Chapter 2

Experimental Techniques

This chapter deals with the various experimental techniques adopted for the formation of hard and high wear resistance surface on the Ti based alloy. The procedure and optimization steps followed for laser nitriding, atmospheric plasma spraying and spray drying for synthesizing agglomerated nano powders are presented in detail. In addition, the various characterization techniques used for the phase, microstructural analysis and mechanical properties evaluation of coatings are discussed along with the description of the test procedure adopted for measuring corrosion and wear behavior of the coatings.

Thus this chapter discusses the following synthesizing and characterization techniques:

(i) Laser nitriding
(ii) Atmospheric Plasma Spraying
(iii) Spray drying
(iv) Microstructure and phase analysis
(v) Raman Spectroscopy
(vi) Roughness and Hardness measurement
(vii) Scratch testing
(viii) Corrosion measurement using potentiostat
(ix) Wear and Friction coefficient measurement using reciprocating wear tester

2.1 LASER NITRIDING

Laser nitriding is an efficient process in which metallic surfaces are irradiated by laser pulses in nitrogen containing atmospheres. It has been found that the nitrogen intake by the metal and hence the nitride formation can improve the surface properties
such as the hardness, corrosion and wear resistance of the metal or alloy. Over the years, many mechanical parts such as tooth wheels, cam shafts, cylinder liners and bio-implants have been subjected to nitriding processes in order to improve their tribological properties (Aravind Vadiraj et al; 2007).

In this investigation, the laser nitriding on Cp Ti and Ti-13Nb-13Zr alloy were carried out using 1.06 μm Nd: YAG pulsed laser in Advanced Material Processing Group, Defence Metallurgical Research Laboratory, Hyderabad, India, using the model SS550 with the maximum rated power of 400 W, Mode: Pulsed. A schematic diagram of the laser nitriding process is shown in figure 2.1.

![Figure 2.1 Schematic diagram of laser nitriding](image)

A high power laser beam is produced using Nd:YAG laser and this beam is made to fall on the work piece (sample). The work piece is mounted on an x-y table, the speed of which is controlled by a computer numerical controller. The laser beam is kept stationary, and the specimen is moved at speed and when the laser beam comes in contact with the specimen the following processes occur (Powell et al; 1988 and Jogender singh et al; 1994). The alloying element nitrogen is fed through a nozzle on
to the laser generated melt pool. Three mechanisms have been identified for facilitating the mixing of component which is liquid state diffusion, convection currents within the melt pool and agitation of the melt pool by laser-sustained plasma. Solidification occurs at the bottom and at the surface of the melt pool, the latter being the result of formation of high melting point (2350°C – 2950 °C). The formation of TiN is made possible by the high concentration of dissolved nitrogen gas near the top of the pool. During surface alloying, large temperature gradients exist across the surface layer as the underlying substrate provides heating and cooling rates of about $10^6 – 10^8$ °C/s. The substrate itself is an excellent sink, so additional cooling medium such as water, is not needed. As a result of rapid heating and cooling, considerable changes in chemical and microstructural features occur. The first set of passes disperses the nitrogen to the desired depth and determines the overall composition of the surface alloy and the subsequent passes will homogenize the effects. The speed at which the substrate is moved determines the time of contact between the source and the specimen and this in turn determines the TiN formation on the surface. Lower speed results in large melt pool, whereas, the higher speed leads to shallow melt pool and hence lower concentration of TiN on the surface. The other important parameters that determine the TiN formation are the partial pressure and laser pulse width. The optimized processing parameters are given in Chapter 3.

2.1.1 SUBSTRATE PREPARATION

Prior to laser nitriding, the surface of the alloys were cleaned to remove dust, grease and oxide layer on the surface of titanium alloys. The procedure adopted to clean the surface is given in flowchart 2.1. Both the Cp titanium and Ti-13Nb-13Zr alloy were processed in pure nitrogen (1 Pa N₂) before passing through the nozzle and delivered coaxially with the beam.
Surface roughening using 220 and 320 grit SiC papers

Etching the samples in a solution containing 5 Vol% of concentrated hydrofluoric acid (HF), 15 vol% of concentrated nitric acid (HNO₃) and 80 vol% of distilled water (H₂O) for 15 minutes

Washing the etched samples in cold water

Washing with laboratory grade acetone

Drying the samples in blowing hot air

Stored in air tight polyethylene cover.

