

**SURFACE TOPOLOGY AND PROPERTIES OF
3D PRINTED TI-6AL-4V & SS316 L**

BY

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A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

MECHANICAL ENGINEERING

DECEMBER 2021

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
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In the name of Allah, the Most Gracious, the Most Merciful. This study is wholeheartedly dedicated to my beloved parents, who always stood by my side as a strong example of perseverance and have been a source of inspiration and strength to me, to my brothers, and to my colleagues. To all my teachers and professors specially Dr. Bekir Sami Yilbas and Dr. Saad bin Mansoor and Dr. Ihsan Ul Haq Toor, who continually provided their moral support, guidance, skills and power of the mind. I hope to always count on everyone's valuable unconditional support throughout my life and career.

ACKNOWLEDGMENTS

First and foremost, all Praise belong to Allah Almighty alone, The Lord of the Universe and The One who created everything. There is no God worthy of worship except Allah and Prophet Mohammed (Sal'Allahu 'alayhi wsalam) is his last messenger. I express gratitude toward Almighty Allah to favour me with sound wellbeing, strength, wisdom, strong determination, assets of life and to manage me in the best way in my life. I might want to thank the Ministry of Education, Kingdom of Saudi Arabia for giving international students an exceptional chance to dominate and excel in their academic fields. I might likewise want to offer my thanks to KFUPM for an exquisite Fully Funded MS Scholarship program and access to advance facilities and equipment in class and laboratories. KFUPM will consistently be recalled in my sweet memories as a home away from home. I feel thankful to have Dr. Bekir Sami Yilbas as my advisor in Master of Science. I express my wholehearted gratefulness to Dr. Yilbas for his valuable ideas, direction, and important time from his bustling timetables all through my Masters. I truly value his unassuming nature and generosity which kept me agreeable all through the excursion at KFUPM. I think without his unconditional help this work could not have been conceivable. It was an advantage for me to enter the realm of exploration under his direction acquiring the abilities needed in this field. Indeed, I say thanks to him for all his help to date and ideally likewise in my prospects. I

would wind up saying that it is an honour to work under his supervision, it inspired and benefited me from his tremendous experience. I am also grateful to my committee members, Dr. Saad Bin Mansoor, and Dr. Ihasn Ul Haq Toor for their valuable suggestions throughout the thesis work and for improvising the quality of my work by exchanging the ideas. I am also very grateful to my colleagues and fellow students, for their continuous assistance and encouragement in helping me complete my experiments. I would like to take this opportunity to thank all the teachers and faculty for their continuous support, guidance, and advice. My overriding debt is to my parents for their help and motivation needed to complete my Master's degree. Also, a great thanks to my family and friends who tried their best to give to encourage me for keeping up with this task. Lastly, I am grateful to all respondents and different people for their important collaboration and furthermore to the individuals who directly or indirectly helped me during this undertaking. Without the assistance of every one of these respected individuals, I would not have had the option to attempt this thesis effectively. Thank you. Abdul Qadeer

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THESIS ABSTRACT

NAME: Abdul Qadeer

TITLE OF STUDY: Surface Topology and Properties of 3D printed Ti-6AL-4V & SS316 L

MAJOR FIELD: Mechanical Engineering

DATE OF DEGREE: DECEMBER,2021

3D Printing is one of the emerging manufacturing processes. With the advent of progress in metallic powder as processing materials arise many new challenges related to surface and material properties of the printed products. The current study covers the investigation of 3D printed Ti-6AL-4V and SS 316L parts in terms of surface topology and material properties. The parts are printed from Ti-6Al-4V powders by using a powder bed Electron Beam Melting (EBM) while Selective Laser Melting (SLM) was used for Stainless Steel 316L (SS 316L) powders. Hence, the primary objective of the study is to identify surface characteristics and material properties of the 3D Printed parts from Ti and Fe Alloy. The analytical tools are used to assess the wetting characteristics, surface texture, and microstructure of the 3D printed parts. The wetting behavior of the surface is evaluated via performing contact angle measurements using a Goniometer. Two sets of samples are printed in different orientations, which allows exam-

ining the effect of printing direction on the topology of the printed surfaces. Surface energy is also determined through the contact angle method. The surface texture is examined using Optical microscopy. SEM is incorporated to analyze the microstructure of the printed samples. EDS and XRD are used for the assessment of the elemental composition and compound formations. The scratch tests are carried out to determine the hardness and scratch resistance of the 3D printed surfaces. The printed samples are later coated with TiN using the cathodic arc physical vapor deposition method and the tests for the coating failure are conducted.

ملخص الرسالة

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عنوان الدراسة: طبولوجيا السطح وخصائص الطباعة ثلاثية الأبعاد Ti-6AL-4V و L SS316

التخصص: الهندسة الميكانيكية

تاريخ الدرجة العلمية: جمادى الأولى ١٤٤٣هـ

تعد الطباعة ثلاثية الأبعاد إحدى عمليات التصنيع الناشئة. مع ظهور التقدم في مسحوق معدني حيث تظهر مواد المعالجة العديد من التحديات الجديدة المتعلقة بالسطح وخصائص المواد للمنتجات المطبوعة. الدراسة الحالية تغطي التحقيق في 3 أجزاء Ti-6AL-4V و 316L SS المطبوعة من حيث طبولوجيا السطح وخصائص المواد. ال تتم طباعة الأجزاء من مساحيق Ti-6Al-4V باستخدام طبقة مسحوق ذوبان شعاع الإلكترون بينما (EBM) تم استخدام الصهر الانتقائي بالليزر (SLM) لمساحيق الفولاذ المقاوم للصدأ (SS 316L). (316L) ومن ثم ، فإن الهدف الأساسي للدراسة هو تحديد خصائص السطح وخصائص المواد للأجزاء المطبوعة ثلاثية الأبعاد من Alloy Ti و 316L. SS تُستخدم الأدوات التحليلية لتقييم خصائص الترطيب ، والملمس السطحي ، والبنية الدقيقة للأجزاء المطبوعة ثلاثية الأبعاد. الترطيب يتم تقييم سلوك السطح عن طريق إجراء قياسات زاوية التلامس باستخدام مقياس الزوايا. يتم طباعة مجموعتين من العينات في اتجاهات مختلفة ، مما يسمح بالفحص تأثير اتجاه الطباعة على طبولوجيا الأسطح المطبوعة. الطاقة السطحية هي أيضاً تحدد من خلال طريقة زاوية الاتصال. يتم فحص نسيج السطح باستخدام الفحص المجهرى البصري. تم دمج SEM لتحليل البنية المجهرية للعينات المطبوعة. يتم استخدام EDS و XRD لتقييم تكوين العناصر والتكوينات المركبة. يتم إجراء اختبارات الخدش لتحديد الصلابة ومقاومة الخدش للأسطح المطبوعة ثلاثية الأبعاد. يتم تغليف العينات المطبوعة لاحقاً بـ TiN باستخدام طريقة الترسيب الفيزيائي للبخار القوسي والكاثودي ويتم إجراء اختبارات فشل الطلاء.

CHAPTER 1

INTRODUCTION

In recent years, Additive Manufacturing (AM) has grown by leaps and bounds. Nowadays, major industries like automotive, aerospace, biomedical and construction utilize additive manufacturing in one form or the other [6]–[14]. AM industry is estimated to reach the mark of \$100 Bn in the next two decades [15]. AM differs from traditional manufacturing in terms of the core principle; instead of subtracting material and reaching the net shape, material is added layer by layer to reach the final product [16]–[18]. This approach allows the freedom of complexity and level of control that traditional manufacturing lacks [19]–[21]. AM provides greater customization without the need of additional cost or tooling. Weights of the parts can be reduced by topology optimization [22]. Complex internal passages for heat transfer in parts/dies can be produced, which are nearly impossible to achieve using other manufacturing processes [23]–[25]. In Biomedical field, AM helps in fabrication of customized implants considering needs of individual patients [26]–[28]. Compliant mechanisms consisting of single part flexible machines [29]–[31] can be manufactured for aerospace application. AM can produce net shaped parts with zero waste and reduced lead time.

1.1 Historical Background of additive manufacturing

Roots of AM spread back 15 decades to topography and photo-sculpture [32]. In 1860 Willeme created 3D replica of a part using cameras [33]. Later in 1890 Blanthier [34] developed topology maps by layering method. In 1951 Munz [35] proposed stereolithography(SL) by hardening photo-polymer which laid the foundation for modern AM. In 1968 Swainson [36] used laser for hardening in SL similar solidification method for photosensitive polymers was researched at Battelle Laboratories [37]. In 1971 Ciraud [38] introduced partial powder melting using heat source such as laser , plasma or electron. Housholder [39] developed the laser sintering of powder in 1981. Kodama [40] developed rapid prototyping using photo-polymer in the same time and Herbert [41] engineered the computerized control for SL system. In 1986 Hull [42] developed SLS [43] which led way for other free-form manufacturing technologies like DMLS LENS and EBM. 3D printing was introduced by MIT by combining ink-jet head and powder bed machines in 1995. LENS of powder using a nozzle delivery was developed in 90s and licensed in 1997 by Sandia laboratories [44]. LENS is similar to DMD except for the control of machine and process execution and both are subcategories of DED. EBF was developed in 1999 by Martin and

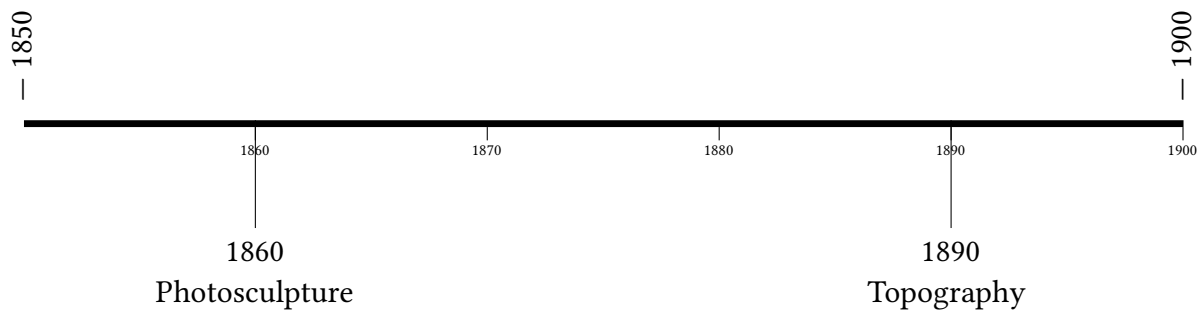


Figure 1.1: Early History

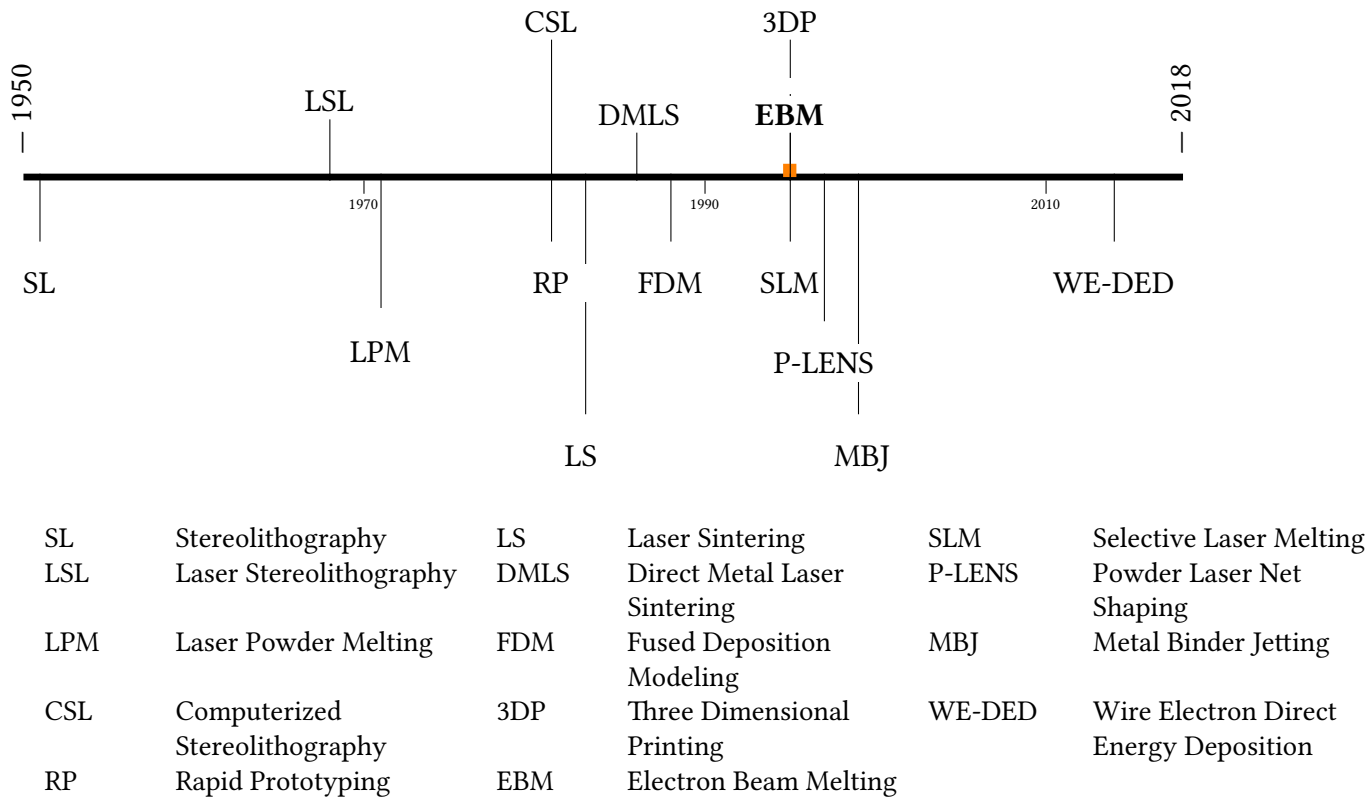


Figure 1.2: Timeline Of Additive Manufacturing

used wire feed [45] [46].

In short, Fusion welding to repair damaged and worn out parts and laser cladding can be considered its precursors. These methods later evolved into free form fabrication. They later gave way to laser engineered net shaping (LENS). DMD introduced wire feed and powder as forms of raw material. At the heart of AM is computer aided design controlling and guiding the tools to finished parts [47].

