Chapter-3

Experimental Details

3.0 Introduction

In this Chapter, the details of the current investigations are discussed, such as the Preparation of the sample (316L Stainless Steel), Wear, Electrochemical Corrosion, and biocompatibility behavior. Varies characterization techniques like Optical Microscopy (OM), Scanning Electron Microscopy (SEM), Electron Diffraction X-ray Spectroscopy (EDAX), Atomic Force Microscopy (AFM), Profilometry, Inductive Coupled Plasma-Mass Spectroscopy (ICP-MS), Contact Angle Measurement (CAM), X-ray Photoelectron Spectroscopy (XPS), and Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy (EIS), Potentiodynamic Polarization also briefly described.

3.1 Material Selection and Sample Preparation

Austenitic stainless-steel type 316L was procured from M/s Mishra Dhatu Nigam Limited (MIDHANI), Hyderabad, India, with dimensions of $472 \times 775 \times 20$. The received sample gets converted into the required dimension of $20 \times 20 \times 2$ mm with the help of a table moving wire Electrical Discharge Machining Machine (WEDM) (Expresscut Series-Ex4023C, India). A fine single-strand metal wire, typically brass, is wound through the workpiece when submerged in a dielectric fluid tank, generally deionized water. The most efficient use of the WEDM process requires properly selecting machining parameters. An electrical spark is formed in WEDM by exposing an electrode to the workpiece. The flow of electricity is evident in the appearance of a spark. The spark is precisely controlled and focused to only affect the material's surface. **Table 3.1** depicts the operating parameters of WEDM for 316L SS. The heat treatment underneath the surface is relatively unaffected by the EDM operation. The spark is always generated in deionized

water. The water cools the equipment and flushes the eroded metal particles away. WEDM, like any other machining tool, uses electricity to eliminate material via spark erosion. As a result, the material must be electrically conductive. The dielectric is a deionized water cover between the wire and the substrate. Because pure water is an insulator, tap water usually contains minerals conducive to wire EDM. Deionized water has been processed through a resin tank to remove most of its conductive elements to control its conductivity. A well-known non-conventional machining method is wire-cut electrical discharge machining; a computer numerically controlled (CNC) system is used for monitoring the wire. **Fig. 3.1** shows the photographic image of a table moving wire Electrical Discharge Machining Machine.

For the experimental analysis in WEDM, stainless steel 316L was chosen as the workpiece material, while brass wire with a diameter of 0.25 mm was used as the electrode. Factors such as pulse on time and peak current must be considered to evaluate the wire-cut electrical discharge machining performance criteria, such as material removal rate, surface roughness, and recast layer thickness. For parametric optimization, Taguchi and ANOVA were used. The wire feed and pulse on time may affect the surface roughness the most. More surface roughness is generated by the higher pulse value on time, with a lower wire feed value; an improved surface condition can be achieved.

Table 3.1 WEDM operational parameters for 316L SS

Parameters/ Sample	**Pulse On (µs)**	**Pulse Off (µs)**	**Group On**	**Group Off**	**Current (Amp.)**	**Voltage (V)**	**VF**	**Max. Speed (µm/s)**	**Time (min.)**
316L SS	35	10	1	0	2	High voltage	49	110	10

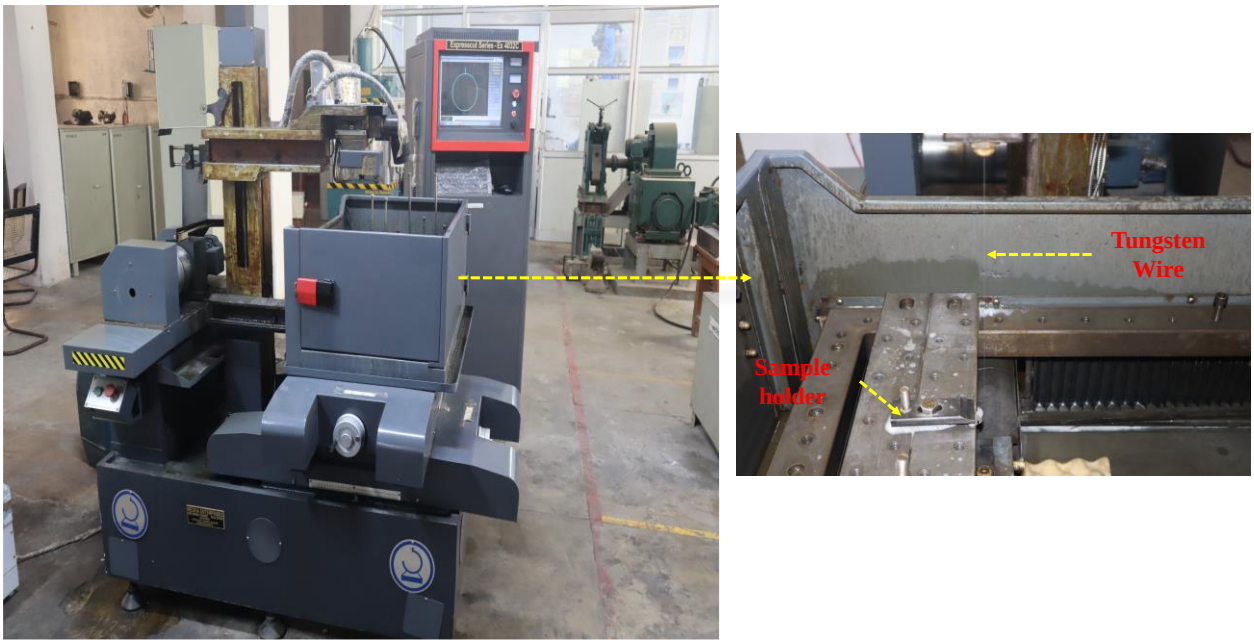

Fig. 3.1 Photographic image of table moving wire Electrical Discharge Machining Machine (WEDM)