**Flow chart 2.1 Surface preparation procedure –prior to laser nitriding**

2.2 ATMOSPHERIC PLASMA SPRAYING (APS)

The nano ceramic powders Al₂O₃-13TiO₂ (AT) and ZrO₂ (YSZ) that were used for plasma spraying were procured from Inframat, USA. Plasma spraying of the reconstituted nanostructured powders was carried out using 80 kW plasma spray system (Sulzer Metco 9MB) (Figure 2.2). The samples were preheated to a temperature of 400º C by means of the plasma torch before plasma spraying so as to enhance the adhesion of the coating. The Ti-13Nb-13Zr alloy substrate (35 x 20 x 4 mm³) was grit blasted prior to plasma spraying. Three different coatings viz, ZrO₂, Al₂O₃-13TiO₂ and Al₂O₃-13TiO₂ over ZrO₂ that were obtained using plasma spraying are schematically represented in Figure 2.3.

2.2.1 EXPERIMENTAL PROCEDURE

Argon is usually chosen as the primary gas because it is chemically inert and because of its ionization characteristics and this gas was allowed to flow between a tungsten cathode and water cooled copper anode. An electric arc is initiated between

---

33
the two electrodes using a high frequency discharge and then sustained using a D.C. power.

![Atmospheric plasma spraying equipment diagram](image)

**Figure 2.2 Atmospheric plasma spraying equipment** (a) control unit, (b) powder feeder, (c) spray booth

The arc ionizes the gas creating high pressure gas plasma. Powders with a particle size up to 100 µm are introduced into the gas stream either just outside the torch or in the divergent exit region of the nozzle (anode). It is both heated and accelerated by increasing temperature, high velocities ranging from 400 to 2,000 ft/s of the plasma gas stream.

The resulting increase in gas temperature which may exceed 30,000º C in turn increases the volume of the gas and hence its pressure and velocity as it exits the nozzle. Power levels in plasma spray torches are usually in the range of 30-80 kW but they can be easily as high as 120 kW.

Various parameters such as the power input, powder feed rate, shape and size of the powder, torch design and the stand off distance (Distance between nozzle and the substrate) control the quality of the coatings. Torch design and operating parameters are critical in determining the temperature and velocity achieved by the powder particles. The operating parameters include not only the gas flow, but also the
distance from the torch to the substrate (stand off) and the angle of deposition. Stand off distance is of substantial importance because adequate distance must be provided for heating and accelerating the powder but too great a distance will allow the powder to cool and lose velocity because the gas stream is rapidly expanding, cooling and slowing. The size and morphology of the powder particles strongly influence their rate of heating and acceleration and hence the efficiency of deposition and quality of the coating. The methodology adopted for optimization and the optimized parameters used for the current study is given in the Chapter 4.

2.3 SUBSTRATE PREPARATION

2.3.1 GRIT BLASTING

In order to obtain an adherent coating, the surface is to be grit blasted and preheated as discussed below.

The main objective of the substrate preparation is to ensure strong bond formation between the coating and substrate in terms of mechanical interlocking which is accomplished by grit blasting. Al₂O₃ and chilled iron are the most widely used abrasive grits for surface preparation. However sand, crushed steel and silicon carbide are also used in some situations. Consideration should also be given to the substrate material in the selection of grit type. Trials of residual grit may adversely affect some coatings. Practical grit sizes ranging from 10/+30 mesh and -30/+80 mesh are generally used. Surface roughness is primarily the result of grit particle size, so the selection of grit size is determined in part by the roughness required for adequate bonding. Excessive grit blasting should be avoided to minimize grit inclusion in the surface.

As mentioned earlier, Ti-13Nb-13Zr substrate was cleaned using acetone so as to remove any thin oil film prior to grit blasting operation. Later, the Ti-13Nb-13Zr
alloy substrate (35 x 20 x 4 mm³) was grit blasted using cabinet type grit blasting machine (Sandstorm equipment, India) using alumina grits (20 μm) for approximately one minute to impart mechanical roughening of the substrate to be coated enabling good bonding. The samples were preheated to a temperature of 400º C by means of the plasma torch before plasma spraying so as to enhance the adhesion of the coating.