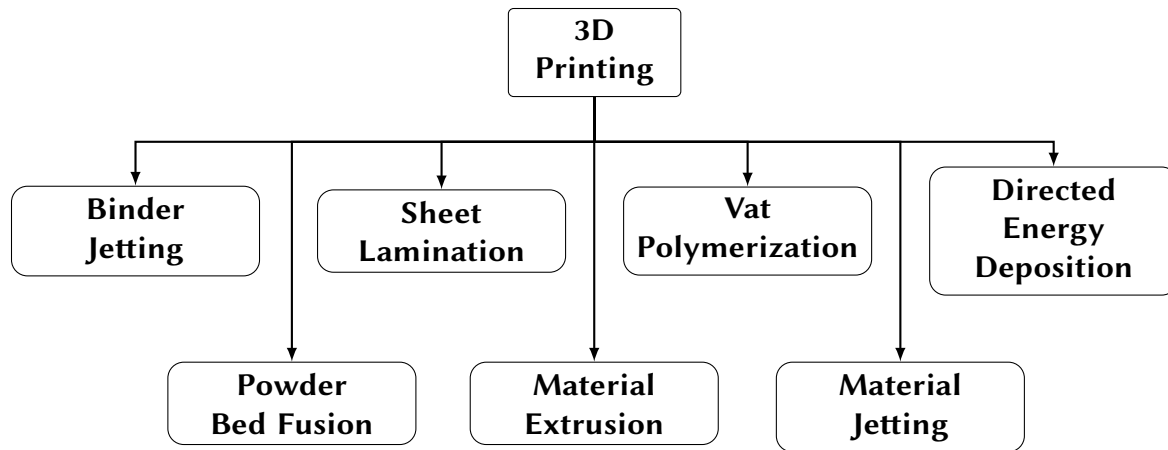


Figure 1.3: AM Process classification(ASTM) 52900:2015

3D printing is a part of additive manufacturing in which the part is manufactured layer by layer. According to ASTM standard 52900:2015 additive manufacturing processes are consolidated under seven different categories as shown in Figure 1.3.

There are many different types of metal 3D printing processes and the most common type is powder based fusion processes. Three widely used metal powder printing processes are Direct Metal Laser Sintering, Selective Laser Melting and Electron Beam Melting. Underlying principle is the same, selective fusion of metallic powder. Raw material is in the form of metal powder which is spread as a layer on the machine bed using a roller. Beam of energy in the form of laser or electron selectively melts and fuses the metallic powder together based on the sliced layers of 3D model of the part. A piston moves the bed down equivalent to the thickness of a single layer. The process is repeated for each layer until the part is finished.

Direct metal laser sintering and selective laser melting both use laser sources for heating the powder but sintering has lesser temperature than laser melting. Laser melting is done in inert gas environments like argon to stop the formation of metallic oxides. Elec-

	DMLS	SLM	EBM
Energy Source	Laser	Laser	Electron Beam
Environment	Nitrogen/Argon	Nitrogen/Argon	Vacuum 10^{-4} – 10^{-5} (mbar)
Scan Speed(m/s)	–	0.3-1.0	Upto 1000
Power(W)	–	120	3500 (varies)
Scan Diameter(μm)	–	30-250	200-1000

Table 1.1: Parameters of DMLS, SLM and EBM [1]

tron beam on the other hand requires vacuum so that beam can travel through the space and reach the specimen. Electron beam has higher power and can achieve higher scanning speeds. Table 1.1 shows the comparison of three techniques values are for commercial machines [1].

1.2 Electron Beam Melting

EBM system works on same principle as an electron microscope. Electron column produces electrons and accelerates them by applying voltage. Scan coils are used to focus the beam on the powder layer. Preheating is done using the beam and the temperature of bed can have substantial effect on the microstructure and phases of the printed parts. Beam is directed based on the slices of the CAD model. Powder melts and forms interconnected pools which cool rapidly and solidify. Solidification occurs in a directional manner giving rise to epitaxial growth [48]. Figure 1.4 shows schematics for ARCAM EBM machine.

Beam energy for electron is given by equation 1.1 and for laser is given by equation 1.2 [47]

$$E_e = \frac{m_e v^2}{2} \quad (1.1)$$

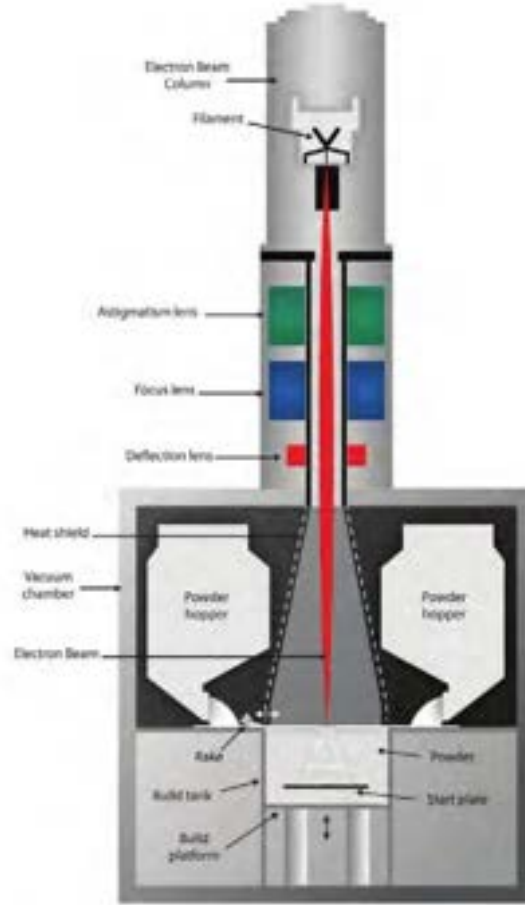


Figure 1.4: EBM Machine schematic (ARCAM) [2]

$$E_l = \frac{hc}{\lambda} \quad (1.2)$$

where:

m_e = Electron mass (kg)

c = Speed of light (m/s)

v = Electron velocity (m/s)

λ = Wavelength (m)

h = Planck's constant ($\frac{m^2 kg}{s}$)

Power Absorption of the surface layer is given by equation 1.3 [47]

$$P_{(s)} \cong 2Q\pi r^2 l \quad (1.3)$$

where:

Q = Power Density (W/m^3)

r = Beam Spot Size (m)

l = Absorption Length (m)

1.3 Selective Laser Melting

Selective laser melting procedure uses energy from laser beam instead of electrons but the underlying principle is similar. Instead of using vacuum inert atmosphere of argon is used

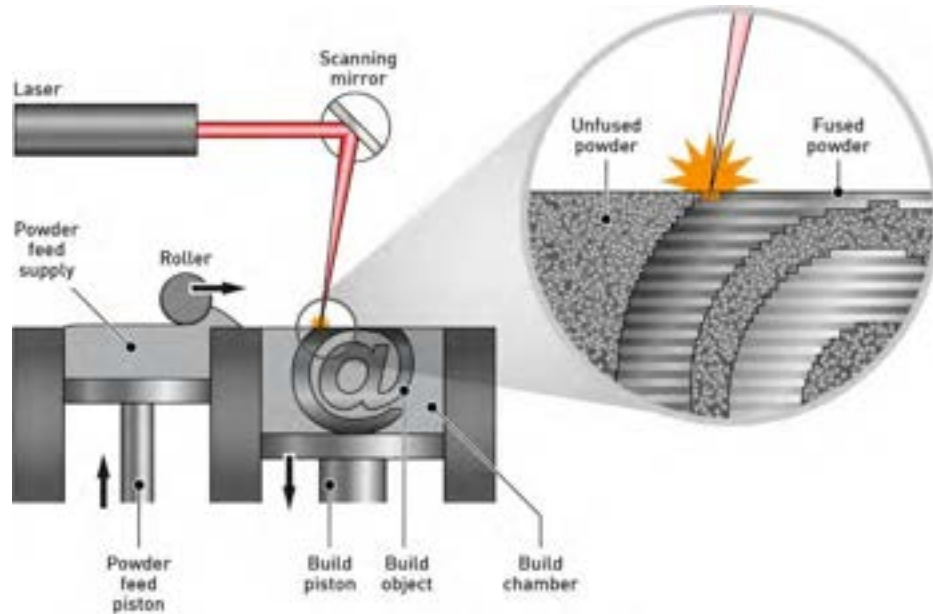


Figure 1.5: SLM Process schematic showing progressive layer formation [3]

to prevent oxidation. Figure 1.5 shows the SLM process. Scanning mirror is used to control the focus location of the laser. Powder is spread using a roller and rake. Energy from laser beam then melts and fuses the powder together and part is manufactured layer by layer. Volumetric energy density from SLM process is given by 1.4 [2]

$$Q_e = \eta \frac{P}{vhl} \quad (1.4)$$

where:

v = Beam velocity (m/s)

P = Beam Power (W)

h = Hatch spacing (m)

η = Absorptance

l = Layer thickness (m)

Q_e = Energy Density (J/m^3)

Properties of 3D printed parts depend on various processing parameters like scanning speed, energy source, powder size and build direction etc. Build direction plays prominent role in the properties of the finished part as some properties show anisotropic behavior. 3D

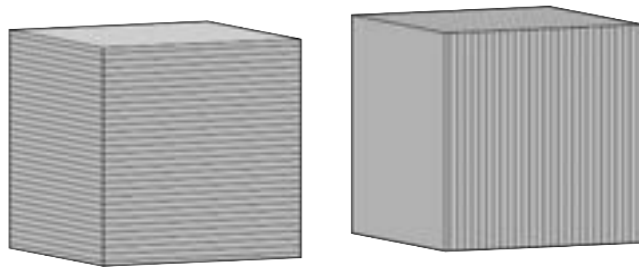


Figure 1.6: Print Layer Direction

Printed parts can be manufactured in either transverse or longitudinal direction. Figure 1.6 shows different alignment of layers of the same part manufactured in different directions.

Samples of the same material can be printed in different directions. Layer direction can be transverse in one sample and parallel in the other. Gravity acts perpendicular to the surface in one sample and parallel in the other sample. This can result in different topography and roughness. Wetting state depends on the contact angle, roughness and surface energy of the sample. 3D printed Ti6AL4V samples have shown both hydrophobic and hydrophilic behavior depending on the printing direction.

1.4 Physical Vapor Deposition

Physical Vapor Deposition(PVD) evaporates or sputters metal from a target material and deposits it onto a substrate material under controlled environment. High kinetic or thermal energy is used to dislodge target metal atoms. These particles are then transported and deposited onto the substrate under controlled environment. PVD can deposit coatings at relatively low temperatures causing a meta-stable phase with desirable properties. Nitride hard coatings are commonly deposited using cathodic arc evaporation, electron beam evaporation, magnetron sputtering, ion beam assisted deposition and chemical vapor deposition. Current study covers the utilization of cathodic arc evaporation for depositing TiN coating onto Ti-6Al-4V and Steel 316L substrates.

Cathodic arc PVD can be utilized for various applications including improving wear and erosion resistance and as a decorative coating. Deposition of hard coatings can help improve tribological properties and increase the life of substrate material. Typical

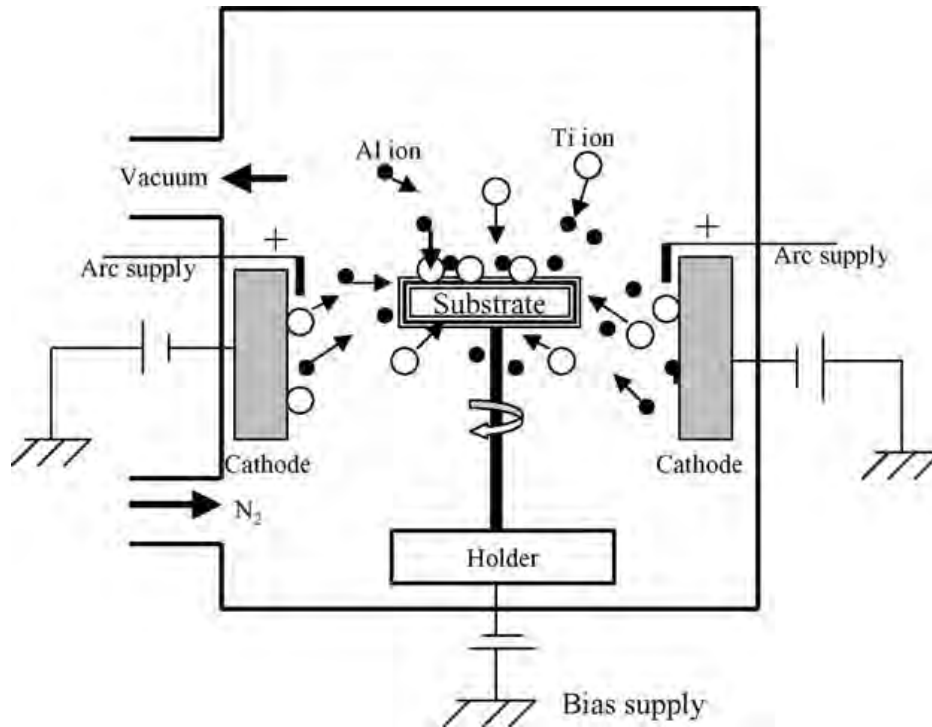


Figure 1.7: Cathodic arc deposition PVD [4]

schematic of the cathodic arc deposition process is shown in figure 3.3. Target material to be deposited is used as a cathode and has positive charge when compared to the rest of the equipment. Electric arc formed strikes the cathode material and this evaporated material is then deposited onto the substrate to be coated. Ions generated during the process have high kinetic energy (upto 200 eV) which facilitates the deposition by improving their mobility> High energy is essential for better adhesion and columnar grain growth. Multiple cathodes can be utilized for co-evaporation. Cathodic arc has a disadvantage due to contamination of plasma from molten cathode droplets. Dense currents create localized meltpools which are ejected onto the substrate by expanding liquid metal and impacting ions creating macro-particle contamination. This macro-particle contamination limits the use of cathodic arc evaporation. Defects can also be introduced due to substrate surface defects so studying the effect of 3D printed surface and its use as a substrate for hard

coatings is quite important for widespread adaptation of 3D printed parts.