The samples were then subjected to chemical analysis by the Foundry Master (Make Oxford Lab). **Table 3.2** shows the chemical composition of the 316L stainless steel alloy used after cutting WEDM as per the required dimensions ($\mathbf{20 \times 20 \times 2\ mm}$). ***T***he samples were ready for the different studies. Samples were mirror polished before deposition of Ta coating using emery paper up to 1600 grit, followed by washing with distilled water and hot air blow drying. The specimens were then ultrasonically cleaned with acetone for 30 minutes to achieve good adhesion with the coating. “The observed composition of 316L Stainless Steel was determined through Optical Emission Spectroscopy, in which carbon is 0.03 wt%. The analysis was conducted five times, and the average reported composition of carbon is 0.0329 wt%.". Optical microscopy was used to check the substrate constantly to ensure the microstructure of the sample surface.

Table 3.2 The chemical composition of the 316L stainless steel

Material	C	Mn	P	S	Si	Cr	Ni	Mo
316L SS	0.03	1.39	0.003	0.005	0.015	17.5	13.6	2.27

3.2 Tantalum Coating by DC Magnetron Sputtering

The high purity Tantalum target (99.95%) with a diameter of 50.80mm and a thickness of 3.175mm was procured from M/S Indo French High Tech Equipments, Mumbai-400053 India. The Ta-coated 316L stainless steel is a thin film of tantalum (Ta) deposited onto the surface of 316L stainless steel using a DC magnetron sputtering system. This coating process involves bombarding a tantalum target with positively charged argon ions, causing tantalum atoms to be ejected and subsequently deposited onto the stainless-steel substrate. The resulting Ta coating provides a uniform and adhesive layer with desirable properties such as high purity, excellent adhesion, corrosion resistance, and a smooth surface finish. The properties and performance of the tantalum coating can be further characterized using various analytical techniques such as scanning electron microscopy (SEM), Atomic force microscopy (AFM), Scratch test, and thickness profilometry**.** **Table 3.3** displays the operational parameters employed in the DC magnetron sputtering process for the coating procedure. Before deposition, the sample underwent ultrasonic cleaning using acetone, followed by drying in a pure argon (Ag) gas flow. Different deposition times were utilized for each sample. The 316L stainless steel substrates were positioned directly below the tracks of the target within the DC magnetron sputtering system. A pre-sputtering step was performed 15 minutes before each layer deposition to cleanse the target surface and remove any impurities or contaminants. Gas flow was regulated using a mass flow controller (MFC).

Prior to deposit, the chamber was evacuated to a base pressure of $5x10^{-4}$ Pa. Coating 316L stainless steel with a tantalum film using DC magnetron sputtering involves the following steps:

- **Substrate Preparation:** Thoroughly cleaned the 316L stainless steel substrate to remove contaminants, which was done using ultrasonic cleaning, and ensured the substrate was completely dry before proceeding.
- **Chamber Preparation: a.** sputtering chamber was appropriately cleaned to remove any residual contaminants. **b.** The chamber was evacuated to create a low-pressure environment suitable for sputtering.
- **Target Mounting: a.** Tantalum sputtering target was mounted onto the cathode within the sputtering chamber. **b.** Ensure the target is securely fixed and properly aligned.
- **Substrate Loading: a.** The cleaned and dried 316L stainless steel substrate was placed onto the substrate holder or stage within the sputtering chamber. **b.** It was made sure that the substrate was positioned securely and correctly.
- **Gas Introduction: a.** Argon (Ar) gas was introduced into the sputtering chamber as the process gas. Argon is commonly used as it provides good ionization and sputtering characteristics. **b.** A gas flow controller regulator was used to control the gas flow and pressure. Typical pressure ranges for tantalum sputtering are between **0.1** and **10 mTorr**.
- **Power Supply Setup: a.** The positive terminal of the DC power supply was connected to the substrate holder or stage. **b.** The negative terminal of the DC power supply was connected to the tantalum target. **c.** DC power supply voltage was set to the desired level.
- **Ignition and Plasma Formation: a.** The DC power supply was turned on to create a high electric field between the tantalum target and the stainless-steel substrate. **b**. This electric field ionizes the

argon gas, generating a plasma discharge. **c.** Electrons are accelerated toward the substrate, while positive argon ions are attracted toward the tantalum target.

- **Sputtering and Film Deposition: a.** The positive argon ions bombard the tantalum target surface, causing tantalum atoms to be sputtered and ejected from the target material. **b.** The sputtered tantalum atoms travel straight and deposit onto the stainless-steel substrate, forming a tantalum coating. **c.** The deposition time was controlled to achieve the desired coating thickness.
- **Process Control and Monitoring: a.** The desired film properties were obtained by monitoring and controlling the DC power supply voltage, gas pressure, and deposition time. **b.** In-situ or ex-situ techniques were used to monitor the coating thickness and quality during or after deposition.
- **Process Completion: a.** Once the desired coating thickness or deposition time is reached at a given time, the DC power supply is turned off. **b.** The sputtering chamber was vented to atmospheric pressure. **c.** The coated 316L stainless steel substrate was removed from the chamber.

