Chapter 2 Materials and methods

The objective of this work was to fabricate Ti-6Al-4V components by additive manufacturing process in three different orientations (0°, 45°, and 90°), to analyse the microstructure, corrosion behaviour, mechanical properties, wear, and biological behaviour. This study consists of various experiments along with their detailed analysis of the results. In this chapter, the experimental procedure used for fabricating the Ti-6Al-4V components in different orientations has been discussed along with the extraction of tensile samples for mechanical testing and preparation of samples for characterization as per the established standards.

In this work, the EOS M280 Laser metal printer was used with optimized process parameters to fabricate samples in different orientations making angle with build platform. The fabricated samples were characterized using various characterization techniques including microstructure examination, mechanical testing, residual stress evaluation, and fractography analysis. The existing surface grinding setup was used with cryogenic attachment to evaluate the effect of cryogenic grinding on surface characteristics of the additively manufactured Ti-6Al-4V samples. Corrosion, wear, and biological studies were also carried out to evaluate the behaviour of additively manufactured Ti-6Al-4V samples fabricated in different orientations.

2.1 Microstructure and mechanical properties of additively manufactured (AM) Ti-6Al-4V alloy

2.1.1 Materials and fabrication of components

In this study, plates of size 100×50×6 mm^3 of Ti-6Al-4V alloy were built at 0° (build direction along thickness), 45°, and 90° orientations, from using powder of the alloy, by a L-PBF printer (Model: EOS M280, Make: EOS) equipped with a 400 W ytterbium fibre laser for making tensile test samples. Also, the three blocks of the size 60×60×5 mm^3 were fabricated with their respective build orientations, keeping the same process parameters and built platform for characterization of microstructure and other properties. The Ti-6Al-4V powder (Figure 2.1a) material prepared from gas atomization process was nearly fully dense with spherical shape (Figure 2.1b) and the size ranging from 4 to 40 µm (Figure 2.1c). Table 2.1 presents the chemical composition of the powder material supplied by the manufacturer.

Table 2.1 Chemical composition of the Ti-6Al-4V powder material used in L-PBF process

Element	Ti	Al	V	O	N	C	H	Fe
Composition	balance	5.8 wt. %	3.89 wt. %	< 2000 ppm	< 500 ppm	< 800 ppm	< 150 ppm	< 3000 ppm

The components were built with optimum process parameters and were almost fully dense. The optimized parameters used for building of the components have been listed in Table 2.2.

Table 2.2 Process parameters used for additive manufacturing

Atmosphere	Argon
Spot diameter	80 µm
Laser power	340 W
Layer thickness	60 µm
Initial bed temperature	35 °C
Hatch distance	120 µm
Scan rotation angle	67°