1.5 Motivation

Most commonly used powder-based AM techniques include Selective Laser Melting (SLM), Electron Beam Melting (EBM) and Direct Energy Deposition (DED). In EBM, parts are generally manufactured under vacuum using electron beam which makes it best candidate for manufacturing of highly reactive metals and alloys [49]–[51]. Titanium proves itself as a promising metal for EBM process due to its high affinity for oxygen [52]–[54] and high melting point. Ti-6Al-4V is most commonly used titanium alloy due to its advantageous characteristics. It has higher strength, fracture toughness, resistance to corrosion and biocompatibility and lower weight compared to other alloys. The strength of Ti-6Al-4V coupled with its low density gives it edge over many other engineering materials which makes it lucrative for many applications. In EBM, energy density is greater than laser which enables it in achieving higher scan speeds than laser. Higher build temperature also results in lesser local cooling rate. In EBM, controlling the build temperature can help to reduce the formation of α' phase in Ti-6Al-4V and also decrease the amount of thermal stresses [55]. On the other hand, SLM utilizes high power laser beam to melt and fuse the metal powder together. . SLM laser beam has lesser power output than electron beam in EBM. Smaller powder size is used due to lesser energy output. SLM can utilize various material alloys and composites such as aluminum, iron, nickel and titanium (AlSi10Mg, Al-SiMg1.4, 18Ni-300 maraging steel, Stainless steel 316L, IN738LC superalloy, Inconel 718, TC4 and Ti6Al4V) [56]–[64] to manufacture parts. SS-316L is used extensively due to its

excellent mechanical behavior and good resistance to corrosion. SLM-based SS-316L has complex structure which results from epitaxial growth [65]–[67] of grains and remelting of melt pools from successive laser scans. Electron microscopy can reveal presence of cellular structures [67]–[71] along with elongated intergranular cells [72]. Despite its many advantages, AM comes with its own set of challenges ranging from material defects to manufacturing time and economic feasibility. Intense thermal gradients and high cooling rates [73], [74] can result in Marangoni flows [75], [76] while manufacturing. Fast scanning speeds along with complicated flows result in several microstructure defects like unmolten particles, pores, cracks, keyholes, and lack of fusion between subsequent layers [ref]. AM samples are subjected to complex thermal cycles due to repeated heating and cooling of subsequent layers[ref] which alter the microstructure. AM parameters affect the thermal history which directly affects the microstructure governing mechanical behavior of printed material. Consequently, mechanical properties of the printed samples depend on printing parameters like scanning speed, scanning strategy [77], [78], hatch spacing, laser power and spot size. Energy is deposited in a localized fashion in EBM and SLM. This results in highly localized heating and rapid cooling which affects microstructure and leaves residual stresses in finished parts. Due to complexity of the microstructure and thermal cycles, it becomes quite challenging and important to analyze the 3D printed part and compare it with traditionally manufactured counterparts. Surface topology of printed parts plays an important role in applications involving tribological properties and wetting. Therefore, investigating wettability, surface topography and surface energy along with scratch resistance and coefficient of friction can help in evaluating the utilization of 3D printed parts in previously unexplored avenues of manufacturing.

1.6 Scope

3D Printing is one of the emerging manufacturing processes. With the advent of progresses in metallic powder as processing materials arise many new challenges related to surface and material properties of the printed product. Current area of study covers investigation of the surface topology and material properties of electron beam melted Ti-6AL-4V and selective laser melted Stainless steel 316L. Investigation of these two materials as substrate for PVD coating of TiN has also been carried out. Scope of the study is to:

- a) Use experimental techniques to analyze the wetting state of the 3D printed samples.
- b) Analyze surface topology and microstructure of the 3D printed sample using microscopic methods.
- c) Determine surface energy of the sample using experimental techniques.
- d) Analyze material composition and structural changes in the printed slab using X-ray diffraction technique.
- e) Coat the samples with TiN using Cathodic Arc physical vapor deposition.
- f) Analyze the tribological behavior and failure of coated samples.

Surface characteristics and properties are the main area of focus in the present study. Wetting state, surface texture, roughness, microstructure and material composition is examined and discussed. Material properties like tensile strength, toughness, hardness, ductility and other similar properties which require specific samples or destructive measure-

ment techniques were not analyzed and are out of scope of this study. Only destructive techniques to be utilized are scratch test for hardness and grinding and etching for optical microscopy. Hard coating are used to improve tribological behavior and wear life of the material. Therefore both substrates were coated with TiN using cathodic arc physical vapor deposition. Analytical tools were then used to investigate the behavior of coatings and feasibility of 3D printed materials as substrates.

1.7 Thesis Overview

Thesis presented has five chapters. Chapter 1 discusses the paradigm of additive manufacturing and brief overview of SLM, EBM and PVD processes. Chapter 2 discusses the current state of additive manufacturing and relevant literature on the techniques used for investigation of samples manufactured using the three processes. Chapter 3 details the equipment used for both manufacturing and investigation of 3D printed and coated samples. Chapter 3 also presents all the characterization tools and parameters used for analyzing the samples. Chapter 4 contains the results and discussion for wetting state, surface energy, roughness, SEM, EDS, XRD, Hardness, Scratch resistance and FTIR for Ti-6Al-4V , SS 316 L and TiN coated substrates. Chapter 5 concludes the present work with finishing remarks and suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

Today additive manufacturing is one of the fastest growing industrial field with estimated \$51.66 Billion in 2026 at the rate of 25.8% CAGR [79]. Figure 2.1 shows the relative trend of global market revenue of both metal additive manufacturing [80] and 3D printing industry as whole side by side. The growth is staggering and is expected to follow same trend in the



Figure 2.1: Market Size 3D Printing

upcoming years. The value of additive manufacturing in 2017 was estimated to be more than \$10 Billion [47]. Companies like GE are working on increasing the throughput of Laser melting machines for parts used in aerospace and automotive industry.

Aerospace is one of the leading market consumer of metal additive manufacturing based on the revenue closely followed by biomedical due to expensive implants customized and manufactured according to the needs of each end user [80]. Other sectors using additive manufacturing include Energy and power sector, Automotive industry, Oil and Gas , Tooling and some other industries contributing minor shares in the total revenue. Figure2.2 shows the comparison of the market share with other industries. Industry is estimated to reach the mark of \$100 Billion during 2031 -2044 [15]. Although additive manufacturing offers number of advantages over traditional techniques for specific applications

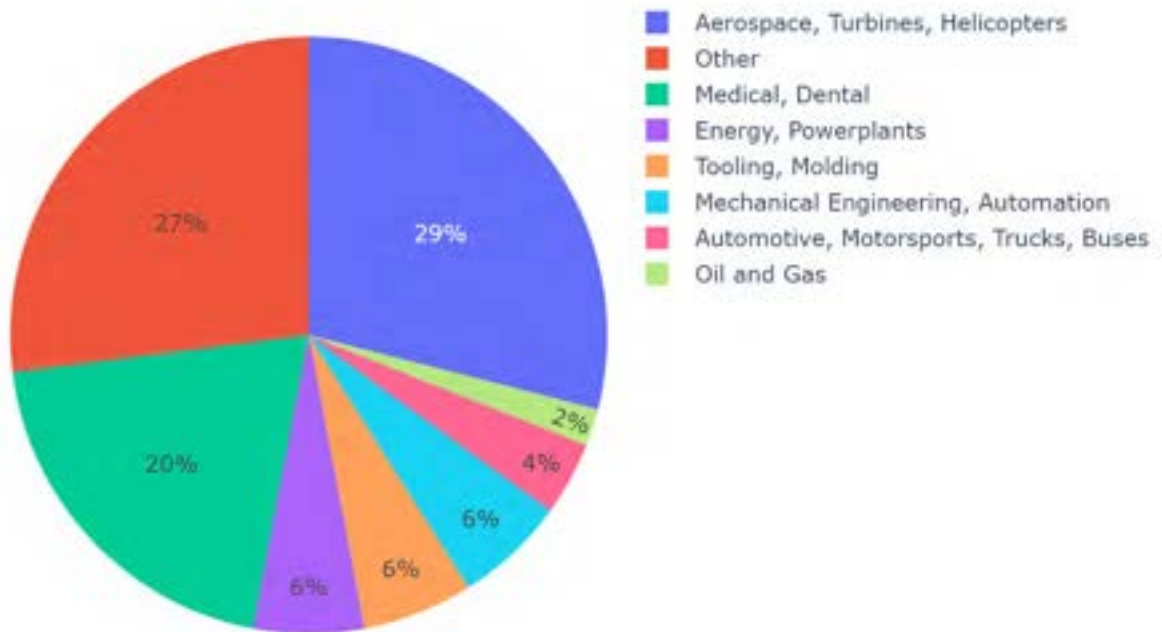


Figure 2.2: Metal AM Sales Revenue by Industry(2019)

still it has very limited market in vital structural applications requiring fine tuned properties. Currently it's making its way into the construction market being a viable solution for building settlements on other planets. Currently complete houses and partly buildings are being built and AM is rapidly earning a name in construction industry. Companies like Reinshaw are testing AM in other fields like mining for printing components(down the hole hammer) [81]. Others are printing custom solutions for animal implants using titanium [82].

Most common feed forms for metal additive manufacturing are powder and filament and the most common process for utilizing these forms is PBF and DED [15]. Powder bed fusion uses an energy source to sinter or melt the powder particles together. Based on the type of energy source it can be further divided into two categories EBM and SLM. As EBM

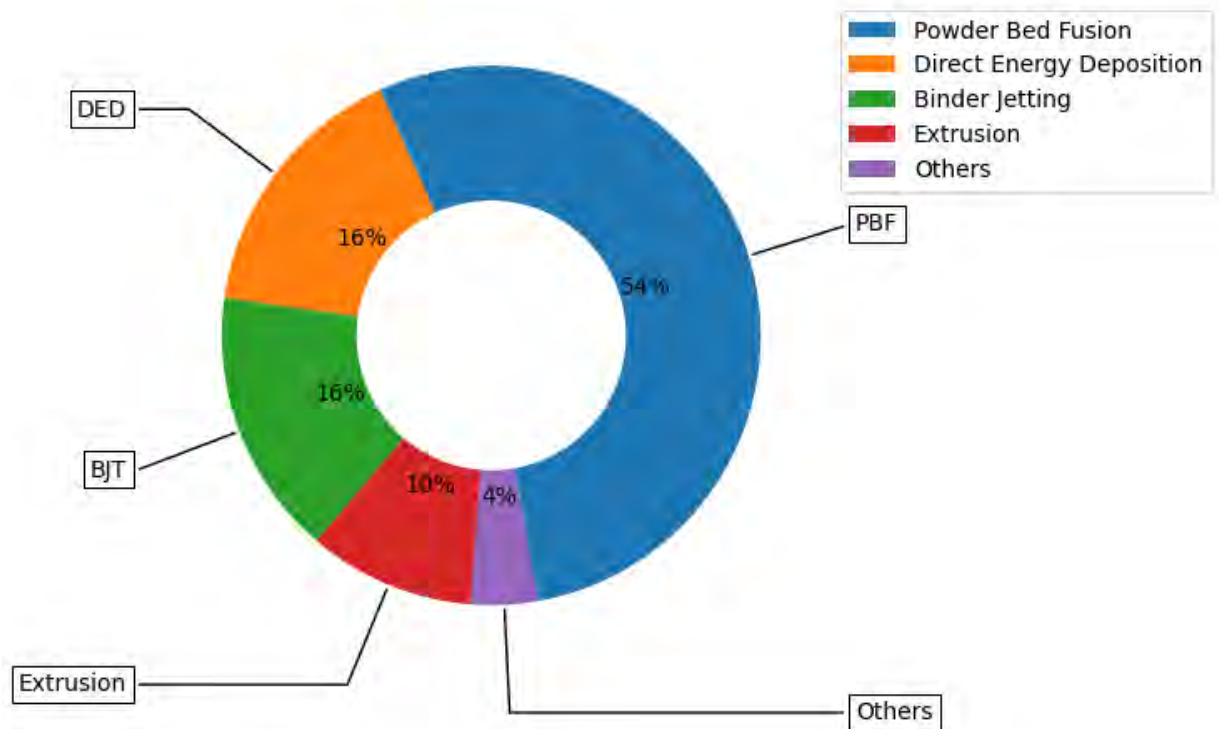


Figure 2.3: By technology Distribution

and SLM are the most used categories it makes PBF the major contributor in metal AM market share as shown in Figure 2.3 [83]

2.1 Importance of 3D printing

3D printing of alloys brings new era in material processing technologies and limitless possibilities. It overcomes the major drawback of conventional processing techniques for fabricating complex parts with intricate features. Layers of fine spherical powders are spread over top of each other and under the influence of high energy in the form of electron beam powder layers melt and fuse together. As the part is manufactured layer by layer it gives precise control over the features of the finished part while saving considerable time from secondary machining processes. Previously only polymers were used for printing the parts due to lower melting points. However, this results in limitation of material properties like toughness, strength, melting point, conductivity and ductility due to use of small group of raw materials. Now with the addition of metals and alloys as raw powder materials, only limit is imagination.

Despite of so many pros of using 3D printing it comes with its own set of challenges. As spherical powder is used as the base layer, it contains tiny gaps of trapped air which can cause irregularities in the heat conduction throughout the layer causing defect sites in the layer. Moreover, melting of the single grain of powder is not uniform as the beam of laser/electron has a Gaussian distribution concentrating energy in center of sphere which can result in irregularities. To mitigate the effect of these problems precise control of the printing parameters is done. Size of powder, scanning speed of the beam, energy of the

beam, peak voltage, energy density and many other parameters are controlled to affect the surface topology of the product

3D Printing is one of the emerging manufacturing processes. With the advent of progresses in metallic powder as processing materials arise many new challenges related to surface and material properties of the printed product. Following sections cover investigation of the surface topology and material properties of 3D printed Ti-6AL-4V and SS316-L.