2.4 PRODUCTION OF AGGLOMERATED POWDERS

The present work demands the use of a spray drier as the nanoceramic particles used are to be agglomerated and coated on the substrate. Spray drying is a technique that utilizes liquid atomization to create droplets which are dried into individual particles while moving in a hot gaseous drying medium, usually air (Masters et al; 1991). Over several thousand spray dryers are presently in use commercially around the world to dry products from agro-chemical, biotechnology products, fine and heavy chemicals, dairy products, dyestuffs, mineral concentrates to pharmaceuticals in sizes ranging from a few kg per hour to 50 tons/h evaporation capacity (Chou et al;2000). Liquid feedstocks, e.g., solutions, suspensions or emulsion, can be converted into powder, granular and agglomerate form in an one-step operation in the spray dryer (Masters et al; 1991 & 2002; Filkova et al; 1995; Huang et al; 2004).

The flow chart 2.2 depicts the procedure adopted in the production of agglomerated nanopowders:

**Flowchart 2.2 Steps involved in the production of agglomerated powders**

2.4.1 PREPARATION OF SLURRY

Slurry preparation greatly affects the quality of the agglomerated powder. For slurry preparation, a known quantity of key ingredients (Al₂O₃) that is 20-30 vol % of alumina was dissolved in distilled water. To this, some quantity of binder
(Polyethylene glycol) was added and stirred well for about five minutes. Finally small amount of dispersant was added and the pH was adjusted using NaOH and HCl. Later the prepared slurry was mechanically milled for 48 hours. The binder was added to keep the powders to be intact with each other and the settling down of the particles was prevented by the addition of dispersant and the mechanical milling.

2.4.2 VISCOSITY AND RELATIVE SEDIMENTATION HEIGHT MEASUREMENT

In this work, the viscosity of the slurries was measured using Brookfield rotational viscometer (DV-III ULTRA, Brookfield, U.S.A) at a shear rate of 51 s\(^{-1}\). Further, settling experiments were conducted to study the effect of pH and solid loading. Relative sedimentation height (RSH) of the slurries was measured over the duration of 170 hrs.

The rotating-cylinder viscometer consists of two concentric cylinders with the annular clearance filled with test fluid. One of the cylinders, usually the inner cone is driven while the other is stationary. There are a number of commercial rotating cylinder viscometers available and these are usually supplied with the cylinders of different diameters giving radial clearances. These can be driven at varying speeds allowing a range of viscosities and shear rates to be accommodated. The main shearing takes place in the annular clearance, but in some cases the shear forces on the ends of the rotating cylinder may be significant and they must then be allowed for (or) taken into account by calibration with a known liquid.

2.4.3 SPRAY DRYING

In the present investigation, spray drying was done with the help of co-current spray dryer. The spray drying apparatus consists of a peristaltic pump which feeds the slurry into the stream of hot gases allowing a rapid evaporation of the liquid and leaving behind the agglomerated alumina particles (Figure 2.4).

A normal spray drying process usually consists of the following three stages:

1. Atomization of feed into droplets: the liquid feed which can be solutions, suspensions, emulsions or slurries is atomized to a spray that consists of
fine droplets. Ordinarily there are two different atomization methods: rotary disc or centrifugal atomizers and nozzle atomizers including pneumatic nozzle and pressure nozzle.

2. Heating of hot drying medium: The drying medium, such as air, is heated by steam, electricity, oil combustion or coal combustion etc. then it will be sent into the drying chamber through the hot air dispenser.

3. Spray-air contact and drying of droplets: The liquid spray is mixed with the hot drying medium in the drying chamber. Then the liquid present in the suspension is evaporated into drying medium and dried into particles or powder.

![Figure 2.4 Experimental setup of Spray drying equipment](image)

**Figure 2.4 Experimental setup of Spray drying equipment**

2.4.4 CHARACTERIZATION OF THE SPRAY DRIED POWDERS

2.4.4.1 POWDER BULK DENSITY

The bulk density (g/cm³) of the powder is determined by taking 5 ml of powder in a 10 ml measuring jar. The powder containing the measuring jar is tapped gently until it reaches a constant height of 5 ml. The final volume and the weight of the
powder is measured. The ratio of the weight of the powder and the change in volume gives the value of bulk density (g/cc).

