Mechanical, Corrosion, and Biological Behaviour of Additively Manufactured Ti-6Al-4V Alloy

Thesis submitted in the partial fulfilment for the

award of degree

Doctor of Philosophy

By

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Pankaj Kumar Singh

DEDICATED

To

My Teachers

&

My Beloved Family Members

ABSTRACT

Titanium based Ti-6Al-4V is the most common alloy, having a high strength to weight ratio and good corrosion resistance, which is suitable for aerospace and biomedical applications. This alloy is kept in a difficult-to-cut material category because of poor thermal conductivity and low elastic modulus. Therefore, additive manufacturing of Ti-6Al-4V alloy has become popular in fabricating complex and customized components in the fields of aerospace and biomedical devices. But, one of the most difficult aspects of additive manufacturing is fabrication of components with reproducible metallurgical and mechanical properties in different build orientations.

In this work, one of the additive manufacturing processes called Laser-Powder Bed Fusion (L-PBF) process has been used to fabricate Ti-6Al-4V components in 0°, 45°, and 90° build orientations. The as-built components have been 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 combined effect of build orientation and heat treatment on surface roughness, residual stress, microstructure, tensile properties, corrosion, wear, and biological behaviour has been examined on the L-PBF Ti-6Al-4V samples. In the as-built condition, the 0° build-oriented flat sample exhibited high tensile strength (1202 MPa) as well as high microhardness (481 HV), but low ductility due to the presence of fine acicular α' martensite. The 90° build-oriented samples had the largest elongation of 8% and high tensile residual stress of 163 MPa. After heat treatment, the α′ martensitic phase transforms into α and β phases, therefore, 0° build oriented samples showed the largest ductility (10.8%) and highest tensile strength (1081 MPa).

Surface grinding setup has been used to finish the L-PBF Ti-6l-4V samples under dry, wet, and cryogenic environments and found that the surface roughness under cryogenic condition can offer a better surface finish (reduced from 5.94 µm to 0.259 µm). Corrosion

tests have been carried out in Ringer's solution by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) analyses have been done on the surface of corroded samples. In as-built samples, the corrosion rate decreases when build orientation increases from 0° to 90°. The heat-treated samples showed higher corrosion resistance than the as-built samples. After heat treatment, the corrosion rate of L-PBF Ti-6Al-4V samples is comparable with conventionally manufactured Ti-6Al-4V samples.

Dry rotary wear test has been performed on L-PBF Ti-6Al-4V samples to study the effect of build orientation and heat treatment, at different sliding velocities and loading conditions. The wear rate exhibited by the heat-treated samples was lower than those of respective as-built samples but comparable with those of conventional samples. Biological test has also been carried out on the L-PBF fabricated Ti-6Al-4V samples by using human osteosarcoma cell line named MG-63. Maximum number of cells were found to adhere on the 45° oriented samples, followed by 0° oriented sample and lowest number of cells were adhered on the 90° oriented samples. This study points out the necessity of considering build orientation as an important variable in the process of optimization.

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AB	:	As-built
AFM	:	Atomic force microscopy
AM	:	Additive manufacturing
ASTM	:	American society for testing and materials
CAD	:	Computer aided design
CLA	:	Centreline average
COF	:	Coefficient of friction
CPE	:	Constant phase element
Cryo	:	Cryogenic
DED	:	Direct energy deposition
DMLS	:	Direct metal laser sintering
DOC	:	Depth of cut
EBM	:	Electron beam melting
EBSD	:	Electron backscatter diffraction
EDS	:	Energy dispersive spectrometer
EEC	:	Equivalent electrical circuit
EIS	:	Electrochemical impedance spectroscopy
EOS	:	Electro optical system
HCP	:	Hexagonal close-packed
HMT	:	Hindustan machine tool
HT	:	Heat-treated
L-PBF	:	Laser-powder bed fusion
OA	:	Orientation angle
OCP	:	Open circuit potential
PBF	:	Powder bed fusion
SCE	:	Saturated calomel electrode
SEM	:	Scanning electron microscopy
SGE	:	Specific grinding energy
SHS	:	Selective heat sintering
STL	:	Standard tessellation language
SLM	:	Selective laser melting
UTS	:	Ultimate tensile strength