Ti-6Al-4V is one of the most commonly used titanium alloy. Aluminum acts as alpha stabilizer and raises the beta transus temperature. Aluminum also decreases the density of titanium as it has $2.7g/cm^3$ compared to titanium's $4.5g/cm^3$. Vanadium on the other hand is beta phase stabilizer and provides ductility to alloy which is useful while hot working. The use of Titanium alloys for 3D printing has several benefits as titanium's toughness to

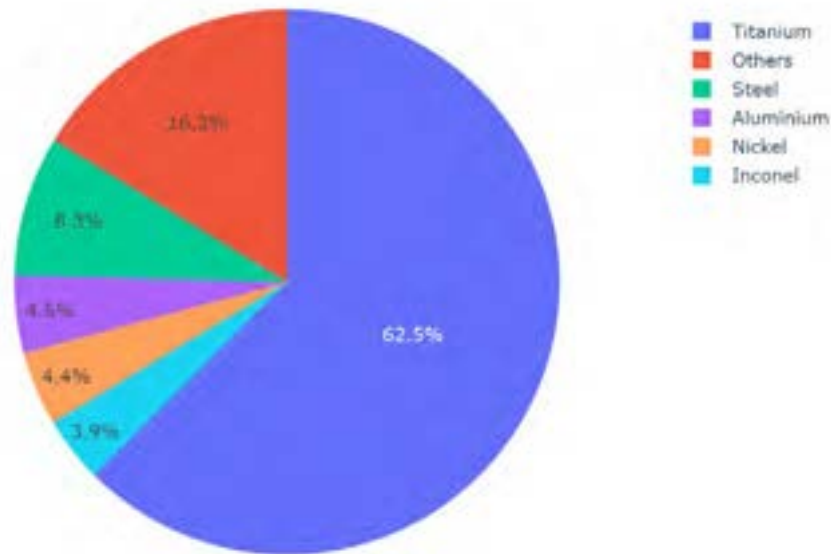


Figure 2.4: By metal type Market

weight ratio is high which makes it ideal candidate for aeronautical and space applications. Titanium is naturally corrosion resistant that makes it useful for bio implants. Wide range of researches have been carried out and published in the area of 3D printing and is still an ongoing process. In case of 3D printing aluminum has higher demand when compared to titanium but based on sales revenue titanium has the lion's share as titanium has specialized applications in aerospace and biomedical due to its strength to weight ratio and bio compatibility [84]. Nowadays, major industries like automotive, aerospace, biomedical and construction utilize additive manufacturing in one form or the other. Understanding the materials properties is important for proper functioning of the parts. Material behavior can also help in predicting part life and failure. Studying surface topology and properties can help open new potential avenues for 3D printed material utilization.

2.2 Contact Angle

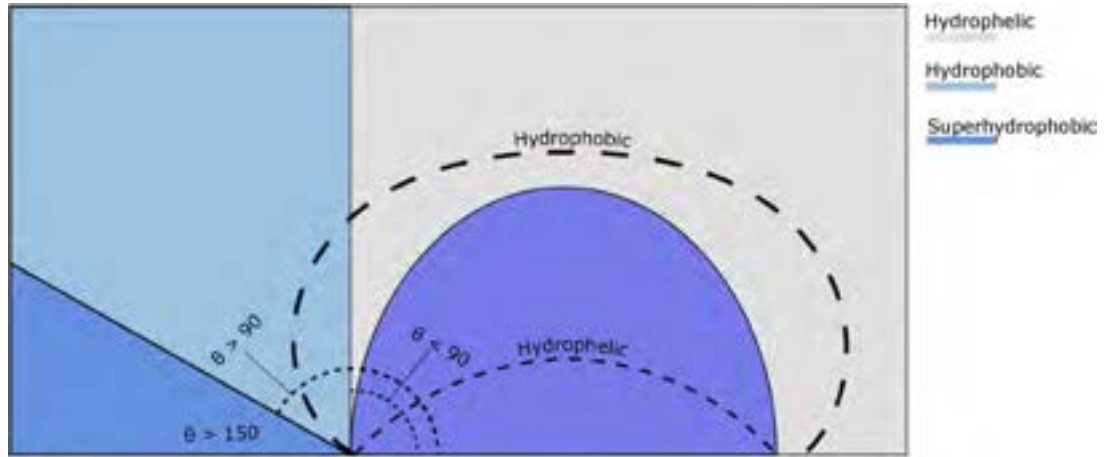


Figure 2.5: Wetting States

Wetting state is very important to identify the behavior of surface when it meets the liquid. Contact angle is measured using goniometer and water. A drop of water is placed on each sample and a picture is taken while keeping the surface perpendicular to the camera and horizontal to the ground. Light is used to illuminate the background to differentiate the boundary of the droplet and measure the contact angle with the surface. Contact angle is the angle between the solid surface and liquid vapor interface at the point of contact. Figure 2.5 shows the range of contact angle which makes surface hydrophilic, hydrophobic and super hydrophobic.

The contact angle depends on the three interfacial tensions. The equilibrium of these three surface energies is given by Thomas Young's equation [85].

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta \quad (2.1)$$

where:

γ_{sv} = Surface energy between solid vapour phase

γ_{sl} = Surface energy between solid liquid phase

γ_{lv} = Surface energy between liquid vapour phase

θ = Angle between γ_{lv} and γ_{sl} interface

Wettability of a surface is analyzed by measuring the contact angle. If the liquid is water and contact angle is less than 90° the surface is called hydrophilic surface and if contact angle is greater than 90° the surface is called hydrophobic. Surfaces with contact angle greater than 150° are considered superhydrophobic surfaces. Complete wetting occurs when the contact angle is 0° which means the droplet forms a puddle and lies completely flat on the surface, this is particularly important in applications requiring lubrication. High wettability means positive spreading coefficient which helps the oil spread easily and homogeneously throughout the surface.

Contact angle also depends on the surface roughness. Roughness can alter the contact angle of the surface. This alteration in contact angle can be explained by the state of the drop in which it lies on a rough surface. The two states are called Cassie-Baxter and Wenzel

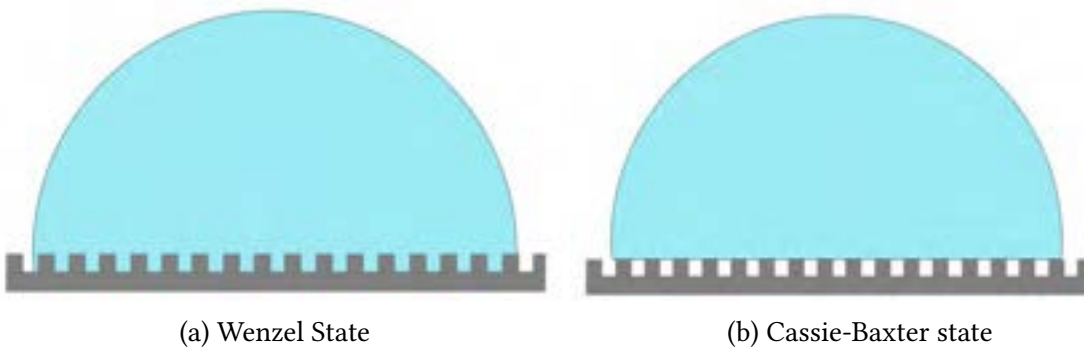


Figure 2.6: Wetting states for rough surfaces

state as shown in Figure 2.6.

In Wenzel state droplet completely contacts with the rough surface. In this state hydrophilic surfaces show a lower contact angle and hydrophobic surfaces have higher contact angle when compared to flat surfaces with the same surface energy. Wenzel relation [86] is given in Equation 2.2.

$$\cos \theta_w = r \cos \theta_y \quad (2.2)$$

where:

$\cos \theta_w$ = Apparent contact angle

$\cos \theta_y$ = Young's contact angle

r = Roughness ratio

In Cassie-Baxter state when the droplet is placed on the solid interface it does not completely contacts the surface due to roughness as shown in the figure above. In this state Contact angle depends on the percentage of solid in contact with the droplet. As percentage decreases the contact angle approaches 180° making the surface super-hydrophobic. Cassie-Baxter relation is given by the following formula [87]. More than three readings should be taken for each surface to establish a pattern if any exists.

$$\cos \theta^* = r_f f \cos \theta_y + f - 1 \quad (2.3)$$

where:

$\cos \theta_y$ = Young's contact angle

θ^* = Cassie Baxter contact angle

f = ratio of surface in contact with liquid to total surface

r_f = roughness ratio of f

2.3 Roughness

Optical Microscopy is used to analyze both macro and microstructure of the material. It can reveal the unmolten powder attached to printed surface due to partial melting and sintering. More over defects in the form of pores and partially molten trapped particles can also be observed. Confocal Microscope can also be used to analyze the surface topology and roughness of the printed samples. Samples can then be etched using acid after grinding and polishing. This can reveal the microstructure of phases, grain boundaries and melt-pools. Observing melt-pools for Ti-6Al-4V can be difficult sometimes but it can be easily observed after etching for other printed materials like Steel316.

Peng et al. [88] have studied the mechanical characteristics of Ti-6Al-4V manufactured using EBM. He found the roughness of the printed sample using Optical microscopy and observed the roughness values to be $0.49 \pm 0.02 \mu\text{m}$.

Another investigation was done by D. Greitemeier et al. [89] on surface roughness of Ti-6Al-4V printed using both DMLS and EBM. He used contact profilometry to measure the surface roughness. He observed that arithmetic average height of roughness R_a for EBM sample was double than the DMLS samples. Same was the case for maximum height profile R_t . The values for R_a were $13 \mu\text{m}$ and $27.1 \mu\text{m}$ for DMLS and EBM respectively and for R_t $109.9 \mu\text{m}$ and $214 \mu\text{m}$ for DMLS and EBM respectively. Greitemeier attributed

Table 2.1: Roughness of 3D printed Ti-6Al-4V

Ref	Process	Material	R_a (μm)	Procedure	R_x (μm)
[88]	EBM	Ti-6Al-4V	0.49 ± 0.02	Optical microscope	...
[89]	DMLS	Ti-6Al-4V	13.0 ± 0.7	Contact Profilometry	R_t 109.9 $\pm$ 0.6
[90]	EBM	Ti-6Al-4V	27.1 ± 0.91		214.0 $\pm$ 9.6
[90]	EBM singlespot	Ti-6Al-4V	24.1 ± 2.3	Stylus profilometer	...
[90]	Vertical		39.3 ± 6.7		
[90]	EBM singlespot		19.7 ± 1.3		
[90]	Horizontal		31.2 ± 4.9		
[90]	EBM multispot		26.1 ± 0.9		
[90]	Vertical		40.5 ± 2.7		
[90]	EBM multispot		25.5 ± 3.2		
[90]	Horizontal		33.5 ± 1.9		
[91]	SLM 0°	Ti-6Al-4V	3.93 ± 0.89	Surface Stylus (Ra)	...
[91]	SLM 45°		15.54 ± 0.69	Confocal microscope	
[91]	SLM 90°		11.74 ± 1.29		
[91]	SLM 135°		22.68 ± 2.27		
[92]	EBM	Ti-6Al-4V	33.9 ± 20	Optical microscope	...
[92]	LS		13.9 ± 11		
[92]	Wrought(Polished)		2.4 ± 1.4		
[93]	SLS As built	Ti-6Al-4V	4.95	Portable Roughness Tester	R_{max} 35.50
[93]	SLS HIPed		5.07		35.20
[94]	DMLS	Ti-6Al-4V	13	Contact Profilometry	...
[94]	EBM		27		
[92]	LS (30)	Ti-6Al-4V	14	Optical microscope	R_v 92
[92]	EBM (50)		34		
[92]	Polished		2		
[95]	LDDED	Ti-6Al-4V	13.83 ± 2.2	Perthometer PRK	R_t 72.8 $\pm$ 12.35
[96]	EBM	Ti-6Al-4V	3.04 ± 0.25 nm	AFM Nanoscope	R_q 4.08 $\pm$ 0.33nm
[96]	Heat Treated 1000°		7.55 ± 0.83 nm		9.46 $\pm$ 0.92nm
[97]	EBM	Ti-6Al-4V		Mitutoyo SurfTest	R_q 71 $\pm$ 22
[97]	SLM				31 $\pm$ 12
[98]	SLM	Ti-6Al-4V	9 ± 6.5	Optical profilometer	...
[99]	SLM	Ti-6Al-4V	5.226	LS confocal microscope	R_v 90
[99]	Laser Polished		0.375		4
[99]	SLM	TC11	7.21		80
[99]	Laser Polished		0.73		4.5
[100]	SLM	Ti-6Al-4V	10.2	LS confocal microscope	...
[100]	Laser Polished		2.1 - 8.05		
[101]	DMLS	Ti-6Al-4V	8.3 ± 0.2	Surface Analyzer	R_z 32
[101]	Sand Blasted		2.3 ± 0.3		10
[101]	AR polished		0.6 ± 0.1		4
[102]	SLM	Ti-6Al-4V	...	Micro-CT	P_a 10
[103]	EBM	Ti-6Al-4V	31.1	3D optical profilometer	...
[103]	SLM		13.7		
[104]	SLM X	Ti-6Al-4V	32.0	Contact profilometry	R_t 198.1
[104]	SLM Y		30.3		197.7
[104]	SLM Z		38.5		235.5
[105]	Wrought	Ti-6Al-4V	280.0 ± 63.8 nm	Optical profilometer	R_t 4396.7 $\pm$ 1166nm
[105]	Polished		9.5 ± 2.4 nm	AFM	749.7 $\pm$ 415.6 nm
[106]	SLM	Ti-6Al-4V	6.00 ± 0.89	Confocal microscope	...
[106]	Roto Polish		0.38 ± 0.01		

roughness to two factors primary factor being the meltpool solidification and secondary factor was the partially melted powder attached to the surface.