2.4.4.2 PARTICLE SIZE ANALYZER

Particle size distribution of ceramic powders is the primary physical parameter that has considerable impact on the properties of the plasma spray coatings. The particle size distribution greatly affects the powder consolidation and densification steps during powder processing through the packing density. One of the principal requirements in ceramic powder processing is the knowledge of the agglomerates and the size distribution of primary particles. Therefore, the measurement of particle size distribution is needed for the starting powders as well as the agglomerated powders so that the desired properties and microstructures can be achieved. The particle size distribution can be analyzed by Particle size analyzer.

In our current study, the particle size of these powders was determined by particle size analyzer (Sedigraph 5100, M/s Micromeritics, USA make) in order to confirm that whether the agglomerated powders are in micron size. The built in program contained in the instrument enables the determination of the particle size by making use of the formula given below which is based on stokes law.

\[
D^2 = \frac{18v\eta}{(\rho - \rho_0)g}
\]

Where, \(v\), \(\eta\) and \(\rho_0\) refer to the velocity, viscosity and density of the liquid, \(\rho\) - density of the particle, \(g\)-acceleration due to gravity.

Depending upon the weight, each particle settles with different terminal velocity \((v)\) that is when the gravitational forces balances the buoyancy and drag forces on this particle. An X-Ray beam is used to detect the changes in suspended sediment concentration during settling, at different vertical distances in the analysis cell and at specific times during settling. This analysis provides a distribution of concentration for different particles sizes.
2.5 CHARACTERIZATION

2.5.1 MICROSTRUCTURAL CHARACTERIZATION

Both the optical microscopes (OM) and Scanning electron microscopes (SEM) were utilized in the present work to analyze the microstructure of the coatings such as morphology, thickness of the coating and to characterize the worn samples. The optical microscope has been in use for the past several decades and it has been used to study grain boundaries and phases present in metallic samples and to observe the coated surface and the cross section. In order to overcome the limitation set by the diffraction limit of visible light in OM, scanning electron microscope (SEM) is used. It images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The use of electrons and x-rays in place of light allows much higher resolution.

In our experimental work, for cross-sectional OM and SEM studies, the samples were mounted using bakelite powder followed by grinding and polishing with emery papers of different grit sizes, ranging from 120 µm to 1600 µm and mirror finished by 1 µm diamond paste. Krolls reagent containing 10 ml of HF, 5 ml of HNO₃ and 85 ml of water was used for etching the surface for optical observation. The SEM was operated in the secondary electron imaging mode (SE) as this is the most common or standard detection mode which can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size.

2.5.2 ROUGHNESS AND HARDNESS MEASUREMENT

Roughness was determined by measuring the $R_a$ (average roughness value) using Talysurf FTS 50 profilometer, in which the probe moves across a surface to detect variations in height as a function of distance. The LVDT incorporated with the equipment will convert the vertical displacement into an electrical signal. This signal can then be processed by the electronic instrument to calculate a suitable roughness parameter.

The hardness of the coatings was determined using Vickers hardness testing machine. The test consists of pressing a square pyramid (diamond) into a flat, polished surface of a material and measuring the dimensions of the resulting
indentation. Since the area of the impression (mean diagonal, d, mm) is proportional to the load applied (L, Kg), a load-independent hardness number can be found from the quotient L/d^2. According to the Vickers prescription, Hv = 1.854 L/d^2. Dimensions of the indentations were measured with the help of microscope attached to it. Minimum five indentations were made to obtain the average hardness value.

2.5.3 PHASE ANALYSIS

In order to analyze the crystallinity, phases of the powders of the coated surfaces and the bare substrate, X-ray diffraction analysis was used. Inspite of the fact that XRD is widely used to study the phases, it is difficult to distinguish the phases in some of the material for which the peaks lie close to each other due to line broadening effect which made Raman studies to be undertaken.