It's essential that the specific process parameters, such as power, gas pressure, and deposition time, may need to be optimized based on the equipment and desired coating properties. To achieve high-quality coatings, it is vital to maintain proper protocol per standard procedure and ensure strong adhesion between the tantalum coating and the stainless-steel substrate with care, using high-purity gases, properly maintaining the target, and monitoring process parameters. **Fig. 3.2** depicts the photographic images of the DC Magnetron Sputtering System.

Table 3.3 The operational parameters of the DC Magnetron Sputtering system

Parameter	Details	Reason
Target Material	Tantalum	Tantalum is chosen for its two crystalline phases (**α**-Ta & β -Ta) **[9-11],** high toughness, and good corrosion resistance [**12**].
Magnetron Source	2 Nos. (each 50.8 mm)	Two magnetron sources are used with a source shutter to enable pre-ionizing and prevent cross-contamination, ensuring deposition only on the cathode.
Special Magnetics	-	Special magnetics are employed to achieve uniform sputtering across the target.
Gas	Argon (Ar)	Argon gas is used as it enhances nucleation density and reduces the surface roughness of the coating.
Working Temperature	180ºC	A temperature of 180ºC is selected to achieve controlled stoichiometry, composition, and a high deposition rate for the thin compounds produced.
Voltage	270-276 V	The 270-276 V voltage range is necessary for operating the system.
Substrate Holder's Distance	70mm	A distance of 70mm is maintained between the substrate holder and the target for optimal results.
Speed	7-9 rpm	The speed of rotation is adjusted as needed.
Base Pressure & Working Pressure	$5x10^{-4}$ Pa & $5x10^{-1}$ Pa	required for the deposition process.
Chiller Temperature	20ºC	A chiller temperature below 15ºC is maintained to ensure plasma generation.

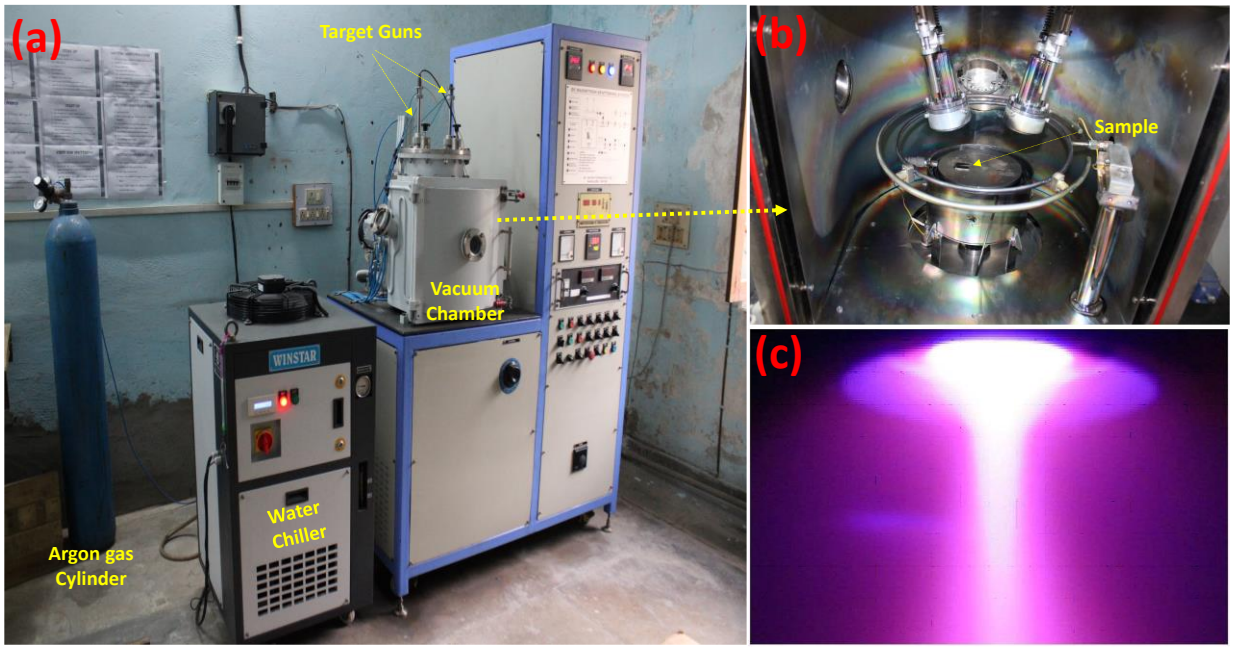

Fig. 3.2 Photographic images DC Magnetron Sputtering System

3.3 Preparation of Simulated Body Fluid Solution (SBF)

Simulated Body Fluid (SBF) is a solution that closely matches human blood plasma regarding ion concentration. It is a metastable solution that is temporarily stable but can change or precipitate under certain conditions. SBF replicates the inorganic components of human blood plasma and does not contain proteins, glucose, vitamins, hormones, and similar substances. In SBF, the concentration of calcium and phosphate ions is saturated, imitating their state in apatite. During the preparation of SBF, it is crucial to exercise extreme caution to avoid any irregularities or the precipitation of calcium (Ca^{2+}) and phosphate (PO_4^{3-}) ions. The specific composition of the SBF solution, as described by **Kokubo et al. [237]**, is provided in **Table 3.4.**