Study on how the processing parameters can effect the roughness of 3D printed Ti-6Al-4V using EBM was done by Pan et al. [90]. EBM was reported to give lower residual stresses and better mechanical properties. The focus is to study the effect of multispot and single spot scanning strategy on the surface topology and irregularities. Both vertical and horizontally printed samples were analyzed. Ti-6Al-4V was chosen as the print material for the study. Roughness was measured using cantilever stylus profilometer that was spring loaded and had a diamond tip. Their study shows that EBM single spot horizontal gave the lowest result ranging from $19.7 \pm 1.3 \mu\text{m}$ - $31.2 \pm 4.9 \mu\text{m}$ with highest roughness in multispot vertical $26.1 \pm 0.9 \mu\text{m}$ - $40.5 \pm 2.7 \mu\text{m}$. Results of the roughness for maximum

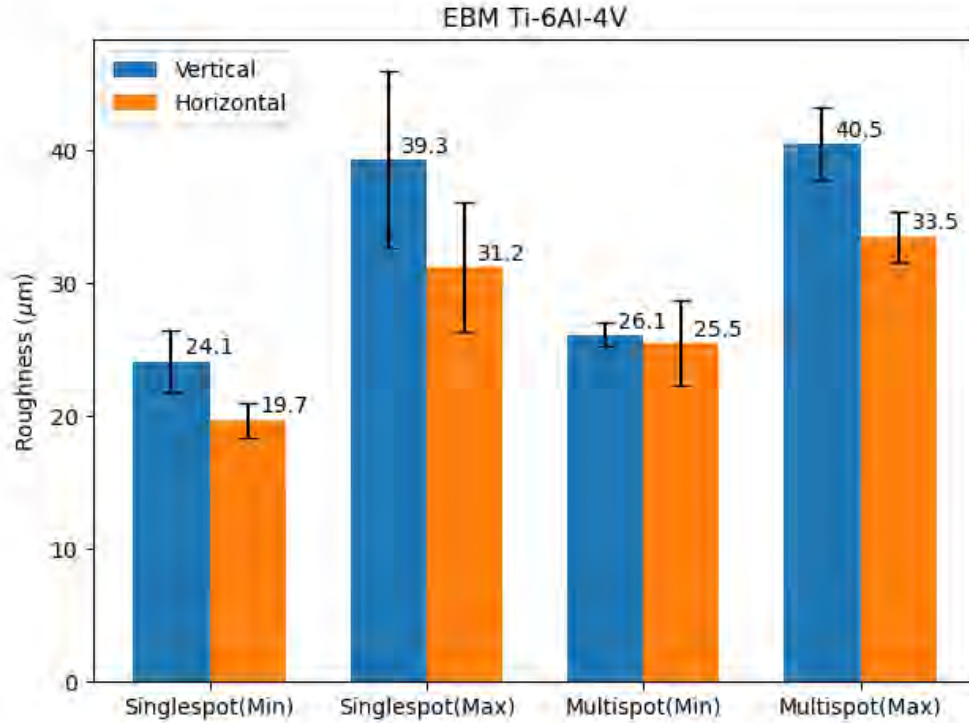


Figure 2.7: Effect of Spot Strategy on Roughness

and minimum for each category has been shown in Figure 2.7. In case of single spot primary parameters affecting roughness were beam current and speed where lower current yielded better roughness. On the other hand in multispot printing key parameters were number of spots, spot time and overlap with higher number and high overlap resulting in better end results.

2.4 Microstructure

Microstructure is of utmost importance in understanding and predicting the material properties. Scientists have researched extensively to understand the grain growth and have always toiled with the question of controlling it. Wide range of researches have been performed to understand the microstructure of the 3D printed parts and effect of different processing parameters (scanning speed, scanning pattern, source power, environment and build direction) on different material properties.

Ryan et al [107] studied the microstructure of four AM processes i. e. SLM, EBM, DMD and WAAM for Ti-6Al-4V and found that all samples consisted of α' -Ti martensitic phase within matrix of $\alpha + \beta$ -Ti. Grain boundaries were prior β -Ti grain boundaries. Morphology was found to have a small amount of differences between the four manufacturing processes. SLM and EBM were found to have needle like martensitic α' laths. DMD samples had shorter and thicker laths while WAAM samples had longer β grain boundaries. Bartłomiej et al [1] analyzed microstructure of Ti-6Al-4V printed by SLM and EBM for bone implants. Both processes exhibited epitaxial grain growth but grains in SLM were wider compared to the EBM samples. Further investigation showed that SLM samples contained

Table 2.2: Grain Structure and phases of 3D Printed Ti-6Al-4V

Ref.	Process	Material	Phases			Grains	Pattern	Growth Direction
[1]	SLM	Ti-6Al-4V	-	β	α'		Widmanstatten	Epitaxial
	EBM		α	β				
[93]	SLS	Ti-6Al-4V	-		α'			
	HIP		$\alpha' \rightarrow \alpha$					
[107]	SLM,EBM,DMD and WAAM	Ti-6Al-4V	α	β	α'			
[108]	SLM	Ti-6Al-4V	-	β	α'	Columnar	Herringbone	
	SLM (HIP)		$\alpha' \rightarrow \alpha$	β				
[109]	DMLS	Ti-6Al-4V	-	β	α'	Columnar		Epitaxial
	Annelaing		$\alpha' \rightarrow \alpha$	β		Equiaxed		
[110]	Laser Sintered (IR)	Ti-6Al-4V	α	$\beta \rightarrow \alpha'$			Widmanstatten	
[111]	SLM	Ti-6Al-4V		β	α'	Columnar	Heterogeneous	Epitaxial
[112]	SLM	Ti-6Al-4V			α'		Herringbone	
[113]		Ti-6Al-4V		β	α'	Columnar	Chessboard	
[114]	Multi Laser	Ti-6Al-4V		β	α'	Columnar	Herringbone	
[115]	SLM	Ti-6Al-4V		β	α'	Columnar		
[116]	DMLS	Ti-6Al-4V	α	β	α'		Widmanstatten	
	Heat Treatment		$\alpha' \rightarrow \alpha$	β				
[117]	SLM	nickel				Columnar		Epitaxial
[118]	EMB	nickel				Columnar		

α' martensitic plates and EBM samples contained needles of α in β -Ti matrix in the form of Widmanstatten structure. They reported higher dislocation density in SLM samples compared to EBM samples and investigation under TEM revealed much finer structure in SLM samples with thickness around five times lesser than EBM plates. Chunlei et al [108] examined the microstructure of Ti-6Al-4V and effect of HIP on it. They found columnar grains along the build direction. Martensitic needle like structure was reported following a herringbone pattern. They also observed that applying Hot Isostatic Pressing resulted in conversion of α' martensite into α - β Ti. Microstructure of 3D printed Ti-6Al-4V using DMLS was investigated by Zaneta et al [109]. They analyzed the surface morphology and found unmolten powder attached to the solidified layer underneath. Other side perpendicular to this surface had one-way scattered pattern of layer revealing the scanning. They attributed porosity of the surface layer to the partially molten powder particles. This

can be beneficial in biomedical applications for facilitating bone growth. They reported fine grain martensitic structure of α' in β columnar grains growing epitaxially. Annealing resulted in decomposition of martensitic α' into lamellar of α and β with equiaxed grains. P. Fischer et al [110] has inspected the structure of IR laser sintered titanium and the powdered titanium. Their findings showed powder consisting of fine primary α grains in α' martensitic which was reported to be transformed from β . Sintered samples contained needle like α grains in α' matrix in the form of Widmanstatten structure but these structures overlapped the grain boundaries. These structures were attributed to slower cooling rates when compared to the cooling of the powder. Study on microstructure done by Atieh Moridi et al [111] shows that Ti6Al4V printed using SLM show heterogeneous structure. Microstructure contains hierarchy of α' within β grains. This hierarchy of primary secondary and tertiary α' which is metastable hcp martensite. is due to complex thermal curve followed by the material. Printing of each layer results in heating of previous layers. These repeated heated and cooling cycles can form a structural hierarchy in 3D printed parts. β grains were columnar due to epitaxial growth and α' showed a preferred growth direction that was at an angle of 40° from the build direction. As primary α' is formed during an early stage of printing so it extends through the β grain boundaries but on the other hand the growth of secondary and tertiary martensitic grains is ceased by the grains that have formed already. Secondary and tertiary grains are much harder due to higher dislocation density and less auto tempering. M Benedetti et al [93] validated the effect of Hot isostatic pressing on Ti-6Al-4V printed using selective laser sintering. They found fine acicular martensitic α' . As the phase is metastable the increase in temperature during heat treatment resulted in its transformation into α . Heat treatment was

done on different temperatures from 900°-950° and they found an increase in α platelets and structure became coarser at higher temperatures. Ductility is noticed to be improved by the heat treatment. Evolution of SLMed Ti-6Al-4V was investigated by Lore Thijs et al [112]. They also observed acicular martensitic structure. Scanning pattern of the printing was visible from the microstructure and hatch spacing could be attributed to resultant microstructure tracks. Herringbone pattern was observed and credited to variation in the scanning direction. There was slanting in the direction of laser beam motion. Coarser grains were result of lower scanning speed. Melt pools were also observed but were easier to differentiate for inputs at higher energy. Grains were elongated when investigated from front and side view with orientation towards the molten pool which is the direction of local heat transfer. They also reported Al segregation and formation of Ti_3Al inter-metallic phase which was helpful in identifying the melt pool boundaries. Formation of martensitic α' in 3D printed Ti-6Al-4V was investigated by Jingjing Yang et al [113]. They observed a chessboard pattern in the structure which was attributed to hatch angle of 90°. Columnar β grains containing α' martensite were found. They noticed that α' nucleated at β boundaries and grew within it but sometimes grew into neighboring grains too. They also found lamellae of α' in coarser α' which were oriented at 45° from coarser α' . Primary α' which was observed to extend across β contained secondary α' which contained tertiary which contained quartic decreasing in size and becoming finer. Finer tertiary and quartic α' 's growth is inhibited by already present α' . When investigated under TEM α' contained higher dislocation density and twins. Fangzhi et al [114] examined the effect of multi laser beam printing of Ti-6Al-4V. They observed a stair effect in the region where scanning of lasers overlapped but it could be minimized by rotating the hatch angle by

90° of one laser with respect to the other. They also obtained herringbone pattern of α' martensitic needles aligned at 45° to building direction in columnar grains of β elongated in the building direction. Investigation of properties of both stainless steel and Ti-6Al-4V parts manufactured using SLM was done by H. Khalid Rafi et al [115]. They confirmed the columnar β grains with martensitic laths of α' growing from grain boundaries in Ti-6Al-4V samples. PH1 steel samples also contained martensitic laths but they contained some of the retained austenite. The striking difference between the two microstructures was prominence of columnar grain boundaries in Ti-6Al-4V and melt pools in PH1 steel. But they lacked showing both structures simultaneously. The appearance of dark bands in Ti-6Al-4V was attributed to higher energy input. Acicular and lamellar morphology of Ti-6Al-4V resulted in better fatigue behavior and improved strength. Todd et al [116] scrutinized the strain behavior in DMLS printed Ti-6Al-4V. They observed α Widmanstätten structure in all their samples. Former β grain phase boundaries were also found and α phase lamellae were growing into the β grains. They also observed 45° aligned α' lathes. In some samples post processing heat treatment was applied to convert α' to $\alpha + \beta$ structure. Strain was observed along the major axis of α as it is free of barrier slip and β grain boundaries also play important role so their orientation is of critical importance. Decreasing or inhibiting the growth of β can improve the properties. Study of nickel superalloy using SLM by Luke N. Carter et al. [117] shows elongated columnar grains in the build direction. This is result of preferential cooling in z direction and epitaxial growth of grains in each layer. Study done by Lawrence E. Murr et al. [118] also shows columnar grains in nickel alloy sample printed using EMB.

2.5 X-Ray Diffraction

X-ray Diffraction gives the value of X-ray intensity vs 2θ . Diffraction behavior is governed by Bragg's Law [119]. Spacing(d-spacing) between the planes can be calculated using Bragg's law which is used to identify phases in the sample. It can also be utilized to analyze the crystallite size using the Scherrer's equation [120] based on the peak width. The shift in peaks can help identify the presence of strain in the sample. Strains in 3D printed samples are result of residual thermal stresses. Compressive stress results in positive shift of the peaks and tensile stress results in negative shift of the peaks. Combination of both stresses causes peak broadening. XRD is very useful in identifying the crystal structure and phases of the samples and can be utilized in conjunction with EDS to analyze the sample composition.

X-ray Diffraction can be very helpful in analyzing various properties of materials like material composition, crystal structure, size and phase identification. It gives the diffraction pattern of the incident wave depending on spacing within the atoms. Bragg's law governs this behavior [119].

$$n\lambda = 2d \sin \theta \quad (2.4)$$

where:

θ = Scattering angle (between plane and incident wave)

d = Interplanar distance

λ = Wavelength of incident wave

$n =$ Positive integer

Diffraction pattern of Ti is shown in Figure 2.8 [1]



Figure 2.8: Ti Crystal planes from XRD [1]

Different crystals give peaks at different values of θ depending on the crystal plane. This helps identifying the type of crystal. Results can be compared with database of known materials to identify the material present within the sample by matching the characteristic lines and their intensity. The size of the crystal can be analyzed by using Scherrer's equation which relates the peak broadening with the crystal size [120].

$$\tau = \frac{K\lambda}{\beta \cos \theta} \quad (2.5)$$

where:

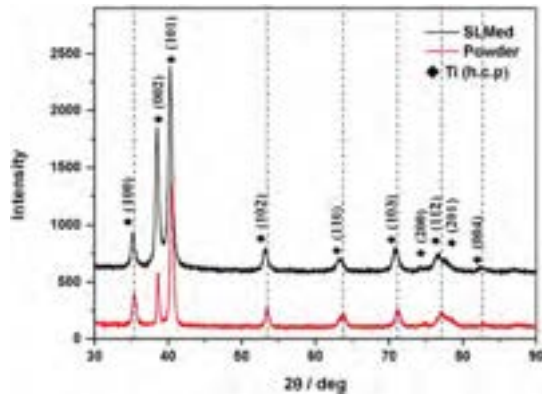
$\tau =$ mean size of the crystalline domain

$\lambda =$ X-ray wavelength

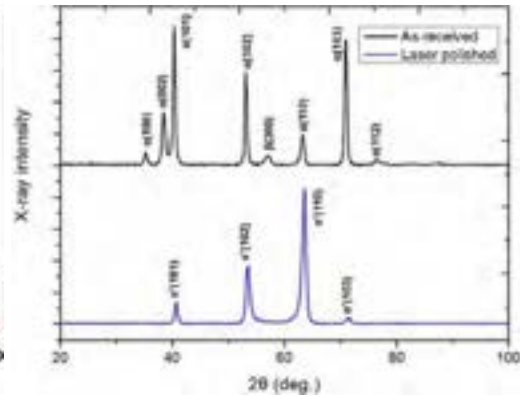
$\beta =$ width at half of the maximum peak intensity

$\theta =$ Bragg's angle

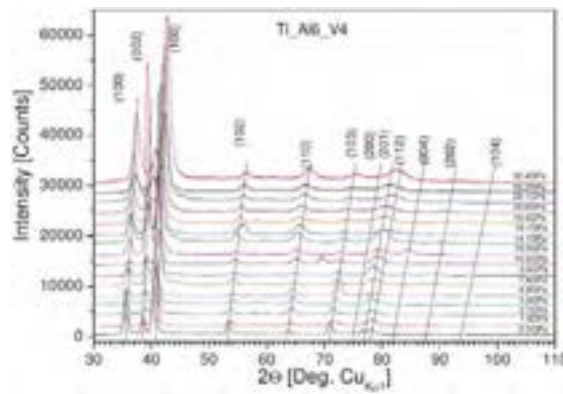
$K =$ Dimensionless shape factor



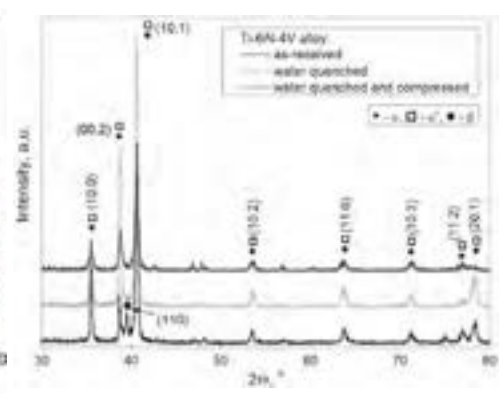
(a) SLMed Ti-6Al-4V [113]