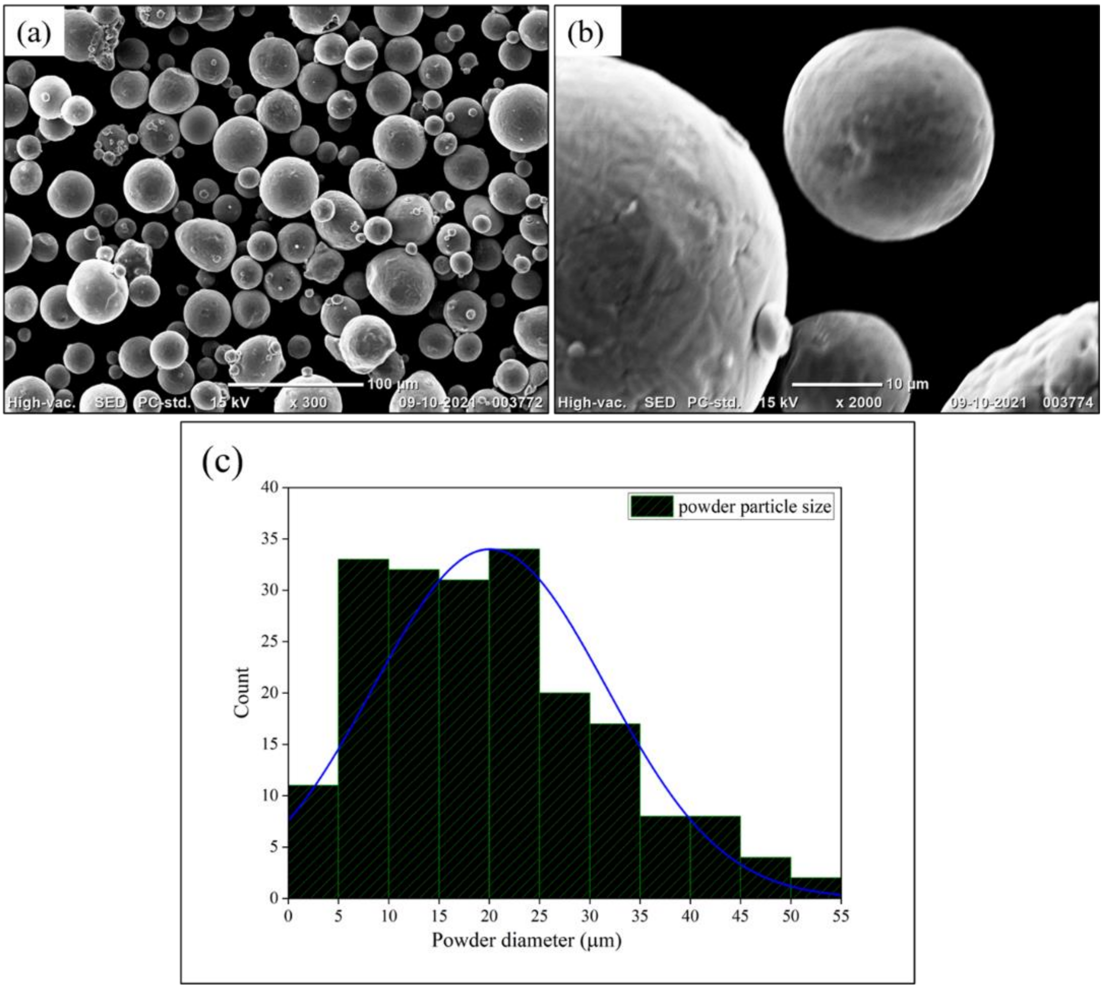

Figure 2.1 Gas atomized Ti-6Al-4V powder: (a) SEM image of particle distribution (X300), (b) surface morphology of powder particle (X2000), and (c) powder particle size distribution of Ti-6Al-4V alloy

During the process, the power of laser was 340 W and the spot diameter was 80 µm. The scan rotation angle (angle between the scan directions in successive layers) and layer thickness were taken as 67° (Figure 2.2a) and 60 µm, respectively. To mix the influence of melt pools, scan lines are inclined in each layer so that the melt pool direction is not the same. The scan rotation angle is usually chosen as 67° because in this way scan directions will not repeat for a large number of layers, providing reduced anisotropy for the product. For this study, the energy density used was 37.78 J/mm^3. The processing parameters were same for building all the components. The process was performed in a protective argon atmosphere and the test samples were cut from the additively manufactured components by wire electric discharge machining (WEDM). The energy density is calculated as:

$$E = \frac{P}{v * h * t} \qquad (1.1)$$

where E is the required energy density, P the laser power, v the scan speed, h the hatch distance, and t is thickness of the layer.

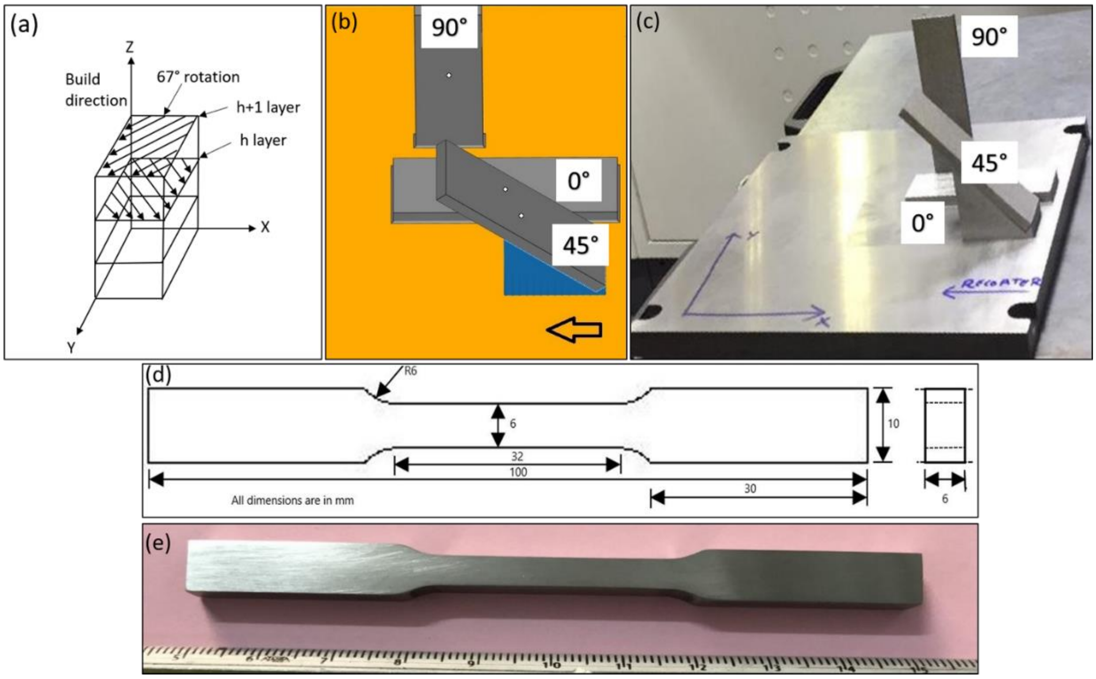

Figure 2.2 Additive manufacturing of samples: (a) Scanning strategy of the L-PBF process, (b) CAD model of fabricating components, (c) as-built components on the build plate used in this research fabricated in three different build orientations of 0°, 45° and 90°, (d) dimensions of the tensile test specimen according to ASTM E8 standard, and (e) heat treated tensile test specimen

2.1.2 Heat treatment

Heat treatment is required after L-PBF process, especially for the components of large sectional size. After building the plates by L-PBF, tensile test specimens were cut with the help of the WEDM process. The tensile test specimens were divided into two sets— the as-built (AB) and the heat-treated (HT). Some tensile specimens were heat-treated at 800 °C for 1.5 h in an argon atmosphere and then cooled in furnace to relieve the residual stress induced during fabrication by the L-PBF process. The heat treatment temperature was suggested by the manufacturer of L-PBF printer (EOS) and was also used by Ren et al. [15].

