

Formation of Thick Anodic Oxide Layers on Zirconium and Zirconium alloys.

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Zirconium oxides present many physical and chemical properties interesting in view of some important applications. For instance, this oxide is the base of high temperature ionic conductors commonly used in SOFC. At low temperature, Zr oxide presents a low mixed conduction. This compound is highly stable. It can be formed anodically on either zirconium [1, 2] or zircalloy [3].

Zirconium alloys are commonly used in the nuclear industry, especially in pressurized water reactors as fuel cladding materials. In the reactor this metal is submitted to drastic conditions in terms of temperature and pressure and undergoes a slow corrosion process. The corrosion is due to the formation of a mixed potential between metal oxidation and water reduction. Schefold et al. [4] have shown by in situ impedance spectroscopy at 360°C and 18.2 MPa that the oxide layer growth is cyclic. The breakdown of the film occurs once the layer thickness exceeds 2 µm. A 200nm thick compact layer remains at the contact of the metal which restarts to grow whereas the external part of the layer becomes porous. The process is slow. It requires more than 110 days to appear and only three kinetic transitions are observed after one year of experiment. This renders the study of this phenomenon uneasy.

Applying an anodic bias accelerates the anodic process. In the present study, we have compared the oxide layer growth on zirconium and two zircalloys, Zr-1.4% Sn (Zr4) and Zr-1% Nb in acidic medium (0.5 M H₂SO₄) at room temperature. The aim was to answer the questions: is it possible to observe a kinetic transition by applying a sufficiently high bias? Does the kinetic transition occur at a similar thickness and is the structure of the layer after the breakdown similar to that formed at high temperature and pressure? The oxide layer has been grown by a potentiodynamic scan between 0 and 8 volts. Above 1.5V a peak of current appears which is attributed to molecular oxygen formation. The peak is higher for the two Zr alloys. The layer thickness has been measured during the potential scan by impedance at fixed frequency. The oxide growth process on either Zr metal and the two alloys is high field assisted. The roughness of the layer has been calculated from the comparison of the capacitive current, deduced from the impedance measurements and the actual current. This factor ranges between 1.5 and 1.7.

Thereafter, films have been grown at constant current density between 8 and 150

volts. It is shown that the growth rate is no more constant with time. At 85V the faradaic efficiency has been calculated assuming a 4 electrons exchange process. 60% is found for Zr and 14 % and 25% for Zr-Sn and Zr-Nb respectively. Some preliminary experiments show that the breakdown occurs above 150 V. The oxide layer thickness before the transition is 300 nm, much less than in the case of high pressure and temperature corrosion.

In conclusion it appears that the oxides formed on alloys present a higher electronic conductivity than those formed on the metal. Under the growth conditions used the layer breakdown appears earlier than expected but this parameter is likely dependent on the anion in solution. The film structures before and after the transition remain to be studied.

References.

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