

# TABLE OF CONTENTS

Index	Page No.
List of Figures.....	ix
List of Tables.....	xv
Abbreviations & Symbols.....	xvii
Preface.....	xxi
<b>Chapter-1 Introduction</b>	<b>(1-22)</b>
<b>1.1 Background and Motivation.....</b>	<b>(1)</b>
1.1.1 Introduction to Biomaterials.....	(3)
1.1.2 Biomaterial Market.....	(4)
1.1.3 Evaluation of Biomaterials.....	(6)
1.1.4 Classifications (Overall).....	(7)
1.1.5 The fundamental requirement of implant materials.....	(9)
<b>1.2 Stainless Steel for Orthopedic Applications.....</b>	<b>(11)</b>
1.2.1 Clinical Studies of 316L stainless steel.....	(11)
1.2.2 A Drawback of 316L Stainless steel.....	(14)
<b>1.3 Surface Modification Techniques.....</b>	<b>(16)</b>
1.3.1 General Overview.....	(16)
1.3.2 Importance of Metallic Coatings.....	(18)
<b>1.4 Role of Tantalum in Orthopedic Implants.....</b>	<b>(20)</b>
<b>Chapter-2 Literature Review</b>	<b>(23-60)</b>
<b>2.1 Background .....</b>	<b>(23)</b>
2.1.1 Criteria for ideal bone implant.....	(25)
2.1.2 Current implant materials .....	(27)
2.1.3 Implant Failure.....	(30)

2.1.4 Biological interactions on metallic biomaterial surfaces .....	(32)
<b>2.2. Corrosion Assessment of Orthopedic Implants.....</b>	<b>(35)</b>
<b>2.3. Mechanical Behavior of Orthopedic Implants.....</b>	<b>(45)</b>
<b>2.4. Biological Evaluation of different types of coated 316L for the orthopedic application.....</b>	<b>(49)</b>
<b>2.5. Need for the metallic coatings and significance of Tantalum (Ta).....</b>	<b>(53)</b>
<b>2.6. Research Gap.....</b>	<b>(55)</b>
<b>2.7. Research Motivation and Objective of the present thesis.....</b>	<b>(57)</b>
<b>Chapter-3 Experimental Details</b>	<b>(61- 80)</b>
<b>3.0 Introduction.....</b>	<b>(61)</b>
<b>3.1 Material Selection and Sample Preparation.....</b>	<b>(61)</b>
<b>3.2 Tantalum Coating by DC Magnetron Sputtering.....</b>	<b>(64)</b>
<b>3.3 Preparation of Simulated Body Fluid.....</b>	<b>(68)</b>
<b>3.4 Evaluation of Ta-coated 316L Stainless Steel.....</b>	<b>(70)</b>
3.4.1 Wear study.....	(70)
3.4.2 Electrochemical Corrosion Study.....	(71)
3.4.3 Biocompatibility study.....	(73)
<b>3.5 Characterization Techniques.....</b>	<b>(76)</b>
<b>3.6 Work Plan.....</b>	<b>(77)</b>
<b>Chapter-4 Wear Behavior of Ta-Coated 316L Stainless Steel</b>	<b>(81- 114)</b>
<b>4.0 Introduction.....</b>	<b>(81)</b>
<b>4.1 Experimental Details.....</b>	<b>(84)</b>
4.1.1 Material and Sample Preparation.....	(84)