2.1.3 Morphological analysis

To measure the density of solid components, Archimedes' principle was used which states that when a solid body is immersed in liquid, it experiences a buoyant force acting upward and the magnitude of this force is equal to the weight of the liquid displaced by the solid part. The density of a solid part depends on the weight of the solid part in air, weight of the solid part in liquid, density of the liquid, and density of air [168]. It can be estimated from the following formula:

$$\boldsymbol{\rho_{solid}} = \frac{\boldsymbol{w_{air}}}{\boldsymbol{w_{air}} - \boldsymbol{w_{liquid}}}\left(\boldsymbol{\rho_{liquid}} - \boldsymbol{\rho_{air}}\right) + \boldsymbol{\rho_{air}} \quad \text{.........(2.2)}$$

where ρ_{solid} is density of the solid body, ρ_{air} is the density of air, ρ_{liquid} is density of the liquid, w_{air} is weight of the solid part in air and w_{liquid} is weight of the solid part in the liquid. The surface roughness of the heat-treated components built in three different build orientations by the L-PBF process was measured on a 2D profilometer (Model: Taylor Hobson, Make: Ametek, UK) machine.

2.1.4 Microhardness

Microhardness was measured with the help of a semiautomatic microhardness tester. It measured Vickers hardness values using a diamond pyramid indenter applying a load of 200 g for a dwell time of 10 s.

2.1.5 Residual stress

During the AM process, residual stress is generated in the components after almost every layer. Residual stress has been measured using an XRD system (Model: Empyrean material research diffractometer (MRD), Make: Panalytical) with Co-Kα radiation at 2θ of 71.225º with a step size of 0.07º and time per step of 3.5 s. For this measurement, the range of angle was taken as 0 to 40º at a step of 8°. To calculate the residual stress, the software "Stress Plus" provided by the Malvern Panalytical was used.

2.1.6 Microstructure analysis

The samples of AB and HT types of each build orientation, were mechanically polished with SiC abrasive papers of 1000, 1200, 1500, and 2000 grit and then were cloth polished using a diamond paste, and etched with solution of 100 ml distilled water, 6 ml HNO_3, and 2 ml HF to reveal the microstructure [169]. Initially, microstructure characterization of the fabricated components in three different build orientations was performed with light optical microscope (Dewinter, classical PL) and then with a high-resolution scanning electron microscope (SEM) (Nova Nano SEM 450) equipped with energy dispersive spectrometer (EDS) (Team Pegasus Integrated EDS-EBSD with Octane Plus and Hikari Pro) for finding out the elemental distribution in the relevant phases.

Electron backscatter diffraction (EBSD) analysis was done on different samples. After polishing, the samples were electropolished in 80% methanol and 20% perchloric acid at –20° C at 12V for 15s, following that EBSD was carried out on the EFI Quanta 3D field emission gun (FEG) system for the micro-texture characterization. A Rigaku Miniflex 600 X-ray diffraction (XRD) system with Cu (Kα) radiation within the angular range (2θ) of 30º - 90º at the scan rate of 5º/min was used to check the peaks and characterize the phases of the different components.

2.1.7 Mechanical properties

Tensile specimens were cut by the WEDM process from the fabricated components as shown in Figure 2.2 (c) as reported by Ren et al. [15]. Two tensile specimens of type AB and two of type HT were prepared from the rectangular pieces of 0°, 45°, and 90° orientations. For building at 45°, a support structure was provided. The 90° tensile specimen consisted of 1700 layers whereas 0° and 45° oriented specimens consisted of 200 and 1203 layers, respectively. The dimension of the tensile specimen was as per the ASTM E8/E8M standard with 100 mm length, 10 mm width, and 6 mm gauge thickness as shown in Figure 2.2 (d and e). Some specimens were heat-treated at 800 °C for 1.5 h in an argon atmosphere to eliminate the residual stress, and were cooled in furnace, as also discussed by Yan et al. [63]. These tensile specimens have been designated as “Heat-treated”. The other specimens have not been stress relieved and these are designated as “as-built”.

Testing of all the tensile specimens was carried out on an INSTRON 8801 universal testing machine (100 kN load cell) at room temperature and a uniform rate of displacement of 1 mm/min and as per the ASTM E8 standard. Yield strength (YS), ultimate tensile strength (UTS), and elongation at failure were determined. The fracture surfaces were characterized using the JEOL (JCM-6000PLUS) SEM operated at 15 kV.