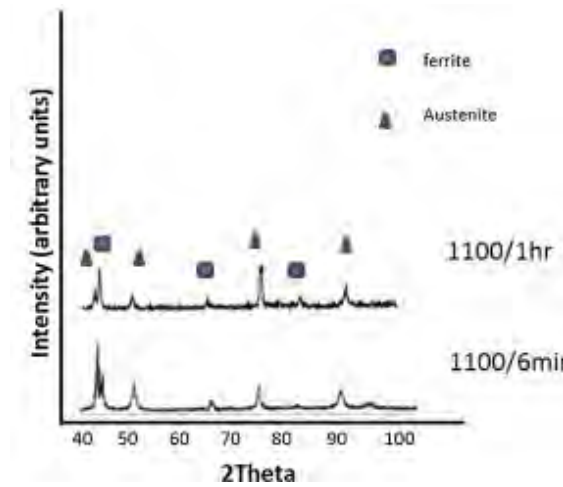
(b) Laser Polishing [99]



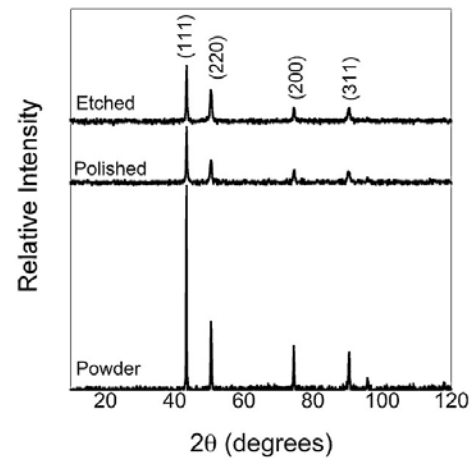
(c) Effect of pressure [121]



(d) Quenching & cold working [122]



(e) Annealed SLMed SS316L [123]



(f) Powder vs SLMed SS316L [124]

Figure 2.9: XRD of Ti-6Al-4V's α , β & α' phases and SS 316L's α & γ phases

XRD patterns of different phases found in Ti-6Al-4V are given in Figure 2.9. Yang et al. [113] have investigated the α' martensite formed after selective laser melting. Effect

of laser polishing of Ti-6Al-4V was studied by Ma et al. [99]. He presented XRD of as received sample containing both α and β phases and laser polishing of sample resulted in α' . Results of pressure and Quenching\Cold Working were discussed by Halevy et. al [121] and Motyka et al. [122] respectively. XRD of SLMed SS 316L is given in Figures 2.9e & 2.9f. Both show presence of γ phase but annealing of the sample results in BCC α phase [123].

2.6 Fracture Toughness

Fracture Toughness is important parameter to gauge the materials ability to resist crack growth. Higher the fracture toughness is, higher the stress required for making the crack unstable. Inquiring fracture toughness of ductile materials only by micro indentation can be pretty challenging but at the same time has far reaching applications. As indentation is nondestructive testing in nature compared to the standard testing procedure of fracture toughness that requires specific sample geometry and experimental procedure and results in destroying the sample such as ASTM standard E399 and E1820 in ASTM E384. The loading range is around 10gf to 100kgf for ISO 6507 and 1gf to 120kgf for ASTM E384. In ASTM recommended sample thickness should be more than 10 times the depth of indentation and in ISO standard more than 1.5 times the length of the diagonal of indent mark.

Min He et al [125] used energy density to measure fracture toughness for ductile materials using Berkovich indenter. He used the theory that indentation fracture energy is the result of plastic deformation energy. He found that in the plastic region of penetration depth load can be represented by a quadratic polynomial. Furthermore, he observed that relation between the logarithmic modulus and depth is linear. He proposed a dam-

age variable which was used to calculate the critical elastic modulus. Model was tested for aluminum & stainless steel and compared with fracture toughness tests. Berkovich indenter is better compared to ball indenter as it requires less penetration depth to evaluate the fracture toughness. Moreover proposed method can be used to evaluate local fracture toughness of specimen and can be used to differentiate the toughness present in different microstructures.

Li et al [126] developed a ductile damage model using continuum damage mechanics and strain behavior of material. Model can be used to find fracture toughness by using indentation to measure fracture-energy. Li used a Berkovich indenter to get loading and unloading graph for indentation test. Li has used loading-unloading tests to quantify the fracture toughness for SS 302 stainless steel and α phase of Ti-6Al-4V. Results only deviated by 7.4% from theoretical calculations. Critical damage variable, fracture stress and strain were also calculated. Critical damage variable is then used to calculate minimum value of young's modulus which in turn provides critical value of plastic indentation depth by extrapolating the logarithmic plot of modulus and indentation depth. Critical value of surface energy and Young's modulus can be used to calculate fracture energy using the formula $k_{1c} = \sqrt{2E\gamma}$ [126]. Obtained value of fracture toughness for α phase of Ti-6Al-4V was around $77.758 \text{ MPa } m^{\frac{1}{2}}$.

Investigation of fracture toughness using Vickers indenter for Ti-6Al-4V was done Riaz et al [127] . They used energy indentation model to estimate the fracture toughness of the material using Vickers hardness test. When the results were compared with stain dependent damage model for ductile materials, they showed a deviation of around 14.5%. Fracture energy was calculated by measuring the deformation of material during inden-

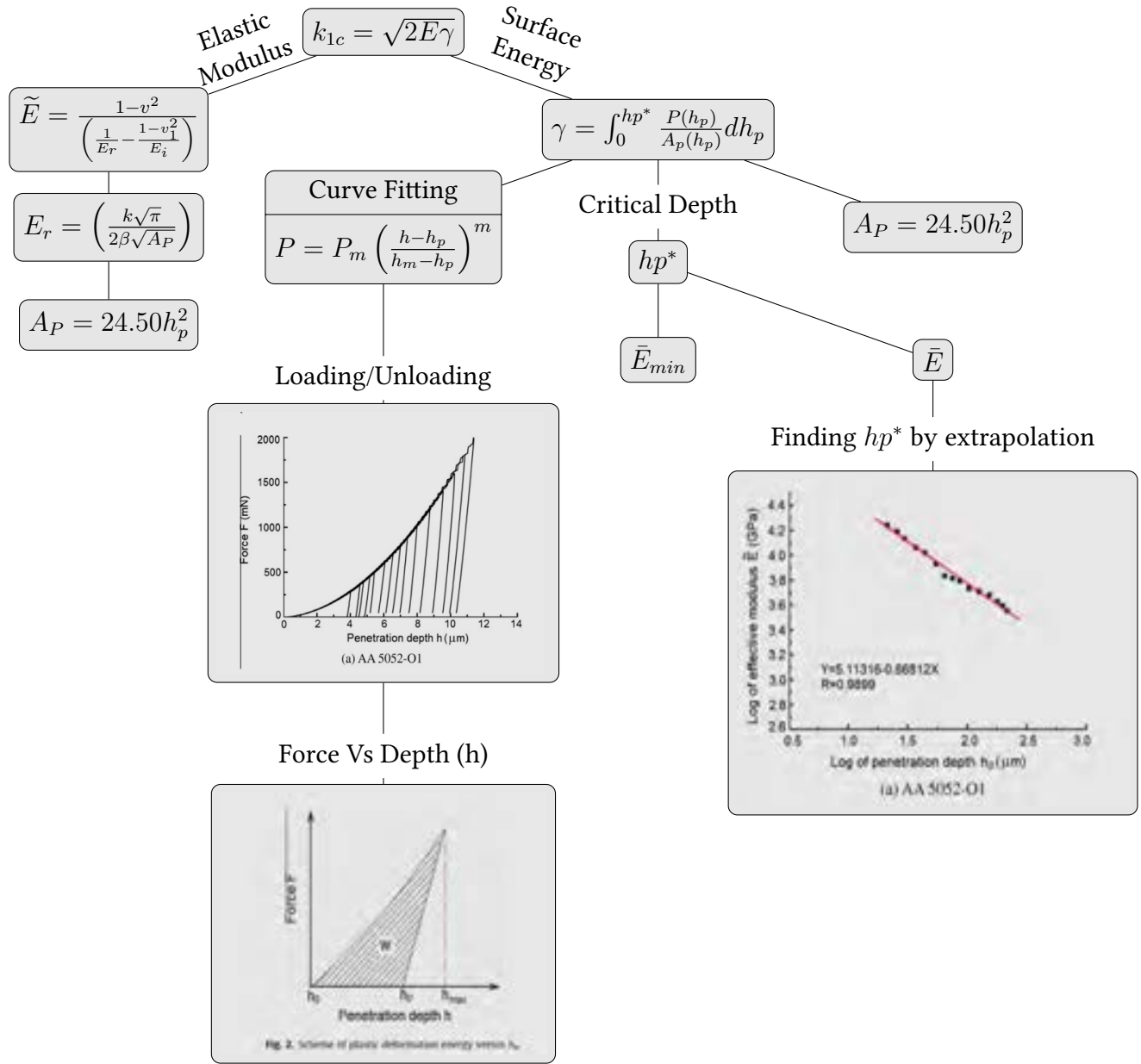


Figure 2.10: Steps for finding Fracture toughness using indentation for ductile materials. The model doesn't consider the effect of pileup and sink-in occurring during the indentation which can sometimes affect the contact area between material and indenter. Fracture toughness was obtained using critical indentation depth calculated using extrapolated logarithmic graph of E and h_p . Average value obtained was $63.35 \text{ MPa m}^{\frac{1}{2}}$.

Cain et al [128] has studied the fracture toughness and fatigue crack behavior on SLM

printed Ti-6Al-4V. They investigated the effect of different orientations and heat treatment on fracture toughness. Fracture toughness is higher when the fracture plane is at 90° to the build direction. Tensile strength of the specimens was around 1248MPa ,after applying stress relief it reduced to 1171MPa and after heat treatment to just 1000MPa. In case of fracture toughness heat treated samples showed highest values around $49 \text{ MPa } m^{\frac{1}{2}}$ and lowest for samples with notched printed parallel to build direction. Microstructure of the specimen showed columnar grains due to epitaxial growth. α' plates of martensitic phase were observed but heat treated samples showed the transformation to Widmanstatten $\alpha - \beta$ structure. Heat treatment of the samples can relief the directional behavior of residual stress and hence reduce the difference in fracture toughness for different orientation samples.

2.7 Topological and Mechanical Properties

Research of 3D printing is an ongoing process. Various researchers have studied the surface topology and mechanical properties of 3D printed materials. Liang et al [129] studied the surface modification effect of 3D printed Ti-6Al-4V on bioactivity for porous implants. Titanium alloys have quite importance in biomedical applications due to their corrosion resistance behavior and weight to strength ratio. Surface modification was achieved using acid etching and anodic oxidation. Elastic modulus was reduced by acid etching. This is desired characteristic for titanium as it has higher modulus than bones. For application in biomedical, elastic modulus of titanium was reduced to match it with elastic modulus of bones. Anodization on the other hand resulted in formation of nano and microscopic scale

structures in the form of tubes and holes. FTIR analysis of the sample showed P-O and O-P-O bond peaks stretching vibration and bending mode respectively that were formed due to induced phosphate from bioactivity evaluation. The other peaks observed were CO_3^{-2} and OH. The current density during surface modification played an important role in the formation of micro and nanosized structures.

Effect of additive angle on 3D printed Ti-6Al-4V bioimplant's biocompatibility and surface properties were investigated by Chen et al [130]. Increase in angle resulted in higher roughness and higher water contact angle. This change in surface behavior was attributed to unmolten particles on the printed surface. Unmolten particles were result of unmolten powder getting sintered to molten layers due to temperature difference. Stair-case effect was observed at an additive angle from $40^\circ - 70^\circ$. Elastic modulus and compressive strengths at 70% porosity were 0.51 GPa and 94.7 MPa respectively. With the increase in additive angle roughness increased and wettability decreased.

Chin et al [131] has reviewed the manufacturing of devices with micro and mesoscale structures using powder based 3D printing. Chin has discussed the impact of manufacturing processes on fabrication of these devices as well as the application of such devices with intricate features. There are several different types of 3D printing with powder-based printing being one of the most popular ones. Reasons for its popularity include low production time, highly reusable powder and no support structures to name a few. Powder based printing is popular for both metal and polymer printing. Selective laser melting and Electron beam melting are the most notable among the powder bed fusion metal 3D printing processes. Selective laser melting differs from laser sintering both in raw power and the amount of fusion achieved.

When surface of as built 3D printed samples is analyzed hydrophobic samples show spherical nano pillar like structures resembling those of lotus leaves which give them naturally hydrophobic behavior and self-cleaning properties. On the other hand, the spherical nanopillars are dispersed into channels of molten layers when surface is aligned with gravity during the printing process. This surface has hydrophilic behavior as there are fewer air pockets under the droplet and in Cassie-Baxter regime the more the area in contact with liquid lesser is the hydrophobicity

Work on fabricating a multi-layer metallic structure was done by Li et al [132]. Their team used SS316 and deposited it on Ti-6Al-4V. Conventionally this results in cracking due to brittle inter-metallic compounds. They used transition route between the two alloys using blown powder laser 3D printing to remedy the cracking problem. Selected inter-layer metals used were V, Cr and Fe. Marangoni flow resulted in concentration gradient between the layers as observed by EDS. When printed using transition route Vickers hardness showed a smooth change as compared to stepped change in hardness for direct deposition.

Bey et al [133] investigated the effect of residual stresses on the anisotropic behavior in 3D printed Ti-6Al-4V using SLM. Residual stresses were mapped using contour method. Samples were clamped then cut using wire EDM. The deformation in cut planes of the resultant two parts after cut was measured using a coordinate measuring machine. The data for two cuts is then averaged to remove asymmetry of the cutting. The resultant deformed cut plane is input to a finite element model to get the stresses necessary to cause that deformation. Case in point , apply stress to deform the measured cut plane into a flat surface. The applied stress will be the residual stress. The data is then filtered using

a spline method to remove errors. Results showed that residual stresses greatly influence the anisotropic behavior of the printed part. Maximum amount of residuals was in the vicinity of yield stress of the material.

