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## Measurements of Zirconium Alloy Oxide Layers

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Introduction - This is an overview of results, presented at APCOM workshops since 2001, achieved at systematic measurements on samples of oxide films on tubes of Zr1Nb, ZIRLO and Zry-4W, used for fuel cladding in light water reactors, which had been grown in the Research Institute UJP [1] at VVER conditions in water of  $360^{\circ}$ C with various times from one day up to 4 years. In a high temperature aqueous environment oxides are formed by diffusion of oxygen ions through the built-up layer, combining with zirconium ionized by electron emission [2]. The corrosion of the zirconium is due to oxide formation by the transfer of electrons from the metal to the water, whereby oxygen ions flow in the opposite direction. Thus the corrosion rate depends largely on the electron motion, which is governed by the conductivity of the oxide layer. The investigation of the electrical properties of the oxide is therefore of interest for the understanding of the corrosion resistance of the Zircaloys. It is well known [2,3,4] that  $ZrO_2$  is predominantly an electronic high-resistivity semiconductor with a low amount of ionic conduction (over room temperature). The band gap is approximately 5 eV, the work function 4.0 eV and the relative permittivity 22.

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## MEASUREMENTS OF ZIRCONIUM ALLOY OXIDE LAVERS

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### I. INTRODUCTION

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## II. Experimental

The oxide layers were grown on Zr1Nb, ZIRLO and Zry-4W tubes 30 mm long and of 9 mm outer diameter. Electrodes were either of 200 nm thick vacuum evaporated Au, or painted on of colloidal Ag



*Figure 1 :* Time dependence of injection and extraction (starting from zero current).

(Degussa), or of sprayed on colloidal graphite to the specimens wrapped in Al-foil with circular openings of 6,0 mm diameter, and the samples mounted in a minithermostat with a maxim. temperature of 220°C. The abraded front ends of the tubes of shining zirconium metal were in direct contact with pressed-on copper electrodes, on which a thermo couple was mounted for temperature control. The current was measured with a two-electrode arrangement using only one contact to each electrode. A stabilized voltage source could be connected with the positive terminal to the zirconium metal contact, while the negative terminal was earthed to the pico-amperemeter common. The input terminal was connected via a contact spring to the sample electrode. The voltage drop of the pico-amperemeter was limited to 10 mV max. and could be neglected for source voltages larger than 2 V.

First the capacity was measured to assess the relative permittivity, then the I-V characteristics were measured, first at room temperature, and then at higher constant temperatures in steps of about 1/10 of the maximum voltage chosen as not to exceed the maximum field strength of 3x10<sup>4</sup> V/cm.

## III. Results

The currents measured ad various voltages, temperatures and times of observation gave data to compute the transport parameters. The electric current measurement was very time consuming. At applying a voltage, the current started at a value limited only by the resistance of the measuring circuit and dropped very slowly, taking minutes up to hours, to





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Asymptotically reach equilibrium condition (Fig.1). Readings were taken after equal time intervals, when the change during 1 minute was less then 1% of the final value.

#### a) I-V characteristics

The I-V characteristics of high-resistivity semiconductors start at low voltages with a linear part obeying Ohm's law. At application of higher voltages the current rises faster due to the injection of majority



*Figure 3 :* Typical I-V characteristic, symmetrical.

consequence of temperature-activated liberation of trapped electrons and/or continuing oxidation in air. The space-charge limited current  $I_{sc}$  i.e. the first term in eq. (1), obeys Child's law [5]

$$I_{sc} = \frac{9}{8} \varepsilon \varepsilon_0 A \mu U^2 / w^3 = a U 2 \qquad (2)$$

Where  $\varepsilon_{\varepsilon_0}$  is the relative and vacuum permittivity, respectively, *A* is the contact area,  $\mu$  is the mobility of the free carriers, *U* the constant voltage and *w* the layer thickness.

The transition from the linear to the square part  $I_{sc}$  occurs at the characteristic voltage  $U_{ch}$ , when the rising space-charge limited current equals the linear ohmic part  $I_o = bU$ , i.e.

$$AU^2 = bU, \text{ or } U = U_{ch} = b/a \tag{3}$$

The ohmic current is

$$I_o = U/R = Uen_o \mu w/A \tag{4}$$

The characteristical voltage  $U_{ch}$ , using eqs.(2 and 4), yields

$$U_{ch} = e n_0 w^2 / \varepsilon \varepsilon_0 \tag{5}$$

By this expression the concentration  $n_0$  of the free carriers can be obtained,

$$n_0 = U_{ch} \varepsilon \varepsilon_0 / e w^2 \tag{6}$$

carriers building up a space charge, finishing with a space-charge limited additional part. The measured current values can be fitted to a second order polynomial

$$I = aU^2 + bU + c \tag{1}$$

The zero current expressed by the constant *c* can be observed above room temperature as a



*Figure 4 :* Temperature dependent I-V *(positive voltage branch only).* 

This is a simple way to assess the concentration of the free carriers  $n_o$  which, with knowledge of the resistivity  $\rho$  measured in the vicinity of the origin, yields also the mobility  $\mu$ .

An other way to assess the mobility is using eq.(2) directly.

#### b) Temperature dependence of the I-V characteristics

A typical example of I-V characteristics measured at rising temperature is in Fig.4.