The phases formed was analyzed using Philips 3121, X-Ray diffractometer using CuKα radiation of wave length (λ=1.5418Å) in Bragg-Brentano geometry. The diffracted 2θ data were collected at a scanning rate of 2°/min and the scanning range is set from 10 to 90 degree.

The diffraction pattern is the characteristic of the substance and forms a sort of fingerprint of the substance to be identified. The particle size was measured from the well known Scherer formula. The peaks of the X-ray diffraction pattern were compared with the available standard data for the confirmation of the phases. For the purpose of comparison, many standards are available, some of which are: Willars Hand Book, Joint Committee on Powder Diffraction Standards (JCPDS) Pcpdfwin and National Bureau of Standards. The JCPDS, Version 2.4 (Joint Committee on Powder Diffraction Standards (JCPDS), International Centre for Diffraction Data (ICDD), Version 2.4, June 2003) was exclusively used for this thesis work.

2.5.4 RAMAN SPECTROSCOPY

Raman spectroscopy is a valuable tool used for the characterization of materials due to its extreme sensitivity to the molecular environment of the species of interest. Plasma spraying of zirconia and titania results in the formation of phases such as cubic and tetragonal zirconia and anatase, brookite and rutile phases based on
the processing conditions. As some phases were absent in the X-Ray, Raman spectroscopy was employed as a complementary technique to confirm the presence or absence of such phases. The phases present in the plasma sprayed coatings were carried out using DILOR-JOBIN-YVON-SPEX Raman spectroscopy.

In Raman spectroscopy, the laser beam is usually focused on the sample using a series of mirrors and lenses. Focusing the beam results in luminous power densities varying from several hundred watts to thousands of watts per square centimeter. For absorbing samples, these power densities can cause significant heating. One of the means of reducing the extent of heating is to focus the laser beam to a line on the sample using a cylindrical lens. This approach also produces scattered radiation in a line shape such that the entrance slit of the monochromator can be completely filled with the slit-shaped image. The output of Raman system is a plot of scattered light intensity as a function of frequency shift in which the shift is calculated related to the laser line frequency.

2.5.5 SCRATCH TEST

The micro-scratch test is an important experimental approach for determining the interfacial strength, toughness and adhesion properties of the coating. The working principle of scratch testing machine is as follows. On the material or specimen surface along the vertical direction an indentation force is exerted and the indenter tip made of diamond penetrates inside the material which is moved in the horizontal and vertical directions simultaneously according to a fixed proportion. When the indenter tip moves near the film/substrate interface, a region of the thin film or coating layer near the indenter tip will be delaminated along the interface. Through measuring the driving forces and the scratch depth, as well as the failure geometry, one may obtain the mode of failure in coatings.

In the current study, scratch test was performed using a commercial micro scratch tester to evaluate the adhesion strength of all the three plasma sprayed coatings. The schematic picture of the scratch testing equipment is as shown in figure 2.5. A spherical Rockwell C diamond stylus of 200 µm radius was used to produce the scratch. The test was carried out under ramp loading mode with the load of 200 N. The loading was varied in steps at 2 N/mm and the stylus scanned the coating surface
perpendicularly at a speed of 0.5 mm/s. The total length of the scratch scar was 10 mm.

**Figure 2.5 Experimental setup of scratch testing machine.**

2.6 ELECTROCHEMICAL CORROSION STUDIES

The corrosion behavior of the laser nitrided and plasma sprayed samples were performed using potentiostat using the three-electrode cell as per ASTM specifications (F2129 standard). The open circuit potential (OCP) and Passive current density are used as the criterion for evaluating the corrosion characteristics of the laser nitrided samples.

2.6.1 SAMPLE PREPARATION

A sample having dimensions of 10 mm x 10mm x 4mm are moulded employing bakelite powder leaving the top side of the specimen exposed. The samples were polished using emery sheets of various grit sizes ranging from 120 to 1000 µm SiC paper. Final polishing is performed on low speed wheel covered with micro cloth using slurry containing 0.05 micron alumina and water with a slight
pressure on the specimen. The samples were then degreased with acetone followed by ultrasonic cleaning with distilled water.