Table 3.4 Chemical Composition for SBF Preparation

Constituents (g)	**NaCl**	**NaH-CO_3**	**KCl**	**$(CH_2OH)_3$. C NH_3**	**$MgCl_2$. $6H_2O$**	**1.0 HCl (ml)**	**$CaCl_2$**	**Na_2 SO_4**
Amount in 1000ml	8.035	0.355	0.225	6.118	0.10	39	0.292	0.072

The SBF solution was prepared using the following method; Firstly, the equipment used for the preparation was thoroughly cleaned by treating it with a diluted hydrochloric acid (HCl) solution. Afterwards, it was rinsed with ultra-pure water and immersed in diluted HCl overnight. The next day, the apparatus was washed multiple times with ion-exchange water. The mouths of the apparatus were covered with wrapping film, and it was placed in a drier set at a temperature below 50°C. 750 mL of double-distilled water was taken in a dried 1000 mL beaker to prepare the SBF solution. The water in the beaker was then maintained at a constant temperature of 36.5°C while continuously stirring it on a clean bench. The chemical reagents listed in **Table 3.4** were added to the solution in the specified order, ensuring each chemical was utterly dissolved before adding the next one. Weighing bottles were used to accurately measure the quantities of the chemicals mentioned in the reagents. Lastly, Tris-hydroxy-methyl amino methane ($(CH_2OH)_3CNH_2$) was added to the solution, and the temperature was carefully maintained at 36.5°C. To adjust the pH of the solution, a pH meter was calibrated using a 1M diluted hydrochloric acid (HCl) solution. Once the pH was adjusted, the solution was transferred to a 1000 ml volumetric flask. Prior to adding the solution, the flask was rinsed multiple times with ultra-pure water, and then the solution was added to the flask. The volume of the solution was adjusted to the mark only after the temperature of the solution dropped to 20°C. After the makeup, the flask was thoroughly shaken. The prepared solution was stored in a refrigerator in a polyethene bottle. A stable solution would not exhibit any residues or suspensions; the SBF solution was renewed every two days throughout the experimental period.

3.4 Evaluation of Ta-coated 316L Stainless steel for the Orthopedic application

3.4.1 Wear Study

The pin-on-disc wear test is performed on a Ducom **(TR-701)** at 37°C in a simulated body fluid environment, according to ASTM G99-95a **[22].** **Fig. 3.3** shows the photographic image of the Bio-tribometer for wear studies. In this study, the chemical composition of simulated body fluid is shown in **Table 3.4**. With a normal load of 10, 20, and 40 N, zirconia pins with a diameter of 6 mm are used as counterparts. The parameters such as time, temperature, and frequency are kept constant in the experiment, and variations in loads throughout all the experiments. The pin on the disc tribometer in which the parts assembly appears is associated with wear function and actual device image. The counter face disc was made of hardened steel (EN31) with an Rc 60 hardness and a Ra 0.15 m surface roughness. Three types of plots are given from the data acquisition system; (a) Height loss versus time; (b) Coefficient of friction versus time, and (c) Frictional force versus time. **Table 3.5** shows the wear test parameters; the weight loss of the samples was determined by weighing each before and after the wear test on a digital balance with 0.0001g accuracy. For each bare and Ta-coated 316L SS sample, weight loss and coefficient of friction (COF) are recorded. These samples' volume loss and wear rates are calculated using equations (2) and (3).

$$\text{Mass loss} = \text{Mass after testings} - \text{Mass before testing} \quad (1)$$

$$\text{Volume loss} = \frac{\text{Mass loss}}{\text{The density of the coating}} \quad (2)$$

$$\text{Wear rate} = \frac{\text{Volume loss}}{\text{Load} \times \text{Sliding distance}} \quad (3)$$

Table 3.5 Wear test parameters

General Parameters		Test Parameters	
Pin material	Zirconia (ZrO_2)	Pin dimensions (mm)	6 × 20
Disc material	-	Normal load (N)	10,20, 40
Loading Profile	Constant	Speed (m/s)	20
Profile Pattern	Linear	No. of Cycle (s)	3600
		Frequency (Hz)	1,2
		Length (mm)	10