WEDM	:	Wire electric discharge machining
XPS	:	X-ray photoelectron spectroscopy
XRD	:	X-ray diffraction
YS	:	Yield strength
E_{corr}	:	Corrosion potential
E_w	:	Equivalent weight
FWHM	:	Full width at half maximum
$FWHM_{\_O}$	:	Full width half maximum at initial condition
$FWHM_{\_F}$	:	Full width half maximum after finishing condition
I_{P_O}	:	Peak intensity at initial condition
I_{P_F}	:	Peak intensity after finishing condition
i_{corr}	:	Corrosion current
LN_2	:	Liquid nitrogen
R_a	:	Average surface roughness for 2D profile
R_{ct}	:	Charge transfer resistance
R_s	:	Solution resistance
R_p	:	Polarization resistance
S_a	:	Average surface roughness for 3D profile
S_q	:	Root means square surface roughness
V_t	:	Table speed
χ^2	:	Chi-square
Z	:	Impedance
ρ	:	Density
v	:	Scan speed
P	:	Laser power
E	:	Energy density
h	:	Hatch distance
t	:	Thickness of layer

PREFACE

Titanium based Ti-6Al-4V is the most common alloy, having a high strength to weight ratio and good resistance to corrosion, which is suitable for aerospace and biomedical applications. This alloy is kept in a difficult-to-cut material category because of poor thermal conductivity and low elastic modulus. The growing interest of using Ti-6Al-4V alloy in biomedical application is primarily due to a combination of suitable mechanical properties, exceptional biocompatibility, desired compressive strength, and good corrosion resistance because of oxide films formed on the surface compared to other metallic materials. Several Ti-6Al-4V products are produced effectively through Additive Manufacturing (AM), which is a process of making three-dimensional (3D) components through computer-aided design (CAD) model by depositing the materials in a layered fashion, feeding the material in the form of either wire or powder, and using various melting sources available such as a laser beam or an electron beam.

Design freedom for making complex components and no tooling cost has made the AM popular in recent years. AM processes have made an entry in aerospace, automobile, and biomedical sectors for making customized products. According to ISO/ASTM standard, AM systems can be categorized into seven subcategories. For Ti-6Al-4V material, there are two types of AM systems — powder bed fusion (PBF) and powder feed (directed energy deposition or DED). The PBF class includes selective laser melting (SLM), direct metal laser sintering (DMLS), electron beam melting (EBM), and selective heat sintering (SHS). For all these techniques, the term laser-based powder bed fusion (L-PBF) is recommended by ISO/ASTM standards.

In a L-PBF process, a required layer of the Ti-6Al-4V powder is applied to the build platform and the laser beam fuses the powder at selective points as per the computergenerated data. The build platform is then lowered, equal to the layer thickness, and another layer of powder is spread out. The material is then fused to form bonds with the layer beneath at predetermined points. This process continues until the component is fully built. To know the performance of L-PBF process, one must understand the microstructure evolved in the process. During fabrication of the Ti-6Al-4V component by L-PBF process, due to the high rate of cooling, the α' martensitic phase completely dominates the microstructure. This α' martensitic phase can transform into $\alpha+\beta$ phases during the heat treatment process.

In this work, Ti-6Al-4V samples have been fabricated by Laser-Powder Bed Fusion process in different orientations (flat, inclined, and upright). Most of the earlier studies are focussed on fabrication and characterization of L-PBF Ti-6Al-4V components with build direction parallel and perpendicular to thickness and only limited studies have been carried out on inclined orientations. Moreover, the combined effect of build orientation and heat treatment of the L-PBF components on their microstructure and mechanical properties has been less explored. Thus, it is essential to carry out systematic investigation on microstructure, mechanical properties, surface characteristics, corrosion, wear, and biological aspect of the specimens of Ti-6Al-4V alloy for biocompatibility with different build orientations in as-built and heat-treated conditions for proper inception of L-PBF as a potential process of manufacturing.

In the present thesis, components of the Ti-6Al-4V alloy have been fabricated by L-PBF process with different build orientations (flat, inclined, and upright) and also subjected to heat treatment for relieving the associated stresses induced in the fabricated components. In this investigation, microstructures, tensile properties, corrosion, wear, and biological aspect of the as-built and heat-treated L-PBF Ti-6Al-4V components, fabricated with three different orientations of 0°, 45°, and 90° have been studied and the effect of heat treatment has also been discussed. The obtained results contribute to a better understanding of build orientation and heat treatment effect (especially for inclined component) on mechanical and metallurgical behaviour of L-PBF Ti-6Al-4V components used in aerospace and biomedical fields.

Following research objectives are drawn for current study:

1. Fabrication of Ti-6AL-4V samples by Laser-Powder Bed Fusion process in different build orientations (0°, 45°, and 90°) followed by heat treatment at 800°C for 1.5 h in an argon atmosphere and cooling in furnace.
2. A comprehensive study concerning build orientation and heat treatment effect on the microstructure, residual stress, mechanical properties, and their fracture mechanism of L-PBF produced Ti-6Al-4V alloy.
3. To examine the effect of grinding environments (dry, wet, and cryo) on surface roughness and microhardness of L-PBF Ti-6Al-4V alloy followed by characterization of grinded surfaces.
4. To evaluate the corrosion behaviour of L-PBF Ti-6Al-4V alloy with potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS) tests followed by characterizations of corroded samples.
5. To evaluate the wear and biological behaviour of L-PBF Ti-6Al-4V alloy fabricated in different build orientations.

The thesis work has been divided into seven chapters as given below:

Chapter 1: This chapter is divided into three sections in which first section discusses about the additive manufacturing, Ti-6Al-4V material used in the present investigation, and different process parameters used during the additive manufacturing process. The second section introduces the literature review on different additive manufacturing processes and related to several aspects of build orientation and heat treatment effect on metallurgical and mechanical properties of laser-powder bed fusion processed Ti-6Al-4V alloy. This section also includes the literature review on methodologies utilized by various researchers to investigate the different additive manufacturing processes, their findings, and important factors that influence the product characteristics. The third section summarizes the research gaps and objectives based on literature reviews.

Chapter 2: This chapter deals with materials and methods used in this work. This section starts with characterization of Ti-6Al-4V powder, optimized process parameters, and fabrication of components by laser-powder bed fusion process using optimized process parameters, and the heat treatment details have been provided. Following this, details regarding different instruments used to measure and perform metallurgical and mechanical properties have been provided. The details of surface grinding experimental setup and process parameters have also been provided. Corrosion test has also been performed to evaluate corrosion rate and corrosion mechanism on L-PBF Ti-6Al-4V samples. The process parameters used for wear test have also been discussed, followed by the characterization techniques used to evaluate the wear mechanism. In the end, the biological test protocol has been provided to check the biological interaction of L-PBF Ti-6Al-4V samples.

Chapter 3: This chapter comprehensively highlights the results of characterization performed on the effect of build orientation and heat treatment on metallurgical and mechanical properties of L-PBF Ti-6Al-4V samples. Tensile tests have been performed on different samples fabricated in different orientations and fracture behaviour is characterized.

Chapter 4: This chapter elaborates the results of the effect of the grinding environments (dry, wet, and cryogenic) on surface characteristics of L-PBF Ti-6Al-4V alloy. The surface roughness, microhardness, and surface morphology of the finished samples were analysed.

Chapter 5: This chapter deals with the results of corrosion behaviour of L-PBF Ti-6Al-4V alloy fabricated in different build orientations. For corrosion test, potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS) tests were conducted and the results are analysed by X-ray photoelectron spectroscopy (XPS). The corroded surfaces of L-PBF Ti-6Al-4V samples were also examined to understand the corrosion mechanism.

Chapter 6: This chapter elaborates the results related to wear behaviour of L-PBF Ti-6Al-4V alloy fabricated in different build orientations. Wear tests were conducted on pin-on-disc machine setup and results are analysed. Wear rate is measured and analysed by measuring the weight of samples before and after wear test. Microstructural characterization of worn surfaces of counter zirconia ball has also been evaluated. This chapter also deals with the results of the effect of build orientation and heat treatment on biological interaction of L-PBF Ti-6Al-4V samples. Cells were cultured for 3 days and the results are analysed.

Chapter 7: This chapter deals with the major conclusions of this research work and the future scopes. The important findings are mentioned below:

- The **orientation of build component** affects the UTS and elongation at fracture of the L-PBF Ti-6Al-4V. Tensile specimens with 0° build orientation demonstrated good tensile strength of 1202 MPa under as-built (AB) condition. However, elongation was reduced due to the presence of fine acicular α' martensite. Samples with a 90° build orientation showed the largest elongation (8.04 %) at fracture.

- The α′ martensitic phase forms and that transforms into α and β phases during heat treatment. The 0° build orientation tensile specimens showed the highest tensile strength of 1081 MPa and the largest elongation at fracture (10.8%). After heat treatment, slip could transfer across the interface of the α and β phases, and increased the ductility.
- High **residual stresses**, the maximum in the 90º oriented component, are induced in the as-built condition. Heat treatment is needed to avoid any distortion in the components.
- **Cryogenic grinding** contributed significantly to reduction of grinding forces and heat produced in the grinding area, thereby surface roughness was less compared to that from dry and wet grinding.
- **Surface roughness** was improved in cryogenic grinding because of low grinding zone temperature and it was reduced by 27.25% and 23.15% for the AM and 30.08% and 29.13% for the conventional samples in comparison with dry and moist conditions, respectively. Also, it was observed that finished AM Ti-6Al-4V samples had better surfaces than finished conventional samples.
- Fast solidification during the L-PBF process and the formation of martensitic α' phase degraded corrosion resistance of the AB samples as per the results shown by Tafel curves. These findings have been further supported by the EIS test, which showed that the AB samples have a less effective passive protective layer than that resulting from the HT.
- The Tafel curve confirmed that HT samples show superior corrosion resistance than the AB samples because of removal of the residual stress and transformation of α' to

$\alpha+\beta$ phases in the microstructure, following the HT.

- The **corrosion rate** decreases when build orientation increases from 0° to 90° in as-built condition. The AM AB-0° oriented samples exhibit lower corrosion resistance due to finer acicular martensitic phase than AM 45° and 90° samples.
- The **wear rates** exhibited by the heat-treated samples were comparatively lower than those of their as-built counterparts, due to improved wear resistance.
- At low loads and sliding velocities, the maximum wear rate occurs in the 90° orientation, followed by the 0° orientation, while the 45° oriented sample demonstrates the minimum wear rate.
- The surface roughness of L-PBF Ti-6Al-4V samples can have a significant impact on cell culture in context of biomedical applications. In the as-built samples, more cells are adhered on 45° oriented samples, followed by 0°, and minimum cells are adhered on 90° oriented samples. After heat treatment, maximum cells are adhered on 45° oriented samples, followed by 90°, and minimum cells are adhered on 0° oriented samples.

This study highlights the impact of build orientation and heat treatment on the mechanical properties of additively manufactured Ti-6Al-4V alloy, with an emphasis on its suitability for biomedical applications where it is critical for mimicking the elastic modulus of bone material. The AM process provides control over porosity levels, which makes it easier to modify the elastic modulus of the alloy to match with elastic modulus of bone material. Furthermore, comprehensive biological assessments, including cell culture growth, are necessary to determine the biocompatibility and bioactivity of the AM Ti-6Al-4V samples.