2.6.2 OPEN CIRCUIT POTENTIAL-TIME MEASUREMENT

Open circuit potential (OCP) versus time and anodic polarization experiments were conducted to characterize the corrosion behavior of the material. OCP measurements were carried out by exposing the samples in an electrolyte for an hour so as to establish a steady state between the electrolyte and the specimen. The change in the potential with respect to time was monitored until the potential reaches a steady state. The potential of the working electrode with respect to the reference electrode after stabilization period is termed as Open Circuit Potential (OCP) or corrosion potential ($E_{\text{corr}}$).

2.6.3 POTENTIODYNAMIC POLARIZATION STUDY

This technique can provide information regarding the corrosion mechanisms, corrosion rate and susceptibility of specific materials to corrosion in designated environments. In anodic polarization study, the potential is changed in the anodic (more positive direction) causing the working electrode to become the anode and causing the electrons to be withdrawn from it.

Polarization methods involve changing the potential of the working electrode and monitoring the current which is produced as a function of time or potential. By using the anodic portion of the polarization curve it is possible to estimate the corrosion resistance of a given metal in an electrolytic medium, which can be achieved by measuring the extension of the range of potential in which the passivation layer exists as well as by determining the current density of passivation. The results of the corrosion studies of the present investigation are well explained in the subsequent chapters.

The evolution of the current density as a function of the potential (versus saturated calomel electrode) can be used in the evaluation of the corrosion resistance of the given material in a corrosive medium. The initial portion of the anodic polarization curves is related to the start of the corrosion process, where the metal
directly interacts with the medium leading to active corrosion. In the following stage, a passivation layer is formed and then the current density becomes constant. The layer consists of metallic oxides, which protect the metal from further corrosion and the kinetics of their nucleation and growth have been well established. In the third stage, further increase in the potential to very higher value leads to an increase in current density and this behavior may be attributed to cessation of the metal protection by the passive layer.

In this current work, potentiodynamic polarization measurements were carried out on all the specimens in Hank’s solution whose compositions are shown (Table 2.1) which was made up to one litre by distilled water and the experiment was performed using a Potentiostat(Gill A.C, ACM make). The parameters used for corrosion testing are shown in Table 2.2.

For performing the electrochemical measurements, a conventional three-electrode system was used. The specimens are used as the working electrode, platinum foil (10mmx5mmx0.5mm) as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The samples were placed in teflon holder, with a 6 mm diameter window exposed to the solution. Just before the electrochemical measurement, the samples were mechanically polished up to 1000 grit SiC paper and were then rinsed with distilled water. Open Circuit Potential (OCP)–time measurements were carried out for one hour to achieve a steady open-circuit potential, which was measured as the corrosion potential $E_{corr}$. When the specimen attained a constant potential after one hour, potentiodynamic polarization was started from an initial potential of 250 mV below the corrosion potential, $E_{corr}$. The scan rate used was 0.166 mV/s as per ASTM F2129 Standards. The experiments were repeated three times for reproducibility of the data. The experimental setup of the corrosion experiment is shown in figure 2.6.
2.6.4 IMPEDANCE SPECTROSCOPY

Impedance spectroscopy is one of the powerful methods for studying both the bulk transport properties of a material and the electrochemical reactions on its surface. Dielectric properties, defects, mass transport, and the influence of microstructure, grain size and composition on the conductance of solids can be studied using an impedance analyzer. This analysis provides quantitative information about the conductance, the dielectric coefficient, the static properties of the interfaces of a system, and its dynamic change due to adsorption or charge-transfer-phenomena. Impedance spectroscopy can also be used to separate the interfacial and bulk phenomena and also the grain and grain boundary effect on electrical conduction in nanomaterials. The basis of Impedance spectroscopy is the analysis of the impedance (resistance of alternating current) of the observed system subject to the applied frequency and exciting signal.

In this work, Electrochemical Impedance Spectroscopy (EIS) measurements were performed with the same experimental setup used for potentiodynamic polarization studies. The frequency response analyzer and potentiostat were driven by Z plot software. Impedance measurements were carried out with a frequency sweep ranging from 10,000 HZ to 1 HZ. The software led to obtain the best fit from the acquired data, which in turn led to smooth and reliable curves. From the impedance
plot an equivalent circuit is generated. The capacitance and the resistance values of
the equivalent circuit are varied to fit the plot and the fitted values provide the actual
information regarding the corrosion resistance of the coatings. The typical impedance
spectra in the complex impedance plane corresponding to the circuits are shown in
figures. 2.7 (a) and 2.7(b).

![Circuit](image)

**Figure 2.7 (a) A common RC circuit and (b) its impedance plane**

2.6.5 WEAR AND FRICTION COEFFICIENT MEASUREMENT

Wear is the main cause of failure of implants directly or indirectly, especially
in the case of knee and hip joint prosthesis. To make the joint more efficient,
minimization of wear is the most important aspect to be taken care of. Wear failure
may happen from two different aspects. Firstly, softer material part (most of the cases,
Ultra High Molecular Weight Polyethylene) of the joint prosthesis may be totally
worn off for reciprocating motion. Secondly, entrapped wear debris between implant
and bone cement is mainly responsible for prosthesis loosening. To avoid those types
of failure, different types of wear tests were performed by several workers using
different types of biocompatible materials. The purpose of the study in the present
work is to investigate the wear characteristics in detail of the biomaterials used for
dental and orthopedic applications.
Table 2.1 Composition of Hank’s solution

<table>
<thead>
<tr>
<th>Reagent</th>
<th>Composition (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCl₂</td>
<td>0.185</td>
</tr>
<tr>
<td>KCl</td>
<td>0.4</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>0.06</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>MgSO₄·7H₂O</td>
<td>0.1</td>
</tr>
<tr>
<td>NaCl</td>
<td>8</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.35</td>
</tr>
<tr>
<td>Na₂HPO₄</td>
<td>0.48</td>
</tr>
</tbody>
</table>

For our current study, the wear studies were carried out using reciprocating wear tester TR-285 M1 machine designed according to ASTM G133 standard (Figure 2.8) with reciprocating motion against 6 mm diameter alumina ball. The wear test was performed with 10N load, 2 Hz frequency and 15 mm stroke length. The Wear testing machine was standardized by measuring the wear of the nano composite against EN31 tool steel which was made to move with a sliding velocity of 0.35 m/s and through a sliding distance of 3600 m. Samples of both the laser nitrided and the plasma sprayed coupons were subjected to wear testing at 37 ± 1°C in Hank’s solution using reciprocatory wear tester. The parameters used for wear testing are shown in Table 2.3. The weight loss was measured using an electronic weighing balance of 0.0001 g of accuracy in order to calculate the wear rate. Three dimensional wear plots were also made using the data collected during the wear test. The wear testing apparatus is shown below (figure 2.8). The studies were used to determine the friction coefficient and wear rate of the coated samples as well as the substrate. The coatings were performed to improve the wear resistance in order to understand how the life span of the biomaterial can be increased.

Table 2.2 Parameters for corrosion testing

<table>
<thead>
<tr>
<th>Reference Electrode</th>
<th>Saturated calomel electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Counter Electrode</td>
<td>Platinum foil</td>
</tr>
<tr>
<td>Scan rate</td>
<td>0.166 m V/s</td>
</tr>
<tr>
<td>Sample dimensions</td>
<td>1 cm x 1 cm</td>
</tr>
<tr>
<td>Environment</td>
<td>Hank’s solution</td>
</tr>
</tbody>
</table>
Figure 2.8 Reciprocatory wear testing machine

Table 2.3 Wear testing parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Load applied</td>
<td>10 N</td>
</tr>
<tr>
<td>Frequency</td>
<td>2 Hz</td>
</tr>
<tr>
<td>Temperature</td>
<td>37º C</td>
</tr>
<tr>
<td>Sample dimension</td>
<td>25 mmx20 mmx 4mm</td>
</tr>
<tr>
<td>Diameter of Alumina ball</td>
<td>5.2 mm</td>
</tr>
<tr>
<td>Test duration</td>
<td>$10^5$ cycles</td>
</tr>
<tr>
<td>Environment</td>
<td>Hank’s solution</td>
</tr>
</tbody>
</table>

The above gives an outline of the various experimental techniques employed in the present study and the details are discussed at length in the respective chapters. Especially, the minute details relating to agglomeration, which forms a substantial part of the work of the present thesis along with atmospheric plasma spraying technique are elaborately dealt with in the chapters 4 and 5.