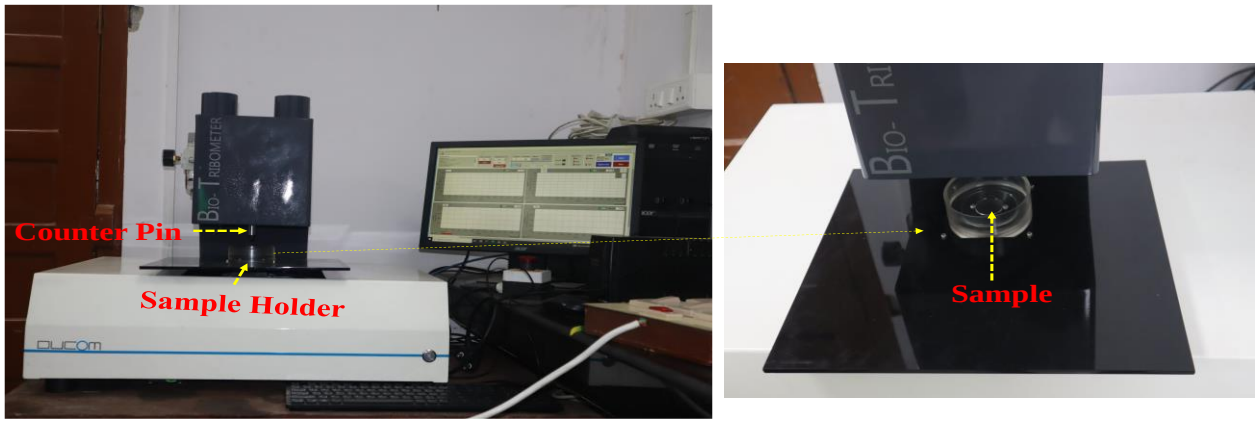

Fig. 3.3 Photographic image of Bio-tribometer for wear studies

3.4.1 (a) Microhardness test

Micro indentation Tester (MHT^3, Anton Paar) was used to determine the microhardness and elastic modulus of austenitic stainless-steel sample 316L SS and Ta-coated 316L SS at an applied load of 10 and 50mN at the frequency rate of 10 Hz.

3.4.2 Electrochemical Corrosion Study

In electrochemical measurements, Open Circuit Potential (OCP), electrochemical impedance spectroscopy (EIS), and Potentiodynamic polarization (PDP) tests were performed. **Fig. 3.4** shows the photographic images of the Electrochemical Corrosion Test Setup. The samples were tested in simulated body fluid (SBF) and prepared using the high-purity chemicals in **Table 3.4**. The typical three-electrode system, in which 316L SS acts as a working electrode, platinum electrode (Pt) acts

as an auxiliary electrode, and silver chloride electrode (Ag/Ag Cl) acts as a reference electrode, was used for the electrochemical corrosion measurement.

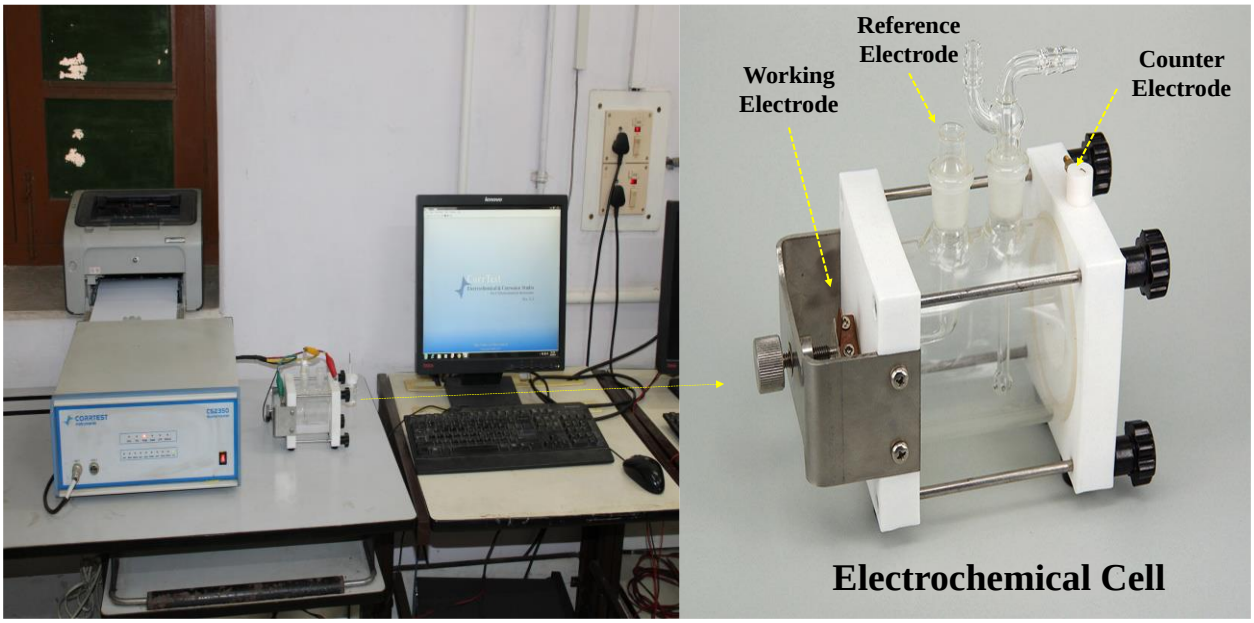

Fig. 3.4 Photographic Images of Electrochemical Corrosion Test Setup

To verify the stability of the specimen's working surface, an open circuit potential (OCP) measurement was conducted (for this study, 1 hour). The OCP measurement involved monitoring the behavior of materials: 316L stainless steel (SS) in its bare form and 316L SS coated with tantalum (Ta). These materials were exposed to a simulated body fluid with a pH of 7.4 and a temperature of 37°C. During the experiment, a potential difference was established between the working electrode (bare 316L SS or Ta-coated 316L SS) and the surrounding environment.