Study done by Bartłomiej Wysock et al. [1] on tensile properties of 3D printed Ti-6Al-4V is given in Table 2.3. Data shows that EBM can achieve same UTS as wrought sample of the material and SLM achieved higher strength but the ductility of the material decreases. This behavior is similar to that of heat treatment of materials when strength is increased ductility is lost as smaller structures can hinder the motion of dislocations. This is expected after analyzing the fine microstructure α' needles within β grains of printed Ti6Al4V. α' is martensitic and has higher hardness. Finer the α' needles the higher is the hardness and lower is the ductility.

SLM sample shows anisotropy in the strength and ductility. Defects can concentrate between the printed layers in form of pores and unmolten powder so alignment of the layer can affect the properties in such cases.

Fatigue of laser sintered Ti6Al4V samples has been studied by M. Benedetti et al. [93]. 3D printed laser sintered samples have a lower endurance limit(340MPa) than wrought samples of Ti6Al4V studied by M. Janeček et al [134] showing around 450 MPa.

Table 2.3: Tensile properties of Ti6Al4V [1]

Process	Cutting Direction	UTS(MPa)	Elongation (%)
ASTN F136		>860	>10
Wrought	XY	933 ± 7	13.0 ± 1.5
	XZ	942 ± 8	12.5 ± 1.2
EBM	XY	976 ± 11	15.0 ± 2.0
	XZ	972 ± 14	14.2 ± 1.5
SLM	XY	1421 ± 120	3.2 ± 0.5
	XZ	1246 ± 134	1.4 ± 0.5

Hot isostatic pressing of the printed part can help decrease the defects by closing inner pores and improving the density of the material. This can help recover the ductility of material in samples with high porosity such as printed DMLS parts. W. H. Kan, et al. [135] did a study on the effect of HIP on 3D printed AlSi10Mg using Laser powder bed fusion. Study by Kan shows that tensile strength and ductility are anisotropic but after post processing with HIP anisotropy is gone. This is due to closing of pores and rearrangement of grains. Tensile strength of the sample decreases and ductility improves.

3D printed metallic materials show anisotropy in the properties depending on the process parameters. Gravity can affect the wetting behavior of the material making it both hydrophobic and hydrophilic depending on the printing orientation. Direction of the print layers can also affect the mechanical properties like strength ductility and fatigue life. These properties are directional mainly due to the concentration of pores and defects between the layers. Pores can decrease the fatigue life of the material considerably, but this can be rectified by using Hot isostatic pressing in samples containing higher porosity. Fatigue life and ductility will improve, and strength will decrease. SLM has better mechanical properties when compared SLS due to smaller number of pores in the sample.

Balogun et al [136] discuss the advances in 3D printing and its application in manufacturing of membranes for water treatment. Research in this area in the next decade will increase the resolution and speed of 3D printing which will lead to manufacturing of different membranes and increase the efficiency of treatment. 3D printing will enable the use of complicated topography and surface textures to improve the performance of membranes. Selimis and Farsari [137] discuss benefits of laser treatment over the conventional methods for surface texturing and 3D printing. Liravi and Toyserkani [138] have researched

on manufacturing of silicone bio structures with optimization of 3D printing and surface characterization. They use hybrid approach of additive manufacturing using material extrusion and material jetting and have increased the fabrication speed by 10 to 20 times in comparison to conventional extrusion. Ji et al [139] researched frictional anisotropy of bioinspired topological surfaces with 3D printing. They used 3D printing to mimic biological surface's interfacial anisotropy and found that flexible supporting layer resulted in low friction in both sliding direction but had higher frictional anisotropy. This anisotropic friction was then drive using directional actuation. Kanafi [140] examined the rubber friction of 3D printed randomly rough surfaces at varying sliding speeds. They measured the sliding friction of rubber on 3D printed compounds with varying roughness. They obtained the viscoelastic modulus curves using mechanical analysis. Investigation of 3D printed porous titanium for orthopedic and dental applications with Calcium Phosphate coating and nanoscale surface modification was done by Bose [141]. They used CaP doped coating to enhance bone tissue integration. The use of porous Ti surface with bioactive doped CaP layer can decrease healing time. Vidales et al [142] examined 3D printed photocatalyst for waste water treatment. They observed that 3D printed photocatalysts improved the activity. PDMS films fabrication using 3D printing having special surface wettability was studied by He et al [143]. They obtained superhydrophobic and anisotropic wettability by adjusting pore structure at millimeter scale. They showed a water contact angle of 155° using this method. Although material properties of different 3D printed materials have been studied as shown above but investigation of hard alloys like 3D printed Ti-6Al-4V and SS316 is still needed.

Recent advancements in metal powder processing technologies and their use in powder bed fusion methods have generated particular interest in their microstructure and mechanical properties. Studies have been carried out to analyze the effect of printing parameters on metallurgical changes in the printed part. These metallurgical changes help understand the difference in mechanical properties between the printed and traditionally manufactured alloy parts. Various research articles have discussed the effect of powder bed temperature and scanning strategy on the finished parts but there is still need for further investigation of the surface properties and wetting state of the printed part. Surface investigations for polymeric materials have been previously conducted but there is still a gap of knowledge on printed metal surface properties. Investigation of surface energy and topology of printed parts can also help in developing potential routes for surface coatings. Effect of nitriding of printed surface using TiN coating hasn't been analyzed. Consequently, for complete understanding of 3D printed metals, Ti-6Al-4V printed using EBM and SS316-L printed using SLM have been selected. Objective of the study is to analyze surface morphology and metallurgy of printed parts using analytical and experimental techniques. Secondary goal is to use the printed parts as substrate for TiN coating and utilize tribological and analytical tools to study coating behavior.

CHAPTER 3

EXPERIMENTAL WORK

This Chapter will discuss the experimental procedure adopted to investigate the properties of 3D printed Ti-6Al-4V. First part consists of parameters and procedure of 3D printing the samples. This is followed by the characterization techniques used for identifying the sample behavior and properties. Techniques used include contact angle measurement for investigating surface energy and wetting state, Roughness analysis using Optical Profilometer and Confocal Microscope, macro-structure, melt-pools(S316) and grain structure analysis using optical microscope, SEM for analyzing microstructure, EDS for analyzing and mapping elemental composition, XRD for identifying phases, Scratch hardness for testing wear behavior of material, Vickers hardness for microhardness and FTIR for analyzing residual stresses due to peak shifts. Each section includes sample preparation , equipment used and experimental procedure.

3.1 Printing Procedure

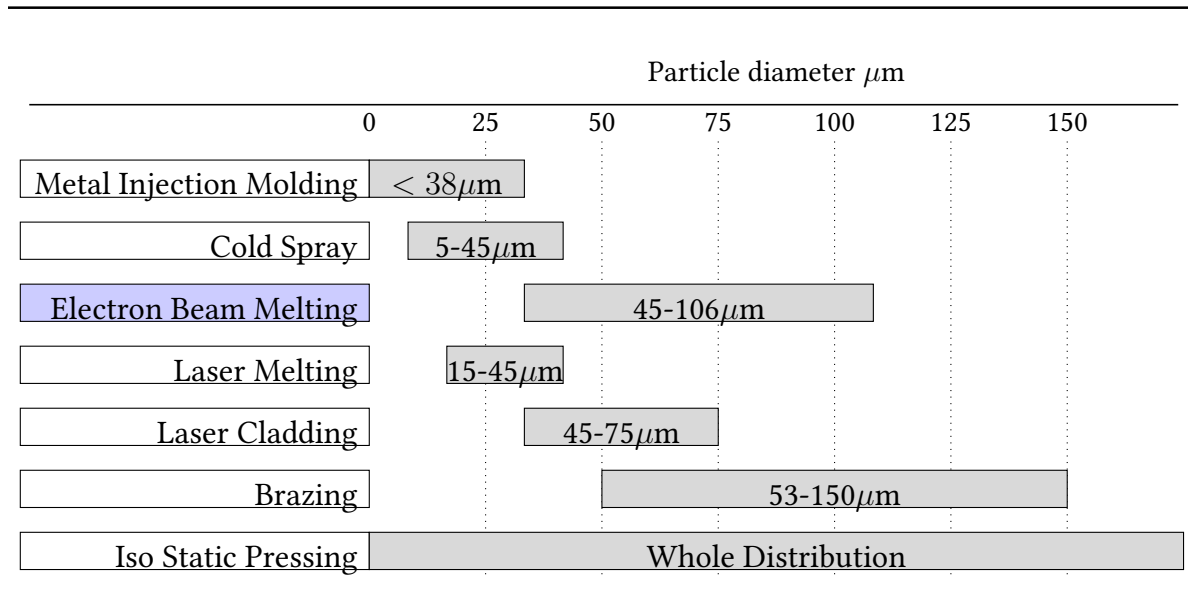
Ti-6Al-4V samples were printed using ARCAM EBM machine. Processing parameters are given in TABLE 3.1 . Beam power is around 3000 W and the beam diameter used is 180 μm . Scanning speed is fixed at about 0.1m/s. Spherical powder is used with an average diameter of 35 μm . Powder particles have a few spherical satellite particles attached.

Table 3.1: Parameters used for printing Ti-6Al-4V

Equipment	Beam Power (W)	Beam Diameter (μm)	Scanning Speed (m/s)	Avg. Powder Dia. (μm)
ARCAM EBM	3000	180	0.1	35

Powder Size has great effect on the melt pool size and layer thickness. Hatch spacing also depends on the powder size. Typical value ranges [3] for 3D printing powder are shown in Table 3.2

Table 3.2: Particle size range for Powder Metallurgy Manufacturing Processes



Flowchart of the manufacturing process is shown in Figure 3.1. First step is to make a CAD model which is sliced into layers. These layers are used to generate the tool paths

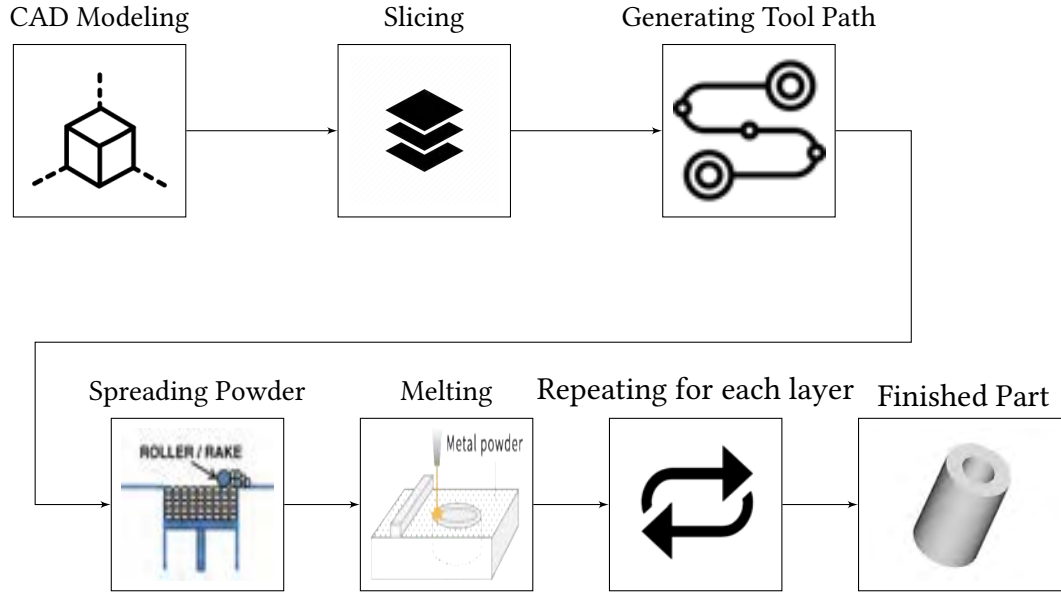


Figure 3.1: Steps for 3D Printing

which will guide the AM machine to manufacture part layer by layer. Each layer will be made by melting ,laminating, curing or sintering the raw material together. Process will be repeated for each layer until the part is manufactured [45]. No mold or fixtures are required. Models can be shared across the globe. Study by Zhai [45] shows that AM can reduce waste and lower raw material consumption by 75%.

3.1.1 Sample Preparation

Sample preparation was done for evaluation of surface energy , Roughness and Microstructure. Samples were grinded using Silicon Carbide papers on Nano 1000T grinder polisher. Speed of the grinder was set at 300 RPM for grinding at rough papers , 500 RPM for fine grinding and 800 RPM for polishing. Table 3.3 shows the grit size and micron grade of the papers used in order. $0.05\ \mu\text{m}$ Gamma Alumina from BUEHLER was used for polishing to have a mirror like surface finish. Small samples were mounted using a specimen mounting

press Qualimount- P. Material used for mounting was Transoptic Powder manufactured by BUEHLER.

Table 3.3: Grit Size for Grinding

Grit Size	60	120	220	320	400	600	800	1200
Micron Grade	260	125	68	35	22	15	10	5

Wetting state of the polished samples was also analyzed. Same grinding & polishing procedure was used before testing for scratch hardness of the samples. Etching was done using Kroll's reagent given in Table 3.4 for 10s. Wrought samples of Ti-6Al-4V were also prepared in a similar fashion as mentioned above in Table 3.3 and then etched for comparison of microstructure under optical microscope.

Table 3.4: Etchant Composition (Kroll's Reagent)

	HF	HNO_3	H^2O
Percentage	1-3 %	2-6%	91-97%

3.2 Coating Procedure

PVD coating of TiN was performed using cathodic arc deposition equipment from Sulzer Metaplas (Germany) available at Center of Research Excellence in Corrosion at KFUPM. Samples of both Ti-6Al-4V and SS 316L were prepared for coating using grinding polishing steps mentioned in Section 3.1.1. After preparation samples are loaded onto the substrate fixture and placed into the chamber. Chamber pressure is then reduced to $4 \times 10^{-5} \text{ mbar}$.