4.1.2 Deposition of Tantalum.....	(85)
4.1.3 Microhardness Characterization.....	(86)
4.1.4 Microhardness studies.....	(86)
4.1.5 Wear Studies.....	(87)
<b>4.2 Results and Discussion.....</b>	<b>(88)</b>
4.2.1 Microstructural Characterization.....	(88)
(A) Optical Microscopy (OM).....	(88)
(B) Scanning Electron Microscopy (SEM).....	(89)
(C) Energy Dispersive Spectroscopy (EDS).....	(94)
(F) Atomic Force Microscopy (AFM).....	(96)
<b>4.3 Microhardness Studies.....</b>	<b>(100)</b>
<b>4.4 Wear Studies.....</b>	<b>(105)</b>
<b>4.5 Conclusions.....</b>	<b>(114)</b>
<b>Chapter-5 Electrochemical Corrosion Behavior of Ta-Coated 316L Stainless Steel</b>	<b>(115- 140)</b>
<b>5.0 Introduction.....</b>	<b>(115)</b>
<b>5.1 Experimental Details.....</b>	<b>(118)</b>
5.1.1 Material and Sample Preparation.....	(118)
5.1.2 Deposition of Tantalum.....	(118)
5.1.3 Microstructural Analysis.....	(120)
5.1.4 Electrochemical Corrosion Analysis.....	(121)
<b>5.2 Results and Discussion.....</b>	<b>(122)</b>
5.2.1 Characterization of Bare 316L SS.....	(122)
5.2.2 Characterization of Ta-coated 316L SS.....	(123)
5.2.3 X-ray Photoelectron Spectroscopy (XPS).....	(128)
<b>5.3 Electrochemical Corrosion Analysis .....</b>	<b>(131)</b>
5.3.1 Open Circuit Potential Study.....	(131)
5.3.2 Electrochemical Impedance Spectroscopy Study.....	(132)
5.3.3 Potentiodynamic Study.....	(136)

<b>5.4 Conclusions.....</b>	<b>(139)</b>
<b>Chapter-6 Biocompatibility Behavior of Ta-Coated 316L Stainless Steel</b>	<b>(141- 182)</b>
<b>6.0 Introduction.....</b>	<b>(141)</b>
<b>6.1 Experimental Details.....</b>	<b>(144)</b>
6.1.1 Material and Sample Preparation.....	(144)
6.1.2 Tantalum Deposition.....	(145)
6.1.3 Microstructural Characterization.....	(147)
6.1.4 Contact Angle Measurement.....	(147)
6.1.5 Scratch Test .....	(148)
6.1.6 Biocompatibility Test.....	(148)
<b>6.2 Results and Discussion.....</b>	<b>(149)</b>
6.2.1 Microstructural Characterization.....	(149)
6.2.1.1 Optical Emission Microscopy (OES).....	(149)
6.2.1.2 Optical Microscopy (OM).....	(150)
6.2.1.3 Scanning Electron Microscopy (SEM).....	(151)
6.2.1.4 Energy Dispersive X-ray Spectroscopy (EDS).....	(158)
6.2.1.5 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) .....	(163)
<b>6.3 Contact Angle Measurement.....</b>	<b>(165)</b>
<b>6.4 Scratch Test.....</b>	<b>(169)</b>
<b>6.5 Biocompatibility.....</b>	<b>(174)</b>
<b>6.6 Conclusion.....</b>	<b>(182)</b>
<b>Chapter-7 Summary and Major Conclusions</b>	<b>(183- 185)</b>
7.1 Summary.....	(183)
7.2 Major Conclusions.....	(184)

Suggestions for the Future Work.....	(186)
References.....	(187)
Publications and International Conferences.....	(221)

## LIST OF FIGURES

Fig. 1.1	Metallic Alloy Used
Fig. 1.2	Evaluations of Biomaterials
Fig. 1.3	Classifications of Biomaterials
Fig. 1.4	316L SS clinical application in implants
Fig. 2.1	Ideal Bone Implant Criteria
Fig. 2.2	Biological interactions on metallic biomaterial surfaces
Fig. 3.1	Photographic image of table moving wire Electrical Discharge Machining Machine (WEDM)
Fig. 3.2	Photographic images DC Magnetron Sputtering System
Fig. 3.3	Photographic image of Bio-tribometer for wear studies
Fig. 3.4	Photographic Images of Electrochemical Corrosion Test Setup
Fig. 3.5	Photographic image of Scratch tester
Fig. 3.6	Photographic images of the Profilometer
Fig. 3.7	Workplan of the thesis (Schematic)
Fig. 4.1	Pin-on-disc tribometer <b>a)</b> Scheme of pin-on-disc assembly, <b>b)</b> device image
Fig. 4.2	Optical Microscopy images of 316L SS; <b>a)</b> Bare <b>b)</b> Ta-coated
Fig. 4.3	SEM images of cross-section cut coating before the wear test <b>(a)</b> Ta-coated