An electrochemical impedance spectroscopy (EIS) test was conducted to analyze the samples, including 316L stainless steel (SS) bare and Ta-coated 316L SS, in simulated body fluid (SBF) at a temperature of 37°C. The EIS test involved sweeping the frequency range logarithmically, starting from 1000 Hz down to 10 Hz. The potential against open circuit potential (OCP) was set at 0.2V. The scan rate was 10 mV per minute, and the test duration was 60 minutes.

For all the samples, including 316L SS bare and Ta-coated 316L SS, the EIS test was performed for 60 min. In the EIS test, 100 data points were collected at different frequencies in the logarithmic range. The data that was obtained was then analyzed using CView software (CS studio, version 5.2) and ZView software (CS studio, version 5.2). These software tools were used to interpret the EIS test results, allowing corrosion rate and corrosion resistance data to be calculated.

In the Potentiodynamic Polarization test, the obtained polarization curve is analyzed to extract key parameters such as corrosion potential (Ecorr), corrosion current density (icorr), and passivation behavior. These parameters provide information about the material's corrosion resistance and electrochemical behavior. The potential is initially set to a starting value and then swept at a constant scan rate in either the anodic (positive) or cathodic (negative) direction. The potential is swept until a final value is reached or until a predefined criterion is met. The polarization curve is obtained by plotting the current density (typically logarithmic scale) versus the applied potential.

3.4.3 Biocompatibility Study

All samples with a dimension of $(20 \times 20 \times 2)\ mm$ were used for the cell culture (Cell Adhesion and Cell Proliferation) investigation. Cells of human bone osteosarcoma named **MG-63** were utilized in this study. The cells were maintained at 37°C in a humidified 5% CO2 incubator (Galaxy®170 S, Eppendorf, Germany) using Dulbecco's modified Eagle's medium supplemented with 10% fetal bovine serum and 1% penicillin (10 000 U ml-1)/streptomycin (10 mg ml-1) (PS). Cell adhesion and proliferation assessment: The assessment was performed on the bare and Ta-coated 316L SS samples placed in a 35mm petri dish, per the standard procedure. The samples were sterilized by using an autoclave. The autoclaved samples were placed in a 35mm perti dish. MG63 cells were seeded with a density of 1×10^4 on each sample and incubated at 37°C and 5%

CO_2. The sample was cultured till day 14. Media was removed from each perti dish for staining and washed thrice with PBS. The sample was fixed with 4% paraformaldehyde.

Further, Triton-X was added for 5 min. to block nonspecific binding, 1%BSA in PBS was added. Finally, rhodamine-phalloidin was added and incubated for 1h. Then, DAPI (1µg/ml) was incubated for 30 min in the dark. The entire experiment was performed in triplicates. Percent cell proliferation was calculated as follows equation 4:

$$\% \text{ cell proliferation} = [A \text{ (sample)}/A \text{ (control)}] \times 100 \quad (4)$$

3.4.3 (a) Wettability

The wettability of the films' surface was evaluated using a contact angle measuring equipment called Drop Shape Analyzer-DSA 25 (Kruss). To calculate the water contact angle, a small drop of liquid was carefully placed on the surface of the test material using a syringe in a technique known as the sessile drop method. After the drop was applied, a goniometer was used to measure the advancing contact angle, which is the angle formed between the liquid drop and the solid material.

The Goniometer was used to examine the contact angle of the uncoated and Ta-coated 316L stainless steel samples. The experiments were conducted under controlled conditions with a relative humidity of 40% and a temperature of 20°C. For each test, deionized water droplets were dispensed onto the samples using a drop rate of 2.66 µL/s and a volume of 2 µL. A high-speed digital camera (U4 series, capturing 520 frames per second) was employed at 5-second intervals to capture images of the droplet shape on the machined workpiece. The ellipse fitting method, precisely the tangent-1 method, was employed to analyze the droplet shape in the pictures. A pipette was used during the experiment to ensure the accurate placement of the deionized water droplet.

3.3.3 (b) Scratch test

The adhesive coating strength was assessed using the Scratch test conducted with the Scratch Tester TR-101 Ducom. **Fig. 3.5** shows the Photographic image of a Scratch tester. The standard diamond stylus used for the test had a spherical tip with a 200 mm radius and Rockwell C geometry featuring a 120° cone shape. The Scratch test involved sliding the diamond stylus over the sample's surface while gradually or continuously increasing normal force until a critical normal force was reached. At this point, a precisely defined failure of the coating occurred. The adhesion strength was determined based on this force. The test employed a progressive vertical force, and as the scratch penetrated through the coating, material fracture and corresponding variations in force were observed, which are considered significant indicators of the critical force. After the scratch test, the worn surfaces (coated and uncoated) 316L stainless steel were evaluated by the profilometer (Multi-Functional Tribometers-RTECH-5000); the photographic image of the profilometer is shown in **Fig. 3.6.**