2.2 Surface characteristics of additively manufactured Ti-6Al-4V alloy

2.2.1 Surface grinding experimental setup

The AM Ti-6Al-4V samples have been cut into small pieces for grinding purposes. For experimental studies, the dimensions of the workpiece for the grinding samples have been taken as 30 × 20 × 6 mm as the length, width, and thickness, respectively. The experimental setup is presented in Figure 2.3 in which force measurement equipment (to measure the force) and cryogenic nozzle (to supply liquid nitrogen during the experiment) are connected. The cryogenic grinding experimental setup consists of flat spray nozzle (Spraytech Systems India Pvt. limited), nitrogen gas cylinder, pressure gauge, pressure regulator and Dewar (TA-55). These are clubbed together with stainless steel pipe. Nitrogen gas was supplied into a Dewar (liquid nitrogen storage container) until a sufficient pressure, in this study, 2 bar, to deliver liquid nitrogen continuously to the grinding zone. During grinding, the liquid nitrogen pressure effectively cools and lubricates the top surface of the sample. The experiments were conducted on 455H HMT surface grinder shown in Figure 2.3 under dry, wet, and cryogenic environments. Aluminum oxide grinding wheel of diameter of 250 mm and width of 20 mm was utilized during the grinding process. A flat spray type nozzle of 3 mm outlet diameter has been used for cryogenic grinding. The stand-off distance of 50 mm remains constant for all the experiments in order to effectively penetrate the liquid nitrogen into the grinding zone, as mentioned in the inset of Figure 2.3. The grinding parameters are enlisted in Table 2.3.

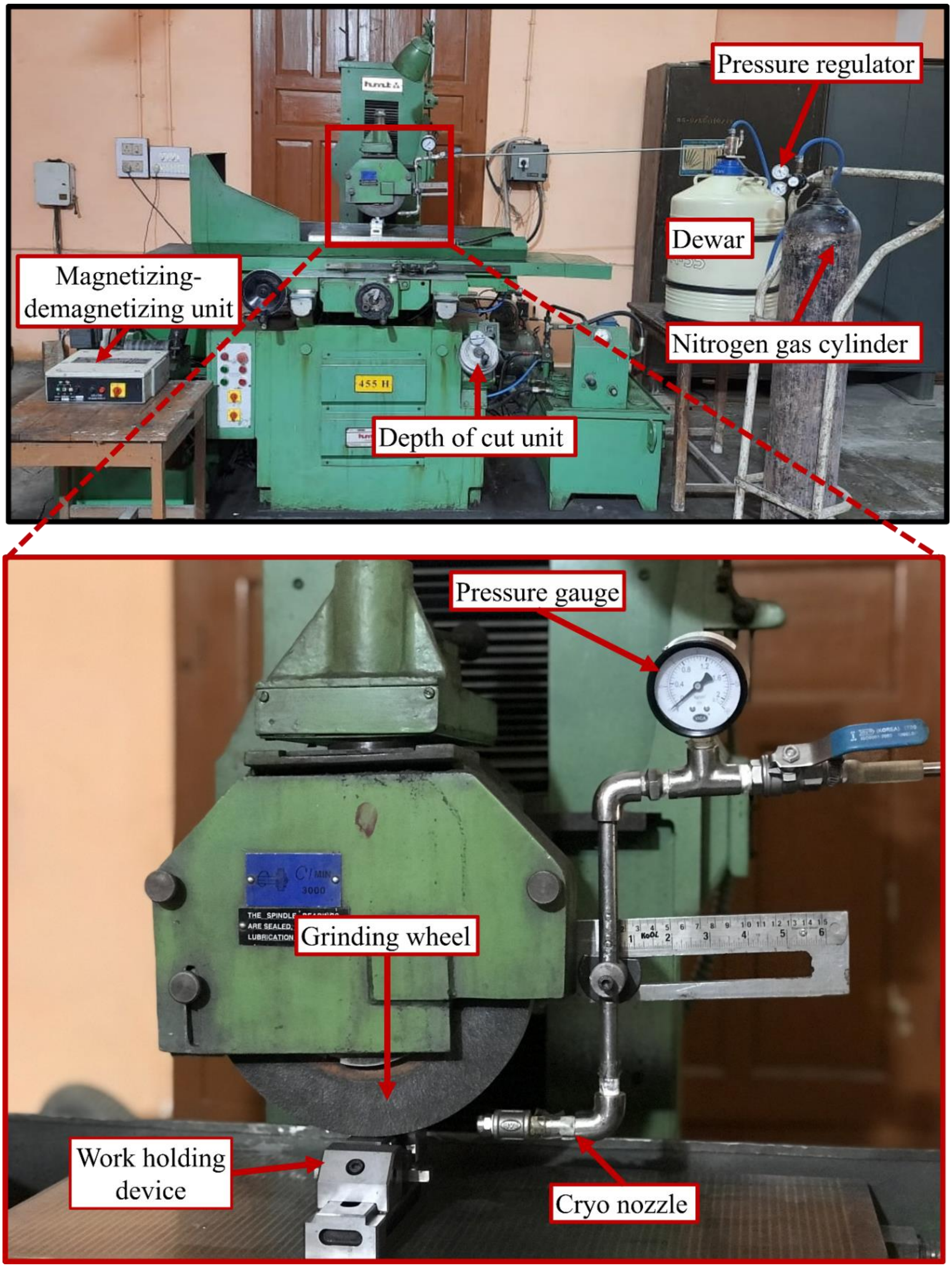

Figure 2.3 Grinding experimental setup with cryogenic attachment for finishing of the AM and conventional samples