	316L SS for 15min. <b>(b)</b> Ta-coated 316L SS for 30min. <b>(c)</b> Ta-coated 316L SS for 60min.
Fig. 4.4	SEM images of zirconia pin after wear test; <b>a)</b> pin diameter <b>b)</b> bare 316L SS treated pin <b>c)</b> Ta coated for 15min 316L SS treated pin <b>d)</b> Ta coated for 30min 316L SS treated pin
Fig. 4.5	SEM images after wear test of bare and tantalum coated samples; <b>(a-c)</b> Bare 316L SS at 10N, 20N, and 40N <b>(d-f)</b> Ta coated 316L SS for 15min. at 10N, 20N, and 40N <b>(g-i)</b> Ta coated 316L SS for 30min. at 10N, 20N, and 40N <b>j-l)</b> Ta coated 316L SS for 60min. at 10N, 20N, and 40N.
Fig. 4.6	EDS images of bare and Ta coated 316L SS; <b>a)</b> bare 316L SS <b>b)</b> Ta coated for 15min 316L SS <b>c)</b> Ta coated for 30min 316L SS <b>d)</b> Ta coated for 60min 316L SS.
Fig. 4.7	Two-dimensional AFM images of the 316L SS; <b>a)</b> Bare <b>b)</b> Ta-coated (15min) <b>c)</b> Ta-coated (30min) <b>d)</b> Ta-coated (60min)
Fig. 4.8	Three-dimensional AFM images of the 316L SS; <b>a)</b> Bare <b>b)</b> Ta-coated (15min) <b>c)</b> Ta-coated (30min) <b>d)</b> Ta-coated (60min)
Fig. 4.9	Load and Displacement curves for 316L SS <b>(a)</b> Bare <b>(b)</b> Ta-coated
Fig. 4.10	Vickers hardness of bare and Ta-coated 316L SS
Fig. 4.11	Modulus of Elasticity, Hardness, and No. Of indentation curves for 316L SS <b>(a)</b> Bare <b>(b)</b> Ta-coated
Fig. 4.12	Micro indentation images of 316L SS; <b>a)</b> Bare 316L SS <b>b)</b> Ta coated
Fig. 4.13	Experimental wear test images of worn surfaces of bare and Ta-coated 316L SS
Fig. 4.14	Coefficient of friction against time results of 316L SS; <b>(a)</b> Bare, <b>(b)</b> Ta-coated for 15min., <b>(c)</b> Ta-coated for 30min, and <b>(d)</b> Ta-coated for 60min.

Fig. 4.15	Wear with load against no. of cycles results of 316L SS; <b>(a-c)</b> Bare 10N, 20N, and 40N, <b>(d-f)</b> Ta-coated for 15min. 10N, 20N, and 40N, <b>(g-i)</b> Ta-coated for 30min. 10N, 20N, and 40N, <b>(j-l)</b> Ta-coated for 60min. 10N, 20N, and 40N.
Fig. 4.16	Wear rate against applied load for bare and Ta-coated 316L SS
Fig. 5.1	Systematic direct current magnetron sputtering (DCMS) process
Fig. 5.2	EDX images of bare samples <b>(a)</b> EDX image of bare 316L SS at spectrum-1 <b>(b)</b> EDX image of bare 316L SS at spectrum-4
Fig. 5.3	SEM image of bare 316L SS
Fig. 5.4	EDX images of Ta-coated 316L SS samples <b>(a)</b> 15 min. <b>(b)</b> 30 min. <b>(c)</b> 60 min.
Fig. 5.5	SEM images before corrosion of Ta-coated 316L SS <b>(a)</b> 15 min. Ta-coating <b>(b)</b> 30 min. Ta-coating <b>(c)</b> 60 min. Ta-coating
Fig. 5.6	SEM images after corrosion of Ta-coated 316L SS <b>(a)</b> 15 min. <b>(b)</b> 30 min. <b>(c)</b> 60 min.
Fig. 5.7	XPS spectra of 316L Stainless steel <b>(a)</b> Bare <b>(b)</b> 15min. Ta-coated <b>(c)</b> 30min. Ta-coated <b>(d)</b> 60min. Ta-coated
Fig. 5.8	XPS spectra (elemental and atomic %) of 316L Stainless steel <b>(a)</b> Bare <b>(b)</b> 15min. Ta-coated <b>(c)</b> 30min. Ta-coated <b>(d)</b> 60min. Ta-coated
Fig. 5.9	Equivalent electric circuit (EEC) for <b>a)</b> 316L SS (bare) and <b>b)</b> Ta-coated-316L SS
Fig. 5.10	Nyquist plot for bare and Ta-coated 316L SS in SBF at 7.4 pH
Fig. 5.11	Bode plot for bare and Ta-coated 316L SS in SBF at 7.4 pH
Fig. 5.12	Potentiodynamic polarization curve for bare and Ta-coated 316L SS
Fig. 6.1	OES results for 316L SS