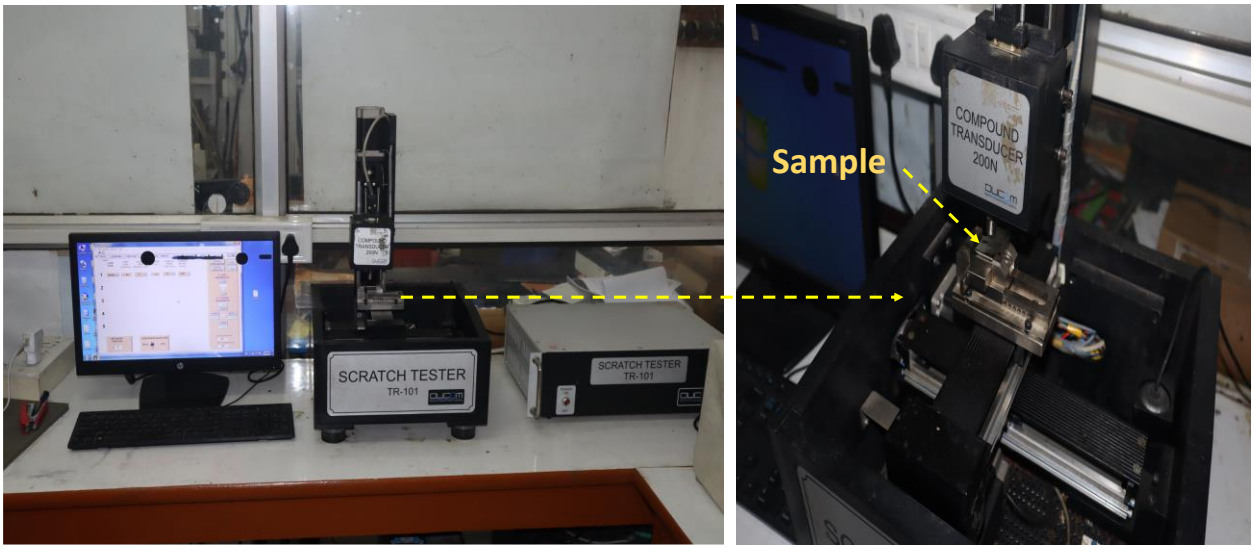

Fig. 3.5 Photographic image of Scratch tester

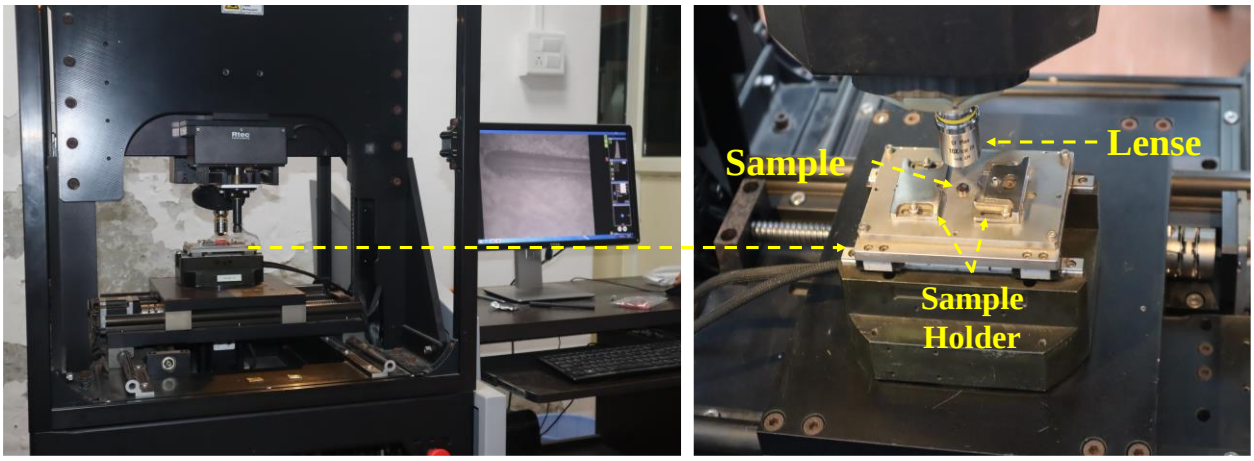

Fig. 3.6 Photographic images of the Profilometer

3.5 Characterization Techniques

The surface of the 316L stainless steel (coated and uncoated) was investigated using various techniques. The surface morphology was evaluated by an optical microscope (OM) [Leica Z6 APO]. Energy Dispersive X-ray Spectrometry (EDS) was employed to examine the chemical composition of the samples. Scanning Electron Microscopy (SEM) [ZEISS MA 15/18 United Kingdom] was used to analyze the surface morphology of the 316L SS. The Scanning Probe Microscope (SPM) [NTEGRA Prima NT-MDT Service & Logistics Ltd., Ireland] was employed. This SPM physically raster-scanned the samples and collected information from the surface using a sharp point. It could detect various signals in real-time with atomic or nano resolution, providing valuable insights into the structural properties of the as-received and Ta-coated 316L SS. X-ray Photoelectron Spectroscopy (XPS) using the K-alpha instrument from Thermo Fisher Scientific was employed to determine the chemical states and elemental composition of both the Ta-coated and bare 316L stainless steel (316L SS). The surface nano analysis XPS system utilized a non-monochromatic Al Kα radiation with an energy of 1486.6 eV, operated at 150W. This technique allowed for the identification and analysis of the chemical composition and states of the elements

present on the surface of the samples. The study of trace elements in physiological fluids was conducted using an analytical method based on Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [Agilent 7800 ICP-MS mainframe, Agilent Technologies]. This technique allowed for the detecting and quantifying of elements in the physiological fluids at low concentrations.

