In-situ electrochemical study of zirconium alloys corrosion in simulated VVER coolant

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Abstract: The corrosion resistance of zirconium alloys in the environment of nuclear reactor coolant depends on formation of an adherent oxide film, which impedes transport of reactive species to the metal surface. Information on the transfer properties and thickness of such oxide films can be obtained from impedance measurements. If the impedance measurements are performed under simulated conditions of primary coolant, then it is possible to obtain a reliable information both on properties of oxide layer and on corrosion parameters of Zr alloys. Electrochemical impedance spectroscopy (EIS) uses a small amplitudinal signal (typically 5-20 mV) which does not disturb properties of the system under study. Sequential measurements can therefore be performed enabling long-term in-situ monitoring of corrosion behaviour of Zr alloys.

In this study, EIS measurements and quasi-potentiostatic polarisation measurements were performed during long-term exposure of different Zr-Sn and Zr-Nb alloys under simulated VVER chemistry (boric acid, potassium hydroxide, lithium hydride) at temperature up to 340 °C and pressure up to 15 MPa. Broad range frequency impedance spectra (usually 300 kHz – 0.1 mHz) were analyzed using equivalent circuits (EC) approximation. Instant corrosion rates were calculated using Stern-Geary approach. Some of the experiments were run for more than 700 days, thus the study of all the corrosion stages (pre-transition, transition, post-transition) was possible.

Good agreement between electrochemical corrosion parameters and those obtained from independent methods (weight gain, electron spectroscopy) was found. Charge transfer properties differences between Zr-Sn and Zr-Nb alloys during transition period are discussed.

Conclusions:
• Long-term continuous in-situ EIS measurements were performed with Zr-Sn and Zr-Nb alloys in simulated VVER coolant at 340 °C. Impedence spectra sensitively reflect the changes in oxide protective properties during oxide transition phase
• Polarization of the IR drop compensated: diffusion control of the anodic reaction, kinetic control of the cathodic reaction (Tafel behaviour)
• Corrosion of Zr alloys in primary VVER coolant follows Stern-Geary equation ⇒ polarization resistance \( R_p \) estimated by EIS expresses the instant corrosion rate
• Difference between the oxide thickness from Stern-Geary/Faraday and the dielectric oxide thickness (\( C_{dl} \)) was usually > 25%. Integral corrosion rate estimated by both methods agreed reasonably with the oxide thickness calculated from the weight gain data
• Transition phase of Zr-Sn and Zr-Nb oxide layer in 340 °C VVER coolant starts after 190 and 430 days respectively
• During the transition phase, more profound changes of oxide transfer properties occurred in Zr-Sn oxide than in Zr-Nb oxide – ratio \( Z_i / Z_{m} \) at LF(64 kHz) was 3:4 for Zr-Sn and 5 at Zr-Nb
• Maximum corrosion rate at Zr-Sn and Zr-Nb was achieved after 70 and 30 days from the transition beginning respectively
• Cyclic nature of corrosion was confirmed for Zr-Sn, but not for Zr-Nb (after 700 d of exposure)

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