, but the form remains unchanged. The temperature dependence of the resistivity, giving  $E = 1.30$  eV, is shown in Fig. 2. The pre-oxidized layer has 1.30 eV and the oxide grown at high temperature (upper layer) has 0.54 eV activation energy.

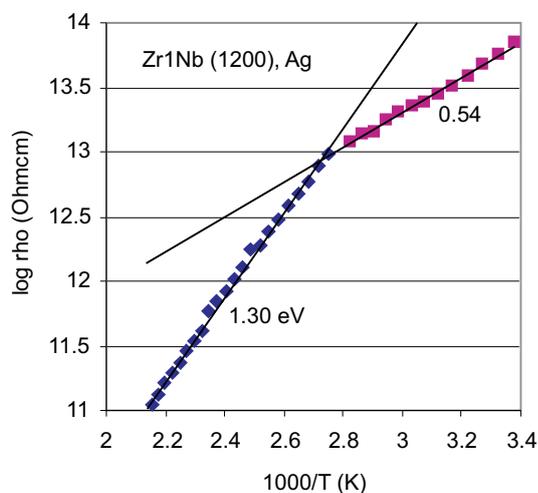


Fig. 2: Zr1Nb, temperature dependence of resistivity

Sample Zry-4W behaved completely differently from Sample Zr1Nb. As shown in Fig. 3a, the I-V characteristic at room temperature was sub-linear up to 50 V, i.e. it obeyed Eq. (1), though with negative coefficient  $a$ , and at higher voltages continued with a linear trend.

With rising temperature the sub-linear part continually diminished, and the linear part gradually changed over to space-charge limited current (Fig. 3b), until this character prevailed completely at temperatures over 150 °C (Fig. 3c). The end point of sub-linear behavior decreased from 50 V at 23.5 °C to 20 V at 120 °C, respectively, with an indication of 10 V at 142 °C, and was not observed at temperatures over 150 °C.

This behavior may be explained by the different properties of the original pre-oxidized layer and the subsequent rapidly grown top layer, thus creating a double layer with attributes similar to p-n junctions. In steam at temperatures below 450 °C, the dark monoclinic oxide phase is formed with activation energy of about 1.3 eV, which prevails at higher measuring temperatures and higher voltages. At temperatures over 450 °C, a whitish oxide is formed with low activation energy of 0.5 eV, determining the current flowing at, and near, room temperature. At the interface between the two oxide types there is a potential drop from 1.3 to 0.5 V, which influences the form of the I-V characteristics.

Using Eq. (1), the coefficient  $a$  in the prevailing region of space-charge limited currents in the I-V characteristics determines the mobility with sufficient precision, but the linear part represents only a small fraction of the characteristic, and coefficient  $b$  is loaded with high error. It is therefore better to compute the resistivity directly, using current readings near the origin at voltages below the onset of the influence of the space charge. Coefficient  $c$  is better determined at zero voltage. Thus the temperature dependence of resistivity, plotted in Fig. 4 using values taken from the I-V characteristics mea-

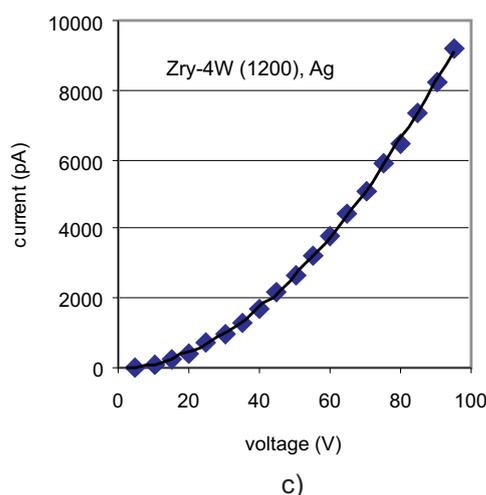
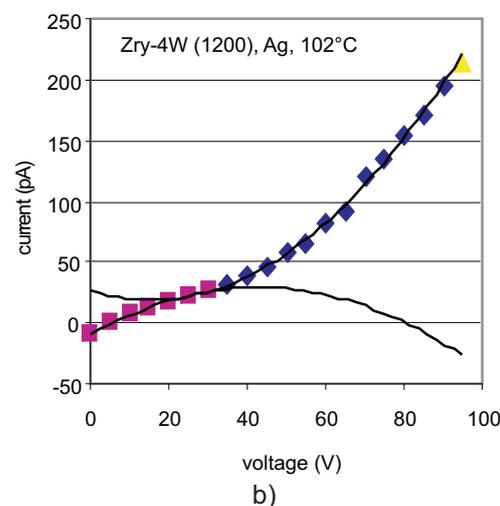
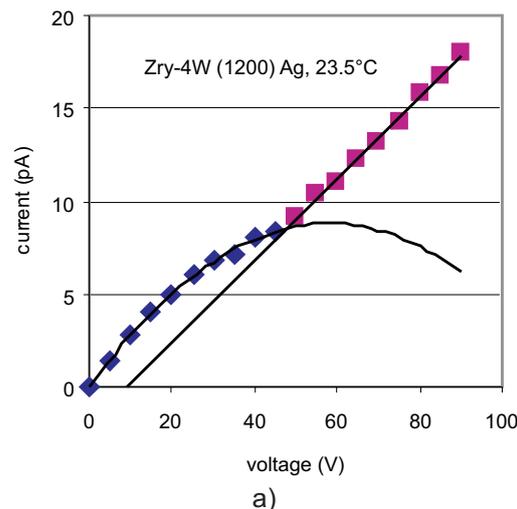