Table 2.3 Experimental operating parameters during grinding process

Parameters	Conditions
Mode of grinding	Surface grinding
Grinding wheel	Aluminum oxide (AA60K5V6)- 250 × 20 × 76.2 mm
Work piece material	Additively manufactured Ti-6Al-4V (427.806 ± 20 $HV_{0.2}$) and conventionally manufactured Ti-6Al-4V (363.13 ± 4.34 $HV_{0.2}$), and heat-treated;
	Dimension: 40 mm (length) x 20 mm (width) x 20 mm (thickness)
Grinding environments	Dry, Wet (moist), and Cryogenic
Wet fluid	Water-based soluble oil
Cryogenic fluid	Liquid nitrogen (LN_2)
Wheel speed	39.42 m/s (constant)
Table speed	7, 10, and 13 m/min
Depth of cut (DOC)	10, 20, 30, and 40 µm
Dresser	Single-point diamond

2.2.2 Microstructure of AM and conventional samples before grinding operation

The as-fabricated L-PBF components were heat-treated at 800°C for 1.5 h and cooled in furnace to transform martensitic α′ phase (Figure 2.4 (a)) into α and β phases to diminish the high residual stresses induced during additive manufacturing. After HT, the martensitic α' structure is converted into α and β phases as shown in Figure 2.4 (b). Also, the conventionally processed samples were subjected to the heat treatment. Although HT reduces the residual stresses of the AM fabricated components, it does not enhance the surface finish of the AM components. The microstructure of AM components is different from that of conventionally processed one. In conventional Ti-6Al-4V, equiaxed α with intergranular β phase forms, as shown in Figure 2.4 (c). The heat-treated samples fabricated by conventional process showed equiaxed grains (Figure 2.4 (d)). The as-fabricated specimens by AM and conventional process were mechanically polished on different grades of emery papers and finally on cloth polishing using diamond paste. The polished specimens were etched using Kroll's reagent to reveal and analyse the microstructure.