Figure 3.2: Cathodic arc deposition PVD Equipment [5]



Figure 3.3: Fixture with substrates attached for planetary rotation [5]

After that pressure rise test is performed followed by etching using arc enhanced glow discharge(AEGD) process. IR heater and planetary rotation were set to 500°C and 2 rpm respectively. Substrates are pretreated using AEGD for 1 hour. AEGD cathode of Ti is used under argon environment. Electrons ionize the argon gas which is then accelerated by the BIAS voltage towards the negatively charged substrate. High energy impact of Ions removes the oxide and residual layers from the substrate. Then bonding layer is deposited at 20 Ah in the presence of nitrogen($8.5 \times 10^{-2}\text{mbar}$). Evaporators are supplied with 130 A current. Evaporator charge is then raised to 150 Ah at $7.5 \times 10^{-2}\text{mbar}$ and then to 200 Ah at $6.5 \times 10^{-2}\text{mbar}$. These conditions are used to achieve a coating thickness of $1.8 \mu\text{m}$ by utilizing a 99.9% Ti cathode evaporator.

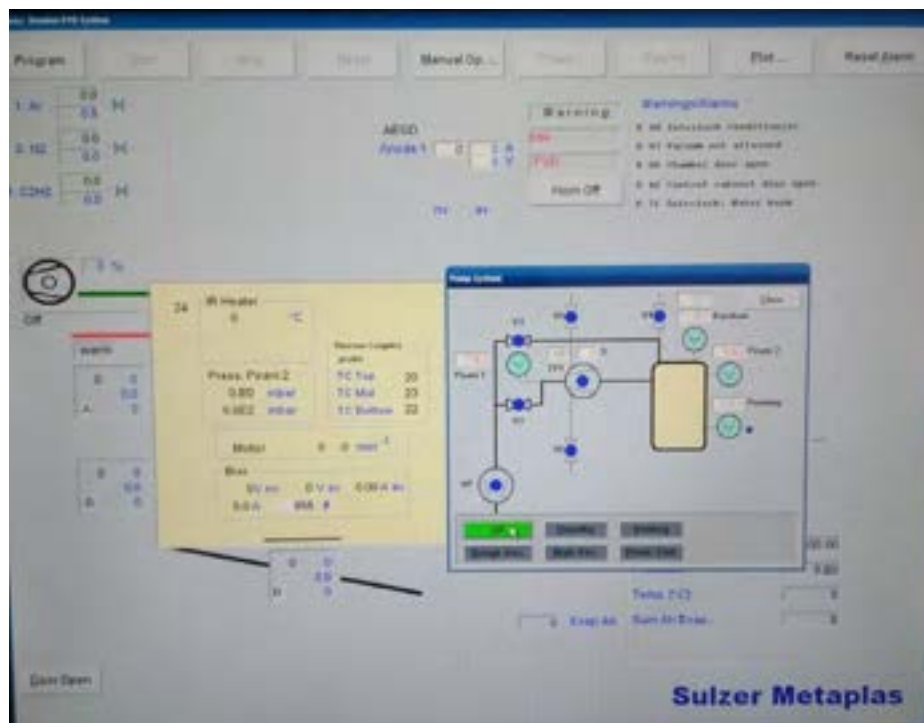


Figure 3.4: Program for controlling/monitoring etching and coating parameters

Figure 3.4 shows the program window used for controlling and monitoring the parameters of both etching and coating processes. Smaller window shows the schematic of pumping system and status of each valves. Parameters used for AEGD etching and coating process for TiN coating are given in table 3.5.

Table 3.5: Parameters used for TiN coating

Program Name		Etching	Coating
Substrate		Ti-6AL-4V/Steel316L	Ti-6AL-4V/Steel316L
Parameters	IR Heater (°C)	500	500
	Evaporator (AEGD)	Ti(99.99%)	Ti(99.99%)
	Evaporator Current (A)	85	130
	Substrate bias (V)	-250	-100
	Duration (min)	40	60
	Gas Pressure	1 X 10 ⁻² Argon (mbar)	50 (sccm) N ₂ -bond
	Gas Pressure	-	215 (sccm) N ₂ -coating

3.3 Characterization Tools

3.3.1 Wetting State

Surface energy for the 3D printed Ti-6Al-4V was determined using sessile drop methods. Contact angle was measured for two liquids water and ethylene glycol. Contact angle was measured for samples printed in both x and z direction. Each group contained 4 samples and readings for each sample were repeated more than 5 times to establish a trend and to minimize instrumental and human error. $3\mu\text{l}$ droplet was used for each reading which is within the recommended range of $1\text{-}10\mu\text{l}$ in a study done on effect of droplet size on the contact angle by biolin scientific. Droplet of water was dispensed using a microliter syringe. Glycol on the other hand was dispensed using a adjustable micro pipette. Water contact angle measurements were performed using goniometer Kyowa(DM 501). Pictures were taken using onboard camera and analyzed using ImageJ and Kyowa's software. For Surface energy Owen-Wendt model [144] given in Equation 3.1 was used which is an extension of Goods equation [145] and Young's Model [85].

$$\gamma_l(1 + \cos \theta) = 2 \left(\sqrt{\gamma_l^d \gamma_s^d} + \sqrt{\gamma_l^p \gamma_s^p} \right) \quad (3.1)$$

Table 3.6: Polar & Dispersive Components of Water and Glycol

liquid	γ_l	γ_l^d	γ_l^p
water	72.8	21.8	51
Ethelene Glycol	48	29	19

Polar and dispersive components required for surface energy calculation through Equation 3.1 are given in Table 3.6. Another extension of this model for measuring surface

energy using Van der Walls and Electron-Donor Parameters is given in Equation 3.2 and subsequently Table 3.7 shows the parameters required for calculation using this equation.

$$\gamma(1 + \cos \theta) = 2\sqrt{\gamma_S^L \gamma_L^L} + 2\sqrt{\gamma_s^+ \gamma_l^-} + 2\sqrt{\gamma_s^- \gamma_l^+} \quad (3.2)$$

Table 3.7: Lifshitz-van der Walls Component and Electron-donor Parameters

Liquid	γ_S^L (mJ/m ²)	γ_L^L (mJ/m ²)	γ_l^+ (mJ/m ²)	γ_l^- (mJ/m ²)
Water	72.8	21.8	25.5	25.5
Glycerol	64	34	3.92	57.4
Ethylene glycol	48.2	31.09	6.59	11.16

3.3.2 Optical Microscopy and Roughness

Optical microscope with 10x, 20x and 50x lenses was used to observe the microstructure and confirm the etching status of the polished samples. Samples were then analyzed using a confocal microscope Olympus DSX 510. EFI images for samples were taken to get a flat 2d image with multiple focal points. 3D images were also taken of as received samples, polished samples with indent marks and after scratch testing. 3D images were later used to analyze line roughness, surface roughness and to construct height contour maps. Resolution of roughness is low for confocal microscope and has a greater amount of error when compared with optical profilometer but considerable researches have been carried out using it. Optical profilometer was also used to acquire the surface roughness

3.3.3 SEM/EDS

FEI Quanta FEG250 was used for scanning electron microscopy and energy dispersive spectroscopy. Machine contains XT microscope console, electron console and FEG vacuum system. It was field width of 5mm at a working distance of 10mm. EDS take off angle is 35° . Take off angle is important for rough samples which can sometimes effect the results of elemental composition in valleys of very rough samples. Mounted samples were gold coated with Quorum Q150RS sputter coater for 15 seconds after attaching to the sample holder with a carbon tape. Other parameter set for sputter coating include tooling factor of 2.30, 20mA current and pressure of 0.08-2.00 mbar. Both SE and back scattered micrographs were taken for reference. Two sets of samples were used first as received samples and Ti-6Al-4V atomized printing powder was analyzed. After analyzing as received

Table 3.8: Energies for Ti-6Al-4V Elemental Peaks

Atomic Number	Element	$K\alpha_1$		λA^0	E(keV)
		λA^0	E(keV)		
13	Al	8.339	1.487		
22	Ti	2.749	4.511	27.42	0.452
23	V	2.504	4.952	24.25	0.511

sample surface sample preparation procedure as mentioned in section 3.1.1 of grinding , polishing and etching was used to analyze the microstructure and defects. Scanning Electron micrographs were taken at acceleration voltage of 20kV, chamber pressure 100Pa , spot size of 3.5mm and working distance of 12-14mm unless mentioned otherwise. EDS/EDX was done at 20KV for 25 frames. Powder samples were analyzed on a FESEM, Lyra3 Tecan from Czech Republic equipped with a Energy dispersive X-ray Spectrometer, X-Max silicon detector from Oxford Instruments.

Table 3.9: Chemical composition of Ti-6Al-4V phases (EDS)

Sample/phase	Ti (%)	Al (%)	V (%)	Ref
α Ti	92.58	6.93	0.49	[99]
β Ti	90.16	5.99	3.85	
Polished Sample	91.48	6.19	2.33	
α Ti	91.71	6.36	1.94	[146]
β Ti	76.13	2.48	21.39	

3.3.4 XRD

X-ray Diffraction was carried out using Brukers D8 Advanced Diffractometer. X-ray target used is $\text{CuK}\alpha$ at 40 kV at 30 mA. Diffraction angle range was set from 20° - 110° . Seven different samples were used from group of both horizontal and vertical printed samples. Phase analysis of the powder was done using Miniflex, Rigaku Benchtop Diffractometer.

Operating conditions for Rigaku were 30kV voltage ,15 mA current and the wavelength was 0.15416nm corresponding to $\text{CuK}\alpha$ at a scan speed of $2^0/\text{min}$ and sampling Width of 0.030 unless mentioned otherwise.

3.3.5 Hardness

Hardness was measured using Vickers indentation test following ASTM C1327-99 and the measurements were done using universal hardness tester ZHU250 ZwickRoell from Germany on machine digital camera Sentech STC-MB152USB with 20x and 40x lens and onboard software. Figure 3.5 shows the purple lines enclosing the indent. Both X and Y diagonals are averaged to calculate d which is used to calculate hardness. Indents were later measured using DSX 510 Olympus confocal microscope to analyze 3D profile and depth of the indents.500gf was used on each sample with a dwell time of 10s. For comparison 1 sample was run on with 1kgf and 3kgf also. Both horizontally printed and vertically printed samples were tested to get a difference in microhardness for different orientations.

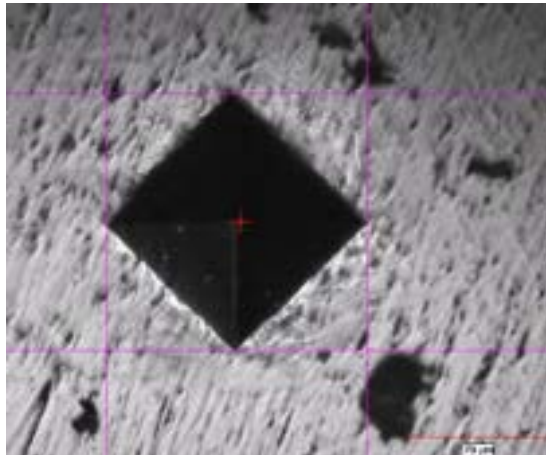


Figure 3.5: Measurement of Hardness indent

Vickers formula is given in Equation 3.3 [ASTM E92] where P is applied load in kgf

and $D(\text{mm})$ is mean diagonal of the indent and $\theta(136)$ is the angle between the opposite faces of diamond indenter.

$$HV = \frac{2P}{D^2} \sin \frac{\theta}{2} \quad (3.3)$$

Coating hardness was analyzed using CSM micro tester equipped with VH 85(vickers) indenter. Modulus and microhardness were determined using data collected from loading and unloading curves and Oliver and Pharr formulations [147]. Figure 3.6 shows the indenter sample projected contact area (A_p). VH was calculated using maximum load P_m and A_p as given in equation 3.4

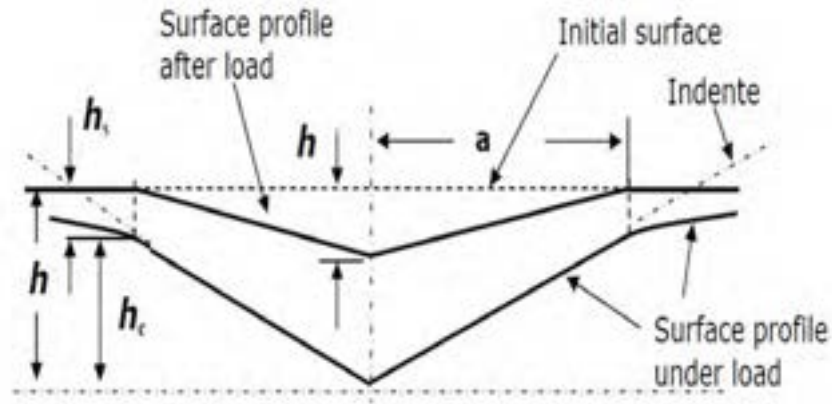


Figure 3.6: Measurement of Hardness indent

$$HV = \frac{P_m}{A_p} \quad (3.4)$$

Load was kept small to ensure penetration depth less than 15% so that effect of substrate hardness is minimized. Stiffness(S) is determined using slope of unloading curve at initial point which is then used to calculate reduced Modulus of Elasticity E_r given in

equation 3.5. Modulus of specimen E_{IT} can be calculated using plain strain modulus E^* and poisson ratio v_s of the specimen and is given in equation 3.7. Effective modulus E can be calculated using E_r , indenter modulus E_i (diamond 1141GPa [5]) and Poisson ratio of indenter v_i (0.07) and is given in equation 3.6

$$E_r = \frac{\sqrt{\pi}S}{2\beta\sqrt{A_p}} \quad (3.5)$$

$$E = \frac{1}{\frac{1}{E_r} - \frac{1-v_i^2}{E_i}} \quad (3.6)$$

$$E_{IT} = \frac{\sqrt{\pi}S}{2\beta\sqrt{A_p}} \quad (3.7)$$

3.3.6 Fracture Toughness

Fracture toughness was evaluated using strain dependent ductile indentation method mentioned in Section 2.6. CSM micro-tester with vickers indenter was used to evaluate fracture toughness. Loading unloading curves were recorded for bulk substrates of Ti-6Al-4V and Steel 316 L at 1N, 2N and 3N. Penetration depth h_p was recorded. Logarithmic scatter plots were drawn for E and h_p and a linear fitting was performed using Origin to obtain the relation for $\ln E$ and $\ln h_p$. Critical value of Modulus was calculated by inserting strain at fracture point ε_f in equation 3.8 [126]. ε_f was taken as 6% for Ti-6Al-4V [128] and 0.7 for Steel 316L [148]. Critical Modulus E^* was used to obtain the critical penetration depth h_p^* