EVOLUTION OF SURFACE FAILURE MECHANISMS IN Zr-ALLOYS UNDER CONTROLLED CONDITIONS

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Evolution of surface failure mechanisms in Zr-alloys under controlled conditions

by

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Dedicated to my parents,
Mr. Bhikam Singh and Mrs. Rakesh Devi

Certificate

This is to certify that the thesis entitled **"Evolution of surface failure mechanisms in Zr-alloys under controlled conditions"**, submitted by **Mr. Bharat Kumar** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of the original, bonafide research work carried out by him under our supervision and guidance. The thesis has reached the standards fulfilling the requirements of the regulations related to the award of the degree.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma to the best of our knowledge.

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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 in 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 the 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 a cross-cylinder configuration under dry and water-submerged conditions. 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 conditions. 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 conditions than that under dry conditions. 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 (260 °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-experimets 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.

सारांश

ज़िर्कोनियम मिश्रधातुओं (Zr-alloys) का उपयोग कई अभियांत्रिकी क्षेत्रों में जाता है (जैसे परमाणु भट्टी, जैव-प्रत्यारोपण, रासायनिक प्रसंस्करण उद्योग आदि), इनकी थर्मल न्यूट्रॉन्स का कम अवशोषण क्रॉस-सेक्शन, अच्छे यांत्रिकी गुणधर्म और अच्छी जंग सहिष्णुता के कारण। इन गुणधर्मों के आधार पर, ज़िर्कोनियम मिश्रधातु न्यूक्लियर कोर संरचनात्मक सामग्री के रूप में व्यापक रूप से प्रयोग की जाती हैं। परमाणु भट्टी के परिचालन के दौरान, संपर्क स्थिति में कुछ मुख्य अंगों को तरल प्रवाह इंदुकित कंपन का सामना करना पड़ता है, जो सतह के विघटन, जैसे सामग्री घिसाव, अलगाव, टूटना आदि, पर निर्भर करता है। यांत्रिकी भार और पर्यावरण घातक प्रक्रियाओं में महत्वपूर्ण भूमिका निभाते हैं। यांत्रिकी भार जैसे आवृत्ति, भार, स्थानांतरण आयाम और चक्रों की संख्या/परीक्षण अवधि दिए गए पर्यावरणीय ढंगों के अधीन विघटन प्रक्रिया को नियंत्रित करते हैं। संपर्क स्थिति पर वर्तमान पर्यावरण, तापमान, जल रसायन, आदि, विघटन प्रक्रिया में महत्वपूर्ण योगदान करते हैं। कुछ अंग लिथियम हाइड्रॉक्साइड युक्त शीतलक पानी के संपर्क में रहते हैं।, जिससे घटकों में जंग और फ्रेटिंग जंग होता है। थीसिस में प्रस्तुत काम विघटन प्रक्रिया पर यांत्रिकी भार और पर्यावरण के प्रभाव को मापता है, जो संपर्क स्थिति पर प्रायिक रूप से प्राधान्य रखता है। अध्ययन यह भी निर्धारित करता है कि पानी की क्षारीयता और संपर्क अवधि का ज़िर्कोनियम मिश्रधातुओं के जंग व्यवहार पर क्या प्रभाव पड़ता है। अध्ययन में ध्यान दिए जाने वाले पदार्थ ज़िर्कोनियम मिश्रधातु (Zr-4, Zr–2.5Nb) और स्टेनलेस स्टील (एसएस-410) हैं। विघटन क्रिया में शामिल घिसाव प्रक्रियाओं की पहचान के लिए व्यापक अन्वेषण किए गए हैं।

प्रत्यागामी घिसाव परिक्षणों को परीक्षण अवधि / चक्रों की संख्या, आवृत्ति और स्थानांतरण आयाम को बदलकर किया गया। परिक्षण सूखी और जल-तटस्थ स्थिति के तहत लंबवत्- बेलन विन्यास का उपयोग करके किया गया। घर्षण और घिसाई प्रतिक्रिया को घर्षण संख्यावाची और मानकीकृत घिसाई गहराई के रूप में दर्ज किया गया। घिसी हुई सतहें क्षेत्रीय-उत्सजर्न क्रमवीक्षण इलेक्ट्रॉन माइक्रोस्कोपी (एफइएसइएम), ऊर्जा प्रसार स्पेक्ट्रोस्कोपी (इडीएस), रमन स्पेक्ट्रोस्कोपी और एक्स-रे फोटोइलेक्ट्रॉन स्पेक्ट्रोस्कोपी (एक्सपीएस) का उपयोग करके वर्तमान घिसाई अधीन विघटन प्रक्रियाओं और संबंधित घटना को मापने के लिए विश्लेषित किया गया।