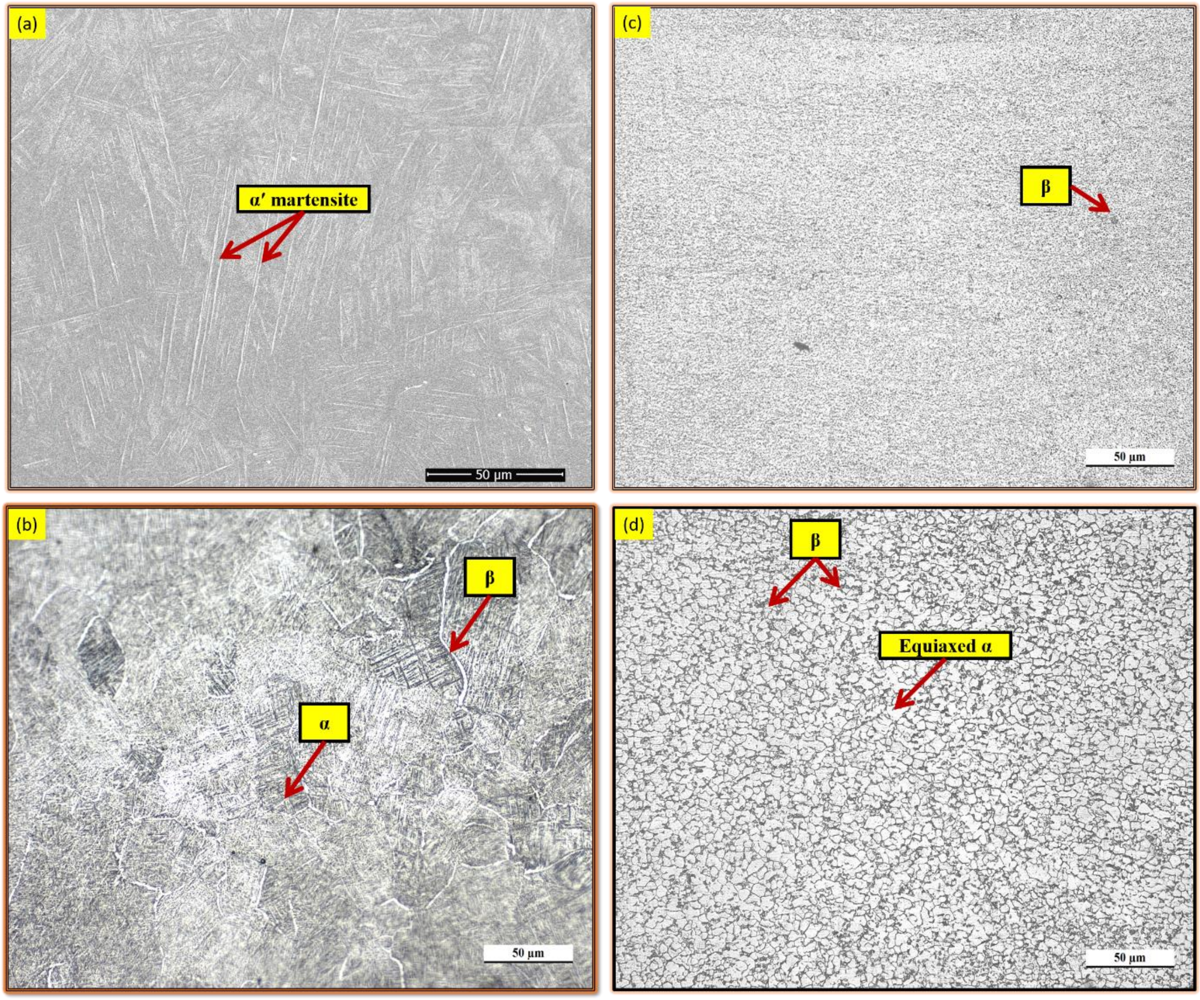

Figure 2.4 (a) SEM micrograph of as-fabricated AM, (b) optical micrograph of HT AM, (c) optical micrograph of conventionally processed and (d) optical micrograph of heat-treated conventionally processed specimen

2.2.3 Grinding forces

For the measurement of grinding forces, a three-dimensional force dynamometer was used and attached to a magnetic chuck, and the components were positioned.

2.2.4 Temperature

The FLIR E75 thermal camera was employed to detect the grinding temperature during the process under different grinding environments. The emissivity of the thermal camera has been taken as 0.34 as per published literature for additively manufactured Ti-6Al-4V workpiece material [170, 171]. The thermal camera was fixed at a distance of 600 mm from the grinding zone using a tripod after performing number of experiments to optimize the distance between the workpiece and the camera for proper focus on the grinding zone.

2.2.5 Surface roughness after finishing

A 2D profilometer (Taylor Hobson (Ametek, UK)) machine has been utilized to measure the initial and final surface finish of the AM samples. The surface roughness has been evaluated at least three times across the direction of grinding, and the average of those values has been provided.

2.2.6 Surface morphology and grinding chip morphology

To investigate the characteristics of the grinding surface, the samples were cut by using WEDM with optimized parameters to avoid thermal deformation. The surface morphology of the grinded surface and the grinding chip morphology were analysed by JEOL (JCM-6000PLUS) SEM operated at 15 kV. In addition to this, the 3D surface morphological characteristics of the grinding surface were evaluated by AFM (NTEGRA Prima, NT-MDT Service & Logistics Ltd.).

2.2.7 Microhardness

Microhardness of the AM samples and grinding samples was measured by a microhardness tester with a 200 g load and 10 s dwell time at three different places, and the average of those values has been provided.

2.3 Corrosion behaviour of additively manufactured Ti-6Al-4V alloy

2.3.1 Corrosion experimental setup

The experimental setup for corrosion test is shown in Figure 2.5.

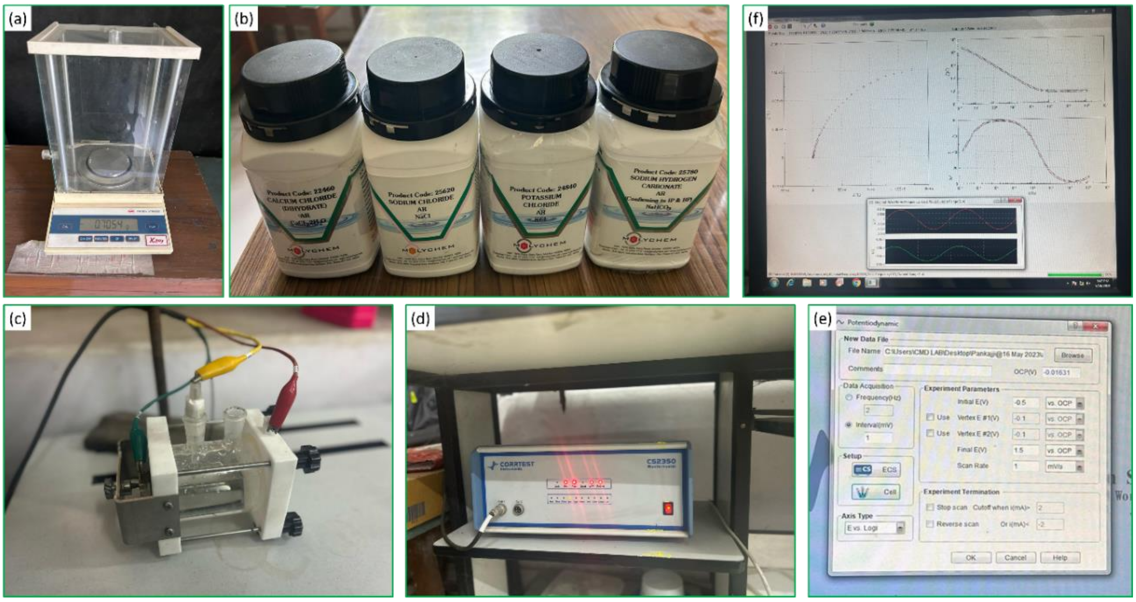

Figure 2.5 (a) Weighing machine to measure the exact weight of powders used for making Ringer solution, (b) Different powders used for ringer solution, (c) Corrosion cell equipped with three electrodes, (d) corrtest instrument, (e) experiment parameters used in corrosion test, and (f) EIS vs. frequency plot during corrosion test

2.3.2 Corrosion rate measurement

Polarization measurements were carried out using a typical corrosion cell equipped with three electrodes including the test sample as the working electrode, a counter electrode (platinum), and a saturated calomel (Hg_2Cl_2) electrode (SCE) as the reference electrode.

Prior to polarization experiment, the Open Circuit Potential (OCP) was allowed to stabilize for about 1800 s. Polarization scans were performed at a scan rate of 0.5 mV/s ranging from −300 mV versus OCP to 500 mV versus OCP. For the electrochemical testing, a PARSTAT 3000A (Make: AMETEK) corrosion test instrument was utilized. To ensure repeatability of the corrosion results, all tests were performed twice. The corrosion current (i_{corr}) and corrosion potential (E_{corr}) measurements were performed using Tafel extrapolation technique. All the experiments were performed in Ringer's solution consisting of 9 g NaCl, 0.24 g $CaCl_2$, 0.43 g kCl, and 0.2 g $NaHCO_3$ in 1000 mL distilled water.

2.3.3 Electrochemical impedance spectroscopy (EIS)

For EIS measurements, experiment was performed with Corr Test Instrument (supplied by Corr Test Instruments Corp., Ltd., Wuhan, China) in Ringer's solution at frequency range of 0.01 to 100 kHz. The impedance and phase angles were measured at each frequency, and based on that of the Bode and Nyquist diagrams were plotted. To make sure the repeatability of corrosion test data, all the tests were repeated at least three times. After collecting the EIS plots, the data were analysed with the ZView software to generate an equivalent circuit. Using a simple fitted model, a suitable equivalent electrical circuit (EEC) model was generated from the real and imaginary parts of the collected impedance information [172]. In this study, the constant phase element (CPE) model was utilized to characterize the majority of samples [89, 173]. A constant phase element is a hypothetical electrical element that is used to model the behaviour of electrochemical interface. CPE's impedance exhibits a constant phase behaviour over a range of frequencies. The solution resistance (R_s), CPE_1 and CPE_2 are obtained from the EIS curves and tabulated.

2.3.4 X-ray photon spectroscopy (XPS) analysis

X-ray photon spectroscopy (XPS) (Model: K_α XPS, Make: Thermo Fisher Scientific) fitted with a monochromatic (1486.6 eV) radiation source established at 150 W was employed to analyse the chemical composition and observe the HT effect on the evolution of oxide layers on AM sample surfaces, as well as to identify the prominent peaks on the surface of the samples. The detection region selected for XPS analysis was 4 × 4 µm. The elements present on the surface of the oxide films were analysed by XPS Avantage software. The XPS spectrums of the surface layer of corrosion samples of AB and HT conditions were obtained. After corrosion tests, the sample surfaces were examined using a SEM (EVO-SEM MA15/18, CARL ZEISS MICROSCOPY) with 51N1000 EDS (Oxford Instruments Nanoanalysis) system operated at 20 kV voltage to evaluate the potential pits.

2.4 Wear and biological behaviour of additively manufactured Ti-6Al-4V alloy

2.4.1 Wear experimental setup

Samples were cut from the as-built and heat-treated samples built in different orientations for wear test. The variation of residual stresses, microstructures and variation in hardness have been thoroughly discussed in our previous work [174]. Dry rotary wear tests were conducted on a ball-on-disc tribometer (Model: DUCOM POD) with diameter of 10 mm zirconia counter ball. An experimental setup of pin-on-disc machine with enlarge view is presented in Figure 2.6 (a). A zirconia ball attached in the ball holder is presented in Figure 2.6 (b). A schematic diagram of the ball-on-disc measurement is presented in Figure 2.6 (c).

Ball-on-disc measurement has been preferred due to high accuracy of the measurement and high contact pressure between ball and disc. The zirconia ball with hardness of ~ 1200 HV was used to avoid the chemical reaction between ball and disc during wear test. Before wear test, conventional and additive manufactured samples were polished with emery papers of grit sizes 600, 1000, 1200, and 1500, followed by cloth polishing with diamond paste to maintain the surface roughness (R_a) of 0.052 – 0.061 µm. In this study, wear tests were performed under normal loads of 5 N and 25 N with sliding velocities of 382 rpm and 891 rpm to investigate the effect of build orientation and heat treatment on the comprehensive tribological behaviour of the L-PBF processed alloy. The test parameters are listed in Table 2.4.

