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Journal of Nuclear Materials 321 (2003) 115–117
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Letter to the Editors

Influence of humidity on the permittivity and conductivity of thin zirconium alloy oxide films

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Received 9 January 2003; accepted 27 March 2003

Abstract

The relative permittivity of thin oxide layers on tubes used for nuclear fuel cells of zirconium alloyed with 1% niobium was observed to change reversibly up to 22% when measured with a permeable thin gold electrode, and the conductivity increased up to several hundredfold when exposed to saturated moist air in several minutes. The effect is believed to be produced by adsorbed water in the pores of the oxide layer.

Continuing our investigations of zirconium alloy oxide films grown on tubes used for fuel cladding in light water reactors [1] we observed changes of capacity bridge readings when the exhaled air of the observer fanned the sample. We therefore investigated the influence of humidity of the surrounding air on the capacity more fully. It was shown that also the current at conductivity measurements was affected by the moisture contents of the surrounding air.

The schematic measuring set-up is shown in Fig. 1. The tubes were of pure zirconium alloyed with 1% niobium, of 30 mm length and of 9 mm diameter. The specimens, characterized by a number code, belonged to a large set used for the investigation of the corrosion resistance under various oxidation conditions. The first specimen, Zr1Nb 1136143, with an oxide layer thickness of 1.13 μm, had been oxidized 18 days in water at 360 °C. The measuring disc-shaped electrode of 6 mm diameter consisted of vacuum evaporated gold, thickness about 100 nm. We used a TESLA BM 498 type capacitance bridge, operating at 1000 Hz with 0.1% precision.

In normal lab air at 23.5 °C with estimated 50% relative humidity, the bridge reading was 4280 pF. When the sample holder was covered with a beaker of 800 ml volume plated inside with moistened filter paper, the capacitance increased after 10 min to 4900 pF. After removal of the beaker the capacitance dropped to 4300 pF. Periodical change of the relative humidity of the air around the sample between 100% with the beaker, and 50% without the beaker in normal air changed the capacitance as it is shown in Fig. 2.

In order to expell all adsorbed water, the sample was heated to 120 °C and measured after cooling down to ambient temperature. After covering the sample with the moist beaker the capacitance rose from 4008 pF in the dried state to 4900 pF in saturated air. This corresponds to a relative capacitance change of $\Delta C/C = 22\%$. The relative permittivity calculated from theses capacitances is $\varepsilon_r = 22.0$ and $\varepsilon_r = 18.0$ for moist and dry air, respectively. In normal air the capacitance dropped to 4310 pF (the same value as in Fig. 2), i.e. higher than in the dried state, due to the lab air of about 50% relative humidity. It should be noted that after drying it took 30 min to reach equilibrium, contrary to periodical changes between 50% and 100% relative humidity in Fig. 2. The sample reacted like a hygrometer [3].

It is known that zirconium oxide layers are porous [2], and filling up of the pores by adsorbed water with a relative permittivity of 81 will increase the measured capacity of the sample. The porosity of the oxide layer is

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doi:10.1016/S0022-3115(03)00202-2

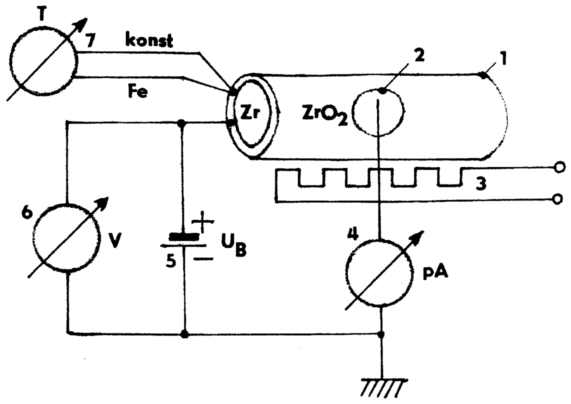

Fig. 1. Schematic drawing of the measuring set-up: 1 – sample, 2 – circular measuring electrode with pressed-on phosphor-bronze wire contact, 3 – insulated heating element, 4 – pico-amperemeter or capacity measuring bridge, 5 – adjustable voltage source, 6 – voltmeter, 7 – thermocouple with millivoltmeter.

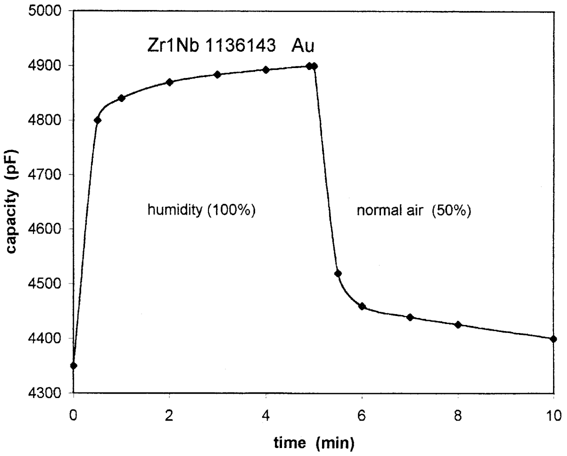

Fig. 2. Time dependence of capacitance of a 1.23 μm thick zirconium oxide layer exposed to air of 100% and about 50% relative humidity, respectively. Gold electrode about 100 nm thick.

manifesting itself by the lower measured relative permittivity of 18.0 in the dry state, whereas for the bulk oxide a relative permittivity of 22.0 is generally assumed. It should thus be possible to evaluate the porous fraction of the layer by the increase of relative permittivity, water being about four times as effective as the oxide.

The influence of moist air on the current measured at room temperature is even more pronounced, as shown in Fig. 3. After applying 0.5 V in normal air, the current dropped from initially 100 pA during 10 min to a nearly constant value of 10 pA, and rose to 2000 pA during 5 min when the sample was covered with the moist beaker and, after removing the moist beaker, dropped again after 2 min to 10 pA in normal air. The current increased 200-fold.

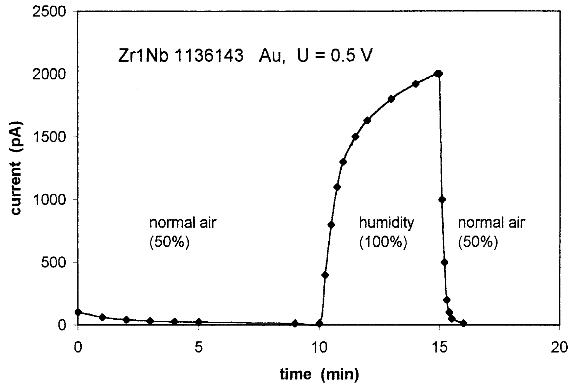

Fig. 3. Time dependence of current at 0.5 V on the relative humidity (same sample as in Fig. 1) at room temperature.

This extreme effect could be observed in this sample only, which had a very thin gold electrode, which was evidently permeable to water vapour. Another sample, Zr1Nb 1136126 of 0.62 μm thickness after three days oxidation in water of 360 °C had a painted-on silver electrode of 3 mm diameter. We used a suspension of fine silver particles (Degussa, Leitsilber 317), which was applied by means of a fine brush. The layer was dried and heated in air at 120 °C for half an hour. The thickness was estimated to be several tenths of a millimeter. The capacitance increased from 605 pF at normal air to 662 pF in moist air not until after 3.5 h, and dropped after 30 min in normal air to the starting value of 605 pF, the relative change being $\Delta C/C = 9.4\%$ (Fig. 3). In this case the compact silver electrode is impermeable, the water vapour can only diffuse sideways after a long time. This assumption is strengthened by the results, shown in Fig. 4, where the measuring electrode on the same sample was formed by three turns of a 0.3 mm thick copper wire wound tightly around the tube. Here the surface was open and water vapour could enter freely. Thus a relative capacitance change of over 20% was achieved after 10 min in moist air. Also the capacitance drop in normal air was short and took only 2–3 min.

The described behaviour can be explained by the porosity of the oxide layer [2]. The ability of the porous oxide, to adsorb water from moist air and thus increasing the permittivity as well as the conductivity can be used for humidity sensors, as was shown by Niranjan et al. [3]. The use of current increase is less suited for humidity sensoring, because of the strong temperature dependence of the conductivity.

On other similar samples, but with thick measuring electrodes, the influence of air with high humidity was mostly very small. Sample Zr1Nb 1136133, oxidized

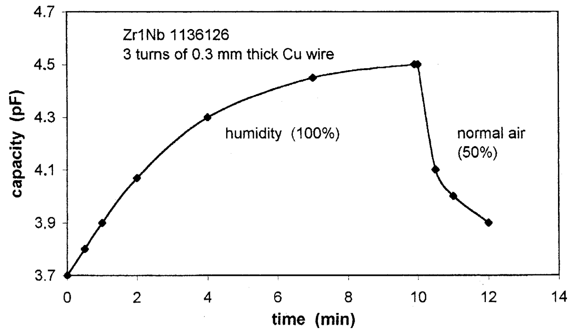

Fig. 4. Time dependence of capacitance of a 0.62 μm thick oxide layer on the relative humidity, electrode consisting of 3 turns of a 0.3 mm thick copper wire at room temperature.

14 days at 360 °C in water with a thickness of 0.96 μm (similar to Zr1Nb 1136143), but with a thicker gold electrode (not measured) had a relative permittivity change of 0.98% only, and sample Zr1Nb 1136107, oxidized 189 days in water of 360 °C and 3.38 μm thick, showed no change of capacity in humid air at all. It is possible that in this case the long oxidation time produced a more compact oxide layer, as is also probable, because the measured relative permittivity was 24. Nevertheless the influence of humid air should be regarded as a possible source of error, especially at current measurements near room temperature.

Acknowledgements

Support of this work by ŠKODA-ÚJP, Praha company is highly appreciated. Special thanks are due to Ms Věra Vrtílková for providing of oxidized specimens of specified thickness.

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