*Figure 5*: I-V characteristics at higher temperatures, showing short-circuit current I(0) and open-circuit voltage U(0) at the origin.



*Figure 6*: Temperature dependence of resi-stivity ,with equal activation energy of doped and undoped Zircaloys.

At higher temperatures a zero current appears due to continuing oxidation in air, causing the characteristic not to pass through the origin, but at a negative zero voltage, as can be seen in Fig.5. The short- circuit current rises exponentially, the voltage only in a linear way.

The slope in Fig.5 corresponds to the ohmic term in eq.1 and determines the resistivity  $\rho$  of the sample. Plotting  $\rho = f(1/T)$ , as in Fig.6, gives the activation energy *E* of the free carriers.

The main result of the analysis of the data of many samples was that the high resistivity of the oxide of the Zircaloys is due to the extremely low mobility of the electrons, of the order of  $10^{-9}$  cm<sup>2</sup>/Vs, but their concentration is practically constant and of the order of  $10^{14}$ cm<sup>-3</sup>.

### c) Injection and extraction of space-charge

At application of voltage the flowing current builds up a space charge, until equilibrium is achieved. By shortening the contacts with the pico-amperemeter, the injected space charge flows out and gives rise to a negative extraction current, which is equal to the former (positive) injection current, see Fig.2, and obeys the power law,

$$I = B t^{-n} , \qquad (7)$$

With time *t* and exponent n < 1 [5]. The extracted charge *Q* can be computed by integration of the extraction current shown in Fig.2,

$$=Q \int_{t_1}^{t_2} Bt^{-n} dt = B(t_2^{1-n} - t_1^{1-n})/(1-n).$$
(8)

It was shown that the charge Q is a linear function of the injection voltage and the slope dQ/dU = C has the dimension of a capacity. The oxide layer behaves like a capacitor, having about tens of  $\mu$ F/cm<sup>-3</sup>, which can be charged and discharged.

## d) Influence of layer thickness

The thickness of the oxide layer depends on temperature and on oxidation conditions (water, steam, air). Near the metal-oxide interface a tetragonal hypostoichiometric layer of dark color with relatively high conductivity is formed (layer of the first kind) [8], which at thickness over 5 µm gradually transforms into a monoclinic white form (of the second kind) with a low concentration of oxygen vacancies and high resistivity. In Fig 7 the connection between resistivity and oxide layer thickness is shown. There is a pronounced tendency of resistivity, shown here with oxide samples of Zr1Nb of the first kind, to drop with slightly increasing thickness to very low values, with a power law dependence of approximately  $\rho \sim w^{-10}$ , whereas with increasing thickness of the oxide of the second kind with layer thickness w, the power law is  $\rho \sim w^3$ . The  $\rho = f(w)$ dependence in Fig.7 then could be explained by varying contributions of the black and white oxide type.



Figure 7 : Dependence of resistivity on layer thickness.



*Figure 8* : Meyer – Neldel Rule InA = f(E).

Since ZrO<sub>2</sub> is a high resistivity oxide semiconductor, it is reasonable that the NMR would apply. Mever and Neldel [9] found that the dependent experimentally assessed temperature conductivity of high resistivity semiconductors,  $\rho = \rho_0 exp$ (-E/2kT), obeys a simple relationship between activation energy *E* and the pre-exponential factor  $\rho_0$ . In Fig.8 the observed activation energies E for the series of specimens, listed in Fig.7, are plotted in dependence of ln A, where  $A = l/\rho_0$ . Although A spans a wide range of 12 orders of magnitude, the experimental values of E follow a straight line with a slope of  $14.9\pm0.04$  with  $T_0 =$ 388 K and the isokinetic energy  $E_0 = kT_0 = 33$  meV. The importance of the MNR consists of the fact that different electrode metals, giving different values of activation energy and resistivity, will nevertheless have points lying on the same straight line with common isokinetic energy. The activation energy E is not a material constant, but is determined by the energy difference between the lattice defects and the lower edge of the conduction band.

## IV. Conclusions

It has been demonstrated that the I-V characteristics consist of a linear part near the origin, followed by a quadratic space-charge limited current obeying Child's law and a constant part. The injected charge can be again extracted as short-circuit current. The I-V characteristics, measured at different temperatures with their activation energy confirm the MNR.

The oxide films are not homogeneous, but consist of a substoichiometrcblack oxide layer of relatively high conductivity near the metal-oxide interface, and of an almost stoichiometric white layer of high resistivity [8]. Competition of both layer types produces a conductivity maximum for layers about 5  $\mu$ m thick. Fully oxidized white layers are of monoclinic structure, whereas substoichiometric black layers with oxygen deficiency can have a tetragonal structure. Moreover, part of the layer near the surface can be porous so that applied electrode metal could enter the pores and alter the effective thickness of the layers, giving rise to erroneous measurement results.

From all carried-out measurements it follows that Zirconium oxide fits into the group of oxide semiconductors, where the (low) conductivity is provoked by stoichiometric deviations and not by doping. ZrO<sub>2</sub> is an n-type reduction semiconductor, conduction depending on missing oxygen, with a small part ionic current at higher temperatures due to continuing oxidation.

## V. Acknowledgement

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