आत्म संगमित ज़िरकलॉय-4 (Zr-4 मिश्रधातु) फ्रेटिंग घिसाई (सूखी स्थिति) में, घर्षण संख्यावाची बढ़ती फ्रेटिंग अवधि के साथ बढ़ता है, लेकिन फ्रेक्टिंग आवृत्ति और आयाम के साथ घटता है। जल-तटस्थ स्थिति के तहत फ्रेटिंग अवधि, आवृत्ति और आयाम के साथ घर्षण संख्यावाची लगभग स्थिर रहता है। जल-तटस्थ स्थिति में घर्षण संख्यावाची और प्रतिकृत घिसाई गहराई सूखी स्थिति की तुलना में कम है। जलतटस्थ और सूखी दोनों स्थितियों में आयाम बढ़ाने के साथ प्रतिकृत घिसाई बढ़ती है। आयाम बढ़ने के साथ, घिसाई प्रक्रिया आग्रहण (फ्रेटिंग के अन्तर्गत) से मिश्रित आग्रहण-खरोंच में परिवर्तित होती है। अध्ययन दिखाते हैं कि घिसाई सतह पर ट्राइबो-ऑक्साइड परत संपर्क स्थिति पर वर्तमान घिसाई प्रक्रिया को नियंत्रित करता है।

$Zr–2.5Nb$ मिश्रधातु और एसएस-410 के बीच कमरे के तापमान (आरटी) और उच्च तापमान (एचटी) पर न्यून आयाम के प्रत्यागामी घिसाई परीक्षण किए गए। उच्च तापमान ($260\ ^{\circ}C$) पर घर्षण संख्यावाची अधिक है कमरे के तापमान की तुलना में । घर्षण संख्यावाची बढ़ते हुए प्रत्यागामी आवृत्ति और स्थानांतरण आयाम के साथ कम होता है, लेकिन बढ़ती हुई अवधि के साथ लगभग स्थिर रहता है। अंतर्निहित घिसाई दर प्रत्यागामी अवधि और आवृत्ति के साथ घटती है, लेकिन स्थानांतरण आयाम के साथ बढ़ती है। घिसाई प्रक्रिया आयाम बढ़ने के साथ आग्रहण से मिश्रित आग्रहण-खरोंच में परिवर्तित होती है। यहाँ, घिसी हुई सतहों पर ट्राइबो-ऑक्साइड परत (यंत्रवत् मिश्रित परत) बन जाती है।

$Zr–2.5Nb$ मिश्रधातु की ट्राइबोलॉजिकल प्रतिक्रिया पर हाइड्राइड बनने के प्रभाव को देखने के लिए, हाइड्रोजन आवेशित (हाइड्राइडेड) $Zr–2.5Nb$ और एसएस-410 के बीच फ्रेटिंग परिक्षण किए गए और अनावेशित (अनहाइड्राइडेड) $Zr–2.5Nb$ मिश्रधातु के साथ तुलना की गई। अनहाइड्राइडेड $Zr–2.5Nb$ मिश्रधातु की तुलना में हाइड्राइडेड $Zr–2.5Nb$ मिश्रधातु पर घर्षण संख्यावाची कम पाया जाता है। हाइड्राइड ($Zr\text{-}H$) अवस्था की ट्राइबोलॉजिकल प्रतिक्रिया को देखने के लिए, एटॉमिक फोर्स माइक्रोस्कोपी (एएफएम) का उपयोग करके ट्रायबो-परिक्षण भी किए गए, जिसमें डायमंड-लाइक कार्बन (डीएलसी) टिप का उपयोग किया गया। एएफएम ट्राइबोलॉजी के दौरान घर्षण बल $Zr\text{-}H$ अवस्था पर Zr-आव्यूह और $Zr–2.5Nb$ मिश्रधातु की तुलना में अधिक है।

