

Abstract

Zirconium alloys (Zr-alloys) are used in many engineering applications (such as nuclear reactors, bioimplants, chemical processing industries, etc.) due to their low absorption cross-section to thermal neutrons, good mechanical properties and good corrosion resistance. Based on these qualities, zirconium alloys are widely used as nuclear core structural material. During the operation of the nuclear reactor, some of the core components are subjected to fluid flow-induced vibrations, which may result in surface degradation, viz., material wear, delamination, spalling etc., depending on the contact conditions prevailing at the contact interface. Mechanical loading parameters such as frequency, normal load, displacement amplitude and number of cycles/test durations control the degradation mechanism under a given set of environmental conditions. The prevailing environment at the contact interface, temperature, water chemistry, etc., significantly contributes to the degradation process. Some components are exposed to the coolant water having LiOH, resulting the corrosion and fretting corrosion of the components. The work presented in the thesis quantifies the effect of mechanical loadings and the environment on the degradation mechanisms prevailing at the contact interface. The study also determines the effect of alkalinity of water and exposure duration on the corrosion behavior of Zr-alloys. Materials considered in the study are Zr alloys (Zr-4, Zr-2.5 Nb) and Stainless Steel (SS-410). Comprehensive investigations have been carried out to identify the wear mechanisms involved in the degradation process.

Reciprocating wear experiments were performed by varying the reciprocating test duration/number of cycles, frequency, and displacement amplitude. Experiments were performed using cross-cylinder configuration under dry and water-submerged condition. Friction and wear response were recorded in terms of coefficient of friction (COF) and normalized wear depth, respectively. Worn surfaces were analyzed using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive Spectroscopy (EDS), Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS) to quantify the prevailing wear mechanisms and the associated phenomenon.

In the case of self-mated zircaloy-4 (Zr-4 alloy) fretting wear, COF increases with increasing fretting duration but decreases with increasing frequency and amplitude

under dry condition. COF remains nearly constant w.r.t. the fretting duration, frequency and amplitude under submerged condition. COF and normalized wear depth are lower under water-submerged condition than that under dry condition. Normalized wear increases significantly with increasing amplitude under both submerged and non-submerged conditions. With increasing amplitude, the wear mechanism changes from adhesion (under fretting) to mixed adhesion-abrasion. The studies show that the tribo-oxide layer formed on the wear surface controls the wear mechanism prevailing at the contact interface.

Reciprocating wear tests at low displacement amplitudes were conducted between Zr-2.5Nb alloy and SS-410 at Room Temperature (RT) and High Temperature (HT). COF is higher at HT ($\approx 260^\circ\text{C}$) than at RT. COF decreases with increasing reciprocating frequency and displacement amplitude but remains nearly constant with increasing duration. The sp. wear rate is higher at RT than that at HT. Sp. wear rate decreases with increasing the reciprocating duration and frequency but increases with increasing the displacement amplitude. The wear mechanism changes from adhesion to mixed adhesion-abrasion with increasing amplitude. Here, also tribo-oxide layer (mechanically mixed layer) is also formed at the worn surfaces.

To observe the effect of hydride formation on the tribological response of Zr-2.5Nb alloy, fretting wear experiments were conducted between hydrogen-charged Zr-2.5Nb (Hydrided Zr-2.5Nb) and SS-410 and compared the friction and wear response with that of uncharged Zr-2.5Nb (Unhydrided Zr-2.5Nb) alloy. The COF is observed lower for hydrided Zr-2.5Nb (Zr-2.5Nb-H) alloy than that for unhydrided (as-received) Zr-2.5Nb (Zr-2.5Nb) alloy. To observe the tribological response of the hydride (Zr-H) phase, tribo-experiments were also conducted using Atomic Force Microscopy (AFM) with Diamond-Like Carbon (DLC) tip. The friction force during AFM tribology is higher on the Zr-H phase than on the Zr-matrix and Zr-2.5Nb alloy.

To study the corrosion response of Zr-alloys, electrochemical corrosion experiments were conducted on Zr-4, Zr-2.5Nb and Zr-2.5Nb-H alloy in the aqueous solution of LiOH. Electrochemical Impedance Spectroscopy (EIS) and potentiodynamic polarization studies were performed for varied concentrations (conc.) of LiOH and exposure durations. Measurements were recorded in terms of impedance, corrosion potential, and corrosion current. The studies showed that the corrosion resistance increases with the increasing exposure duration and decreases with the increasing

concentration of LiOH in the water. An oxide layer is observed to form on the surface of the Zr-alloys during the corrosion process, which protects the substrate from further corrosion. The corrosion resistance of Zr-2.5Nb-H alloy is observed to be lower than that of Zr-2.5Nb alloy. Zr-4 alloy shows slightly more corrosion resistance than Zr-2.5Nb alloy for the same environment.