Fig. 3: Zr1Nb, I-V characteristics changing with temperatures, a) 23.5 °C, b) 102 °C, c) 180 °C, respectively

sured at 102, 120, 142, 159, and 180 °C, respectively, is well defined, but not so at lower temperatures. In order to fill this gap, the resistivity in Fig. 5 was determined by current measurement at constant 5 V with slowly rising temperature up to 100 °C, thus completing the inaccurate range under 100 °C in Fig. 4.

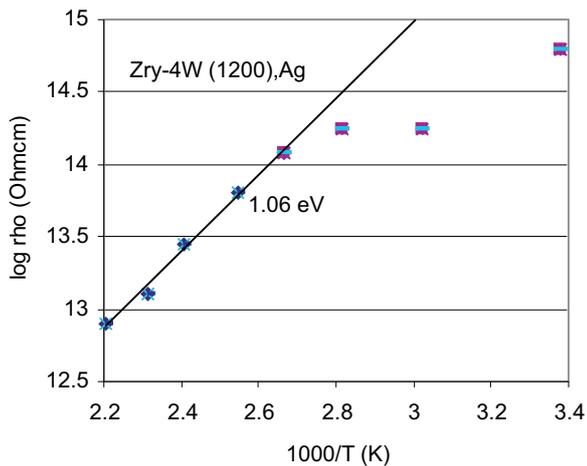


Fig. 4: Zry-4W, resistivity at temperatures over 100 °C

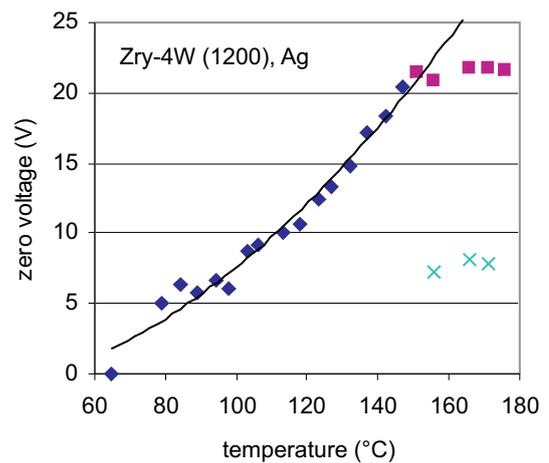


Fig. 7: Zry-4W, negative zero voltage

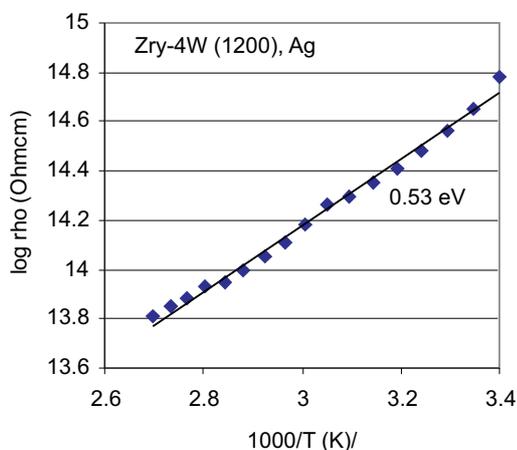


Fig. 5: Zry-4W, resistivity under 100 °C

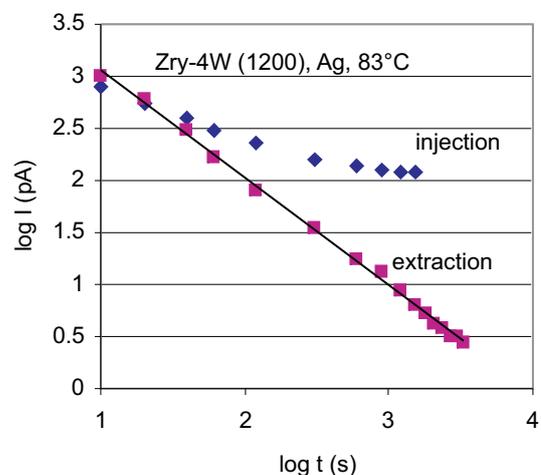
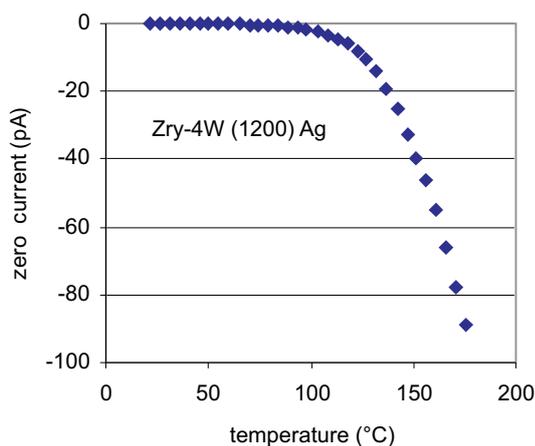
Fig. 8: Zry-4W, injection (at 75 V) and extraction at  $T = 83\text{ }^{\circ}\text{C}$ 

Fig. 6: Zry-4W, negative zero current (extraction)

The observed negative zero current (without external voltage) in Fig. 6 was due to extraction of the formerly injected charge, and was not caused by continued oxidation, which would have produced a positive ion current. At flow of current  $I$ , the resistance  $R$  of the layer and the input resistance  $R_i$  of the pico-amperemeter form a closed circuit, thus acting as a voltage source. It is defined by the sum of the voltage drops of

the resistors, caused by current  $I$ , giving  $U = I(R + R_i)$ . This is an open-circuit voltage and can be assessed by compensating the current, or can be computed, if the resistance of the layer is known. The result shown in Fig. 7 is astonishing. The extremely high voltages up to 22 V are the consequence of former high injection at 90 V into the very thick oxide layer.