ज़िर्कोनियम मिश्रधातुओं की जंग प्रतिक्रिया का अध्ययन करने के लिए, लिथियम हाइड्रॉक्साइड के जलीय घोल में $Zr\text{-}4$, $Zr–2.5Nb$ और $Zr–2.5Nb\text{-}H$ मिश्रधातु पर विद्युतरसायनिक जंग परिक्षण किए गए। विभिन्न सान्द्रता और संपर्क अवधि के लिए इलेक्ट्रोकेमिकल इम्पेडेंस स्पेक्ट्रोस्कोपी (ईआईएस) और पोटेंशिओडाइनामिक पोलराइज़ेशन अध्ययन किए गए। मापन विधियों को प्रतिरोध, जंग क्षमता, और जंग प्रवाह के रूप में नोट किया गया। अध्ययन दिखाते हैं कि जंग प्रतिरोध विकास बढ़ती संपर्क अवधि के साथ बढ़ता है और पानी में लिथियम हाइड्रॉक्साइड की बढ़ती सान्द्रता के साथ घटता है। जंग प्रक्रिया के दौरान ज़िर्कोनियम मिश्रधातुओं की सतह पर एक ऑक्साइड परत देखी जाती है, जो उपभूमि को आगे के जंग से बचाता है। $Zr–2.5Nb\text{-}H$ मिश्रधातु का जंग प्रतिरोध $Zr–2.5Nb$ मिश्रधातु से कम पाया जाता है। $Zr\text{-}4$ मिश्रधातु उसी वातावरण के लिए $Zr–2.5Nb$ मिश्रधातु से थोड़ा अधिक जंग प्रतिरोध दिखाता है।

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Abbreviations

PHWRs	**P**ressurized **H**eavy **W**ater **R**eactors
LPIS	**L**iquid **P**oison **I**njection **S**ystem
Zr-alloys or Zircaloys	**Z**irconium **a**lloys
Zr-4 alloy	**Z**ircaloy-4
Zr-2.5Nb alloy	**U**nhydrided or as-received Zr-2.5Nb alloy
Zr-2.5Nb-H alloy	**H**ydrided Zr-2.5Nb alloy
Zr-matrix	**Z**irconium **m**atrix
Zr-H phase	**Z**irconium **H**ydride **p**hase
Wt.	**W**eight
BCC	**B**ody **C**entered **C**ubic
HCP	**H**exagonal **C**losed **P**acked
Avg.	**A**verage
COF	**C**oefficient **o**f **F**riction
w.r.t.	**W**ith respect to
Sp. wear rate	**S**pecific **w**ear **r**ate
Tribo-experiments	**T**ribological **e**xperiments
Tribo-corrosion	**C**orrosion during wear
Fretting-corrosion	**C**orrosion during fretting wear
RT	**R**oom **T**emperature
HT	**H**igh **T**emperature
PPM	**P**arts **P**er **million**
OFAT	**O**ne **F**actor at **A** **T**ime
AFM	**A**tomic **F**orce **M**icroscopy
DLC tip	**D**iamond **L**ike **C**arbon tip
SEM	**S**canning **E**lectron **M**icroscopy
FESEM	**F**ield **E**mission **S**canning **E**lectron **M**icroscopy
EDS	**E**nergy **D**isperssive **S**pectroscopy

XPS	**X**-ray **P**hoton **S**pectroscopy
VMC	**V**ertical **M**illing **C**enter
EIS	**E**lectrochemical **I**mpedance **S**pectroscopy
OCP	**O**pen **C**ircuit **P**otential
LiOH	**L**ithium **H**ydroxide
KOH	**P**otassium **H**ydroxide
$\mathbf{H_3BO_3}$	**B**oric **A**cid
pH	**P**otential of **H**ydrogen
Conc.	**C**oncentration
$\mathbf{R}_S$	**S**olution **R**esistance
$\mathbf{R}_{CT}$	**C**harge **T**ransfer **R**esistance
$\mathbf{R}_{out}$	**O**uter oxide layer **R**esistance
$\mathbf{R}_{in}$	**I**nner oxide layer **R**esistance
$\mathbf{C}_{CT}$	**C**harge **T**ransfer **C**apacitance
$\mathbf{C}_{out}$	**O**uter oxide layer **C**apacitance
$\mathbf{C}_{in}$	**I**nner oxide layer **C**apacitance
$\mathbf{CPE}_{out}$	**C**onstant **P**hase **E**lement for outer oxide layer
$\mathbf{CPE}_{in}$	**C**onstant **P**hase **E**lement for outer oxide layer

Symbols

f	Frequency
ω	Angular frequency
°C	Degree celcius
Ω	Ohm
μ	micro
n	nano
%	Percent
h	Hour
M	Molar and Megha