Fig. 6.2	Optical Microscopy images of 316L SS (a) Bare (b) Ta-coated
Fig. 6.3	SEM images of cross-section cut coating before the biocompatibility test of Ta-coated 316L SS (a) Ta-coated (15min.) (b) Ta-coated (30min.) (c) Ta-coated (60min.)
Fig. 6.4	SEM images of MG-63 Osteoblast culture for <b>1-day</b> incubation on bare and coated 316L SS (a) Bare (b) Ta-coated 15min., (c) Ta-coated 30min., (d) Ta-coated 60min.
Fig. 6.4 (Continued)	SEM images of MG-63 Osteoblast culture for <b>07-days</b> incubation on bare and coated 316L SS (a) Bare (b) Ta-coated 15min., (c) Ta-coated 30min., (d) Ta-coated 60min.
Fig. 6.4 (Continued)	SEM images of MG-63 Osteoblast culture for <b>14-days</b> incubation on bare and coated 316L SS (a) Bare (b) Ta-coated 15min., (c) Ta-coated 30min., (d) Ta-coated 60min.
Fig. 6.5	EDS images for <b>1-day</b> of bare and Ta-coated 316L SS (a) Bare (cell adhesion) (b) Bare (cell Proliferation) (c) Ta-coated (cell adhesion) (d) Ta-coated (cell Proliferation)
Fig. 6.5 (Continued)	EDS images for <b>7-days</b> of bare and Ta-coated 316L SS (a) Bare (cell adhesion) (b) Bare (cell Proliferation) (c) Ta-coated (cell adhesion) (d) Ta-coated (cell Proliferation)
Fig. 6.5 (Continued)	EDS images for <b>14-days</b> of bare and Ta-coated 316L SS (a) Bare (cell adhesion) (b) Bare (cell Proliferation) (c) Ta-coated (cell adhesion) (d) Ta-coated (cell Proliferation)
Fig. 6.6	Element, concentration, and count per second (CPS) images of bare and Ta-coated