The typical time dependence of injection and extraction currents is shown in Fig. 8. It takes long times to reach equilibrium after applying the voltage, up to 30 min. The injected charge is stored and can be observed as a negative extraction current by short-circuiting the sample with the pico-amperemeter, obeying a power law of the form  $I = I_0 t^{-n}$ , with the exponent  $1 > n > 0.5$ . The time integrals of the extraction and the negative injection current (minus the equilibrium current) are equal to the injected space charge, divided by the injection voltage, and define the capacity  $C/V$  of the layer.

## 5 Conclusions

The changes provoked by high temperature shock are best seen by comparing their properties with those of the pre-oxidized samples, as shown in Table 2.

The main difference consists in the formation of double layers of pre-oxidized grey monoclinic phase with high activa-

Table 2: Comparison of samples before and after thermal shock

Sample	Zr1Nb		Zry-4W	
	425 °C	1200 °C	425 °C	1200 °C
$\epsilon_r$	18	36	11.5	31
$\rho$ ( $\Omega\text{cm}$ )	$7 \times 10^{13}$	$6.6 \times 10^{13}$	$2.5 \times 10^{14}$	$4 \times 10^{14}$
E (eV)	1.3	1.3/0.5	1.4	1.1/0.5
C/V ( $\mu\text{F}/\text{cm}^3$ )	3.9	–	1.0	0.9
Permittivity $\epsilon_r$	low	high	low	high
Resistivity $\rho$	nearly equal		twice higher	
Energy E	1.3 eV only	change at 85 °C	change at 85 °C	
Capacity C/V	high	–	unchanged (lower)	

tion energy (1.3 eV) and the subsequent growth at 1200 °C of a whitish phase of low activation energy (0.5 eV), thus acting as  $n^+n$  structures.

In Zr1Nb the alloyed Nb does not form active centers, and therefore the I-V characteristics are normal space-charge limited current curves, whereas in Zry-4W there are active centers of Sn, Fe and Cr, which influence the I-V characteristics.

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