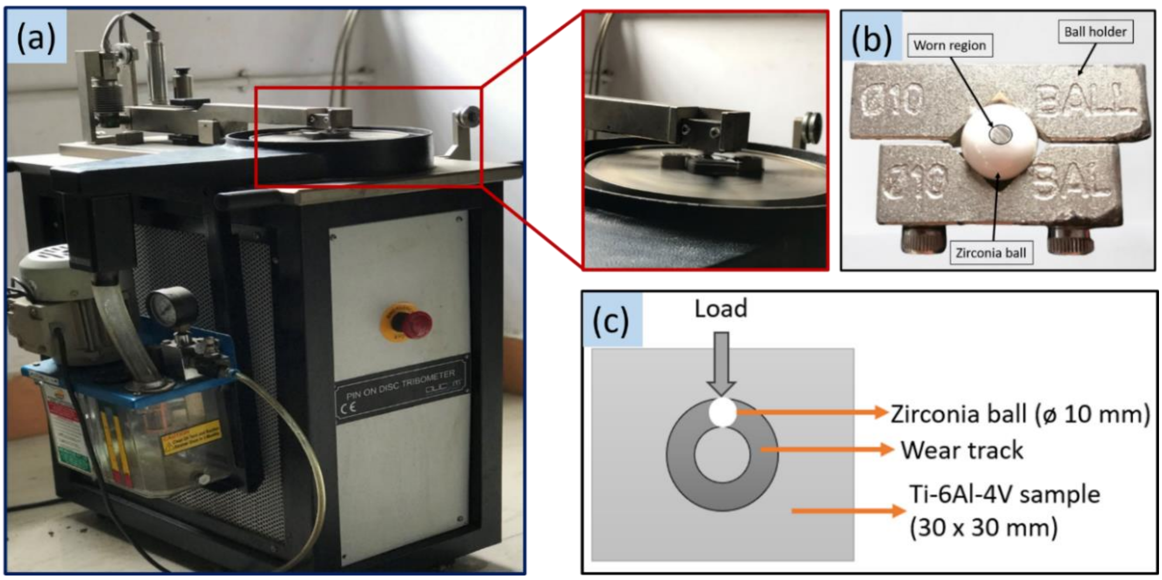

Figure 2.6 Experimental setup (a) for wear test with enlarge view of red rectangular position, (b) zirconia ball fixed on ball holder with wear mark shown, and (c) schematic diagram of ball-on-plate measurement

Table 2.4 Conditions of the dry rotary wear tests used for this investigation

Parameters	Conditions
Workpiece sample	Conventional, L-PBF as-built and heat-treated 0°, 45°, 90° orientation samples
Normal load (N)	5, 25
Sliding velocity (rpm)	382, 891
Ball diameter (mm)	10 (fixed)
Track radius (mm)	15 (fixed)

The worn volume of wear samples was measured by weighing the initial and final weight of samples using weighing machine with least count of 0.0001 g (Model: K-EA 200, Make: K.Roy instrument Pvt. Ltd.). For each condition, the experiments were repeated three times to confirm the reproducibility of results. The wear scar widths were measured using SEM and for each sample, measurements were taken at least three different positions and the average value was reported. The worn surface morphology of conventional and L-PBF processed samples, as well as counter surface of zirconia ball were characterized by high resolution SEM (Model: Nova Nano SEM 450, FEI Company of USA (S.E.A.) PTE, LTD) attached with energy dispersive X-ray spectrometer (EDS). The presence of TiO_2 formed on the worn surfaces was analyzed by high resolution Raman spectroscopy (Model: Alpha 300, Make: WiTech Germany) with an excitation wavelength of 532 nm.

2.4.2 Biological test

All samples with a dimension of 10 mm diameter and 6 mm height were used for the cell culture investigation. The L-PBF Ti-6Al-4V samples were cleaned in an ultrasound bath with acetone, ethyl alcohol, and deionized water for 60 min prior to biological evaluation. After that, the samples were dried and sterilized at 121°C for 20 min in an autoclave. The human osteosarcoma cell line named MG-63 were utilized to investigate the biological effect on the L-PBF Ti-6Al-4V alloy. The cells were maintained at 37°C in a humidified 5% CO_2 incubator (Galaxy® 170 S, Eppendorf, Germany) using Dulbecco's modified eagles medium supplemented with 10 % fetal bovine serum and 1% penicillin (10,000 U ml^{-1})/streptomycin (10 mg ml^{-1}) (PS).

The assessment was performed on the L-PBF fabricated Ti-6Al-4V samples placed in a 35 mm petri dish, as per the standard procedure. The samples were sterilized by using an autoclave. MG-63 cells were seeded with a density of 400 cells on each sample and incubated at 37°C and 5% CO_2. The samples were cultured till day 3. For staining, media was removed from each petri dish and washed thrice with PBS. The sample was fixed with 4 % para-formaldehyde. Further, Triton-X was added for 5 min. To block non-specific binding, 1 % BSA in PBS was added. Finally, rhodamine-phalloidin was added and incubated for 1 hour, followed by DAPI (1 µg/ml) incubated for 30 min in the dark region. All the entire experiments were repeated thrice to ensure the reproducibility of the results.

With the above materials and methods on mechanical, corrosion, and biological behaviour of additively manufactured Ti-6Al-4V alloy, results and discussion of microstructure and mechanical properties of AM fabricated Ti-6Al-4V alloy has been discussed in chapter 3.