	316L SS <b>(a)</b> Bare, <b>(b)</b> Ta-coated (15min.), <b>(c)</b> Ta-coated (30min.), and <b>(d)</b> Ta-coated (60min.)
Fig. 6.7	Contact Angle Measurement of 316L SS <b>(a)</b> Bare <b>(b)</b> Ta-coated (15 min) <b>(c)</b> Ta-coated (30 min) <b>(d)</b> Ta-coated (60 min)
Fig. 6.8	Scratch test surface topography of 316L SS <b>(a)</b> Bare <b>(b)</b> Ta-coated for 15min. <b>(c)</b> Ta-coated for 30min. <b>(d)</b> Ta-coated for 60min.
Fig. 6.9	BT-SEM images of scratch test over the bare and Ta-coated 316L SS <b>(a)</b> Bare <b>(b)</b> Ta-coated (15min) <b>(c)</b> Ta-coated (30min) <b>(d)</b> Ta-coated (60min)
Fig. 6.10	3D topography of scratch test images 316L SS <b>(a)</b> Bare <b>(b)</b> Ta-coated (15min) <b>(c)</b> Ta-coated (30min) <b>(d)</b> Ta-coated (60min)
Fig. 6.11	Thickness and adhesion strength diagram
Fig. 6.12	Photographic images of bare and Ta-coated 316L SS for biocompatibility test
Fig. 6.13	Fluorescent microscopy images of Osteoblast (MG-63) over 316L stainless steel <b>(a)</b> Bare surfaces <b>(b-d)</b> Ta-coated surfaces. <b>(1-Day)</b>
Fig. 6.13 (Continued)	Fluorescent microscopy images of Osteoblast (MG-63) over 316L stainless steel <b>(a)</b> Bare surfaces <b>(b-d)</b> Ta-coated surfaces. <b>(7-Day)</b>
Fig. 6.13 (Continued)	Fluorescent microscopy images of Osteoblast (MG-63) over 316L stainless steel <b>(a)</b> Bare surfaces <b>(b-d)</b> Ta-coated surfaces. <b>(14-days)</b>
Fig. 6.14	Cell viability and Time image of bare and Ta-coated 316L SS <b>(a)</b> SEM-based analysis <b>(b)</b> Software (Image J) based analysis



## LIST OF TABLES

- Table 1.1 Clinical applications of the 316L SS
- Table 1.2 Different Surface Modification Techniques
- Table 2.1 An overview of biomaterials used in biomedical applications
- Table 2.2 The benefits and drawbacks of biomedical materials
- Table 2.3 Mechanical properties of the bone and bone implant materials
- Table 2.4 An overview of a few kinds of literature on the electrochemical corrosion behavior of  
**(a) uncoated** 316L stainless steel
- Table 2.4 An overview of the few kinds of literature on the electrochemical corrosion behavior  
**(b) of different types of coated stainless steel (Grade-316L) published in the recent decade  
(2023-2013)**
- Table 2.5 Mechanical Properties of 316L Stainless Steel as per ASTM A240
- Table 2.6 Summary of the Wear behavior of different types of coating over 316L Stainless steel  
(2023-2012)
- Table 2.7 Overview of tantalum (Ta) properties per **ASTM B 365** and **708**.
- Table 3.1 WEDM operational parameters for 316L SS
- Table 3.2 The chemical composition of the 316L stainless steel
- Table 3.3 The operational parameters of the DC Magnetron Sputtering system
- Table 3.4 Chemical Composition for SBF Preparation
- Table 3.5 Wear test parameters
- Table 4.1 The chemical composition of the as-received 316L SS
- Table 4.2 Test parameters for wear studies

- Table 4.3** Roughness results of bare and Ta-coated 316L SS
- Table 4.4** Test parameters and results at the rate of 10Hz microhardness for bare and Ta-coated 316L SS.
- Table 4.5** Wear rate results for bare and Ta-coated samples at different parameters.
- Table 5.1** Orthopaedic characteristics of stainless-steel metallic implant
- Table 5.2** The chemical composition of 316L stainless steel in wt.%
- Table 5.3** Composition of simulated body fluid at 7.4pH
- Table 5.4** Ta-coated thickness by DC magnetron sputtering on 316L with time interval.
- Table 5.5** Compounds and Binding Energy (BE) of bare and coated 316L stainless steel
- Table 5.6** Parameters of the equivalent electrical circuit model bare and coated samples in 7.4 pH
- Table 5.7** Polarization parameter for bare and Ta-coated 316L SS in 7.4pH at 37°C
- Table 6.1** The chemical composition of the as-received 316L SS
- Table 6.2** DC Magnetron sputtering operational parameters for the coating process.
- Table 6.3** Experimental results of ICPMS of Bare and Ta-coated 316L SS
- Table 6.4** Contact angle measurement values for 5 iterations of bare and Ta-coated 316L SS
- Table 6.5** Scratch test parameters for bare and Ta-coated 316L SS
- Table 6.6** Sample plan (Bare and Ta-coated) for biocompatibility test