3.6 Work plan

The work plan was made before the initiation of the study, and it was executed accordingly. The present work plan schematically is shown in **Fig. 3.7.** This work plan outlines the strategy and approach for utilizing Ta-coated 316L stainless steel in orthopedic applications. This plan explores the potential benefits, challenges, and implementation strategies of using Ta-coatings on 316L stainless steel. This work plan aims to enhance the wear and corrosion resistance, improve biocompatibility performance, and increase the durability of tantalum-coated surfaces of 316L stainless steel in human body environments.

The work has been divided into the following parts:

- **Materials Selection**: To study and prepare 316L stainless steel for orthopedic implants.
- **Ta-Coating through DC Magnetron Sputtering**: The austenitic stainless steel 316L was coated at different times (15, 30, and 60 min.) to obtain the specific thickness of coating with the application of the DC Magnetron Sputtering (DCMS) system.
- **Characterization and Validation of Coating:** After coating the tantalum over 316L stainless steel, Ta-coated substrates were validated by Scanning Electron Microscopy for thickness measurement with cross-section cut via wire EDM-CNC machine, Atomic Force Microscopy (AFM) for surface roughness measurements, and Scratch test for coating adhesion strength measurement.

- **Wear Behavior:** Ta-coated 316L SS were characterized by wear behavior at different loads (10, 20, and 40 N), and the hardness and modulus of elasticity were checked by microhardness test.
- **Corrosion Behavior:** Open Circuit Potential (OCP), Electrochemical Impedance Spectroscopy, and Potentiodynamic Polarization methods were used to evaluate the corrosion behavior of Ta-coated 316L Stainless steel in Simulated Body Fluid (SBF).
- **Biocompatibility Evaluation:** Cell Adhesion and Cell Proliferation for the period of 1, 7, and 14 days with MG-63 Osteoblast were performed for biocompatibility test of bare, and Ta-coated 316L SS, wettability by Contact angle measurement test, and Coating adhesion was checked through the scratch tester.
- **Analysis of results Obtained:** \The results obtained from the above studies were critically analyzed and compared with the literature.
- **Deriving Conclusions:** Finally, the conclusions were made based on the results obtained.

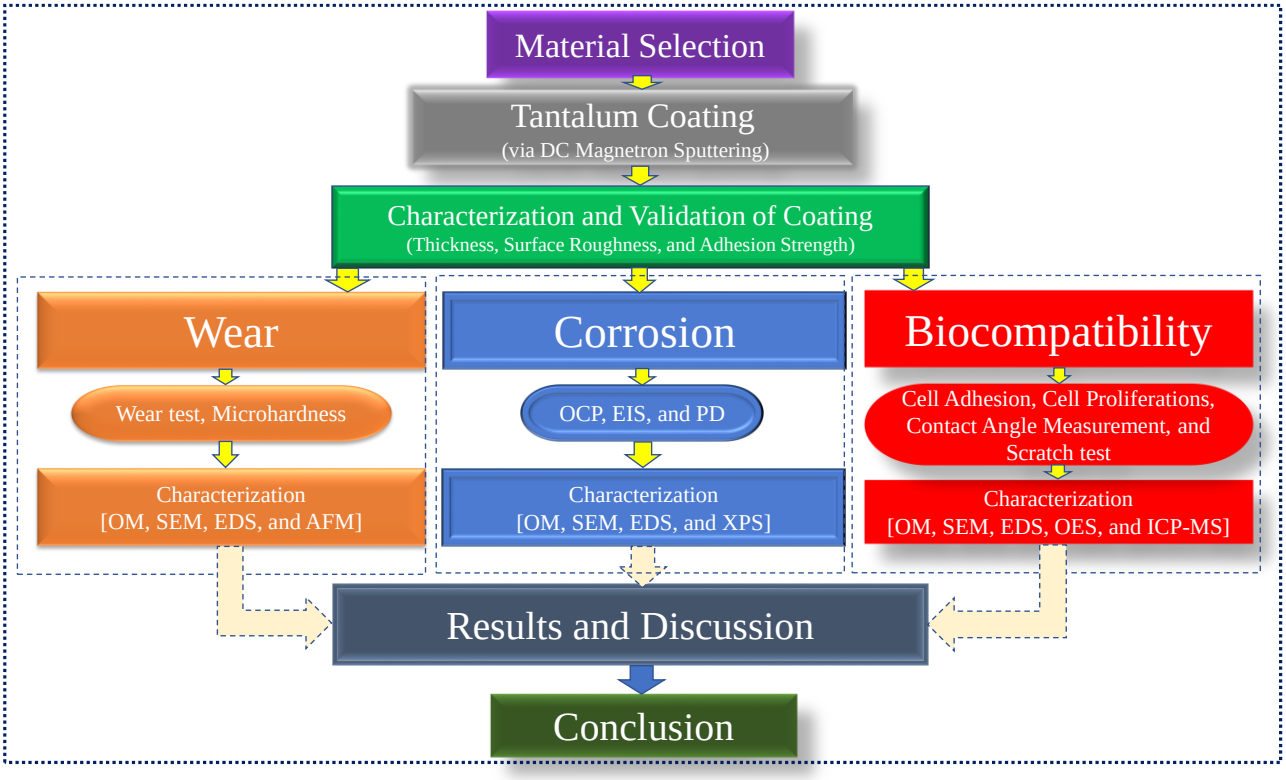

Fig. 3.7 Work plan of the thesis (Schematic)