# Abbreviations

<b>ASTM</b>	American Society for Testing and Materials
<b>316L SS</b>	Low Carbon Stainless Steel type 316
<b>DC</b>	Direct Current
<b>Ta</b>	Tantalum
<b>SBF</b>	Simulated Body Fluid
<b>CNC</b>	Computer Numerical Controller
<b>EDM</b>	Electrical Discharge Machining
<b>SCCM</b>	Standard cubic centimetres per minute
<b>MFC</b>	Mass Flow Controller
<b>DCMS</b>	Direct Current Magnetron Sputtering System
<b>DOE</b>	Design of Experiment
<b>OM</b>	Optical Microscopy
<b>OES</b>	Optical Emission Spectroscopy
<b>SEM</b>	Scanning Electron Microscopy
<b>EDS</b>	Energy Dispersive X-Ray Spectroscopy
<b>BT-SEM</b>	Bench Top Scanning Electron Microscopy
<b>AFM</b>	Atomic Force Microscopy
<b>XPS</b>	X-ray Photoelectron Spectroscopy
<b>SPM</b>	Scanning Probe Microscopy
<b>ICP-MS</b>	Inductive Coupled Plasma-Mass Spectroscopy
<b>CAM</b>	Contact Angle Measurement
<b>WEDM</b>	Wire Electrical Discharge Machining
<b>PVD</b>	Physical Vapor Deposition
<b>COF</b>	Coefficient of Friction
<b>min</b>	Minute
<b>THA</b>	Total Hip Arthroplasty

<b>OCP</b>	Open Circuit Potential
<b>EIS</b>	Electrochemical Impedance Spectroscopy
<b>PD</b>	Potentiodynamic Polarization
<b>SHE</b>	Standard Hydrogen Electrode
<b>CPE</b>	Constant Phase Element
<b>CPS</b>	Counts Per Second
<b>EEC</b>	Equivalent Electrical Circuit
<b>FBS</b>	Fetal Bovine Serum
<b>PBS</b>	Phosphate-buffered saline
<b>CA</b>	Cell Adhesion
<b>CP</b>	Cell Proliferation
<b>DAPI</b>	4',6-diamidino-2-phenylindole

# Symbols

<b><math>K_2HPO_4 \cdot 6H_2O</math></b>	Di-potassium hydrogen phosphate hexahydrate
<b><math>MgCl_2 \cdot 6H_2O</math></b>	Magnesium dichloride hexahydrate
<b><math>(CH_2OH)_3 \cdot CNH_2</math></b>	Tris (Hydroxymethyl) amino methane
<b>NaCl</b>	Sodium Chloride
<b>KCl</b>	Potassium chloride
<b>NaHCO<sub>3</sub></b>	Sodium bicarbonate
<b>Na<sub>2</sub>SO<sub>4</sub></b>	Sodium Sulfate
<b>CaCl<sub>2</sub></b>	Calcium chloride
<b>Ta<sub>2</sub>O<sub>5</sub></b>	Tantalum oxide
<b>R<sub>q</sub></b>	Root Mean Square roughness
<b><math>\bar{z}</math></b>	Arithmetic average height
<b>F<sub>n</sub></b>	Normal Force
<b>F<sub>t</sub></b>	Tangential Force
<b>mN</b>	Micro Newton
<b>μm</b>	Micrometer
<b>Ag/Ag. Cl</b>	Silver Chloride
<b>Pt</b>	Platinum
<b>W</b>	Warburg Impedance
<b>Hz</b>	Hertz
<b>β<sub>a</sub></b>	Anodic Tafel Constant
<b>β<sub>c</sub></b>	Cathodic Tafel Constant
<b>R<sub>p</sub></b>	Polarization Resistance
<b>E<sub>corr</sub></b>	Corrosion Potential
<b>i<sub>corr</sub></b>	Corrosion Current Density
<b>wt%</b>	Weight Percentage
<b>μL/s</b>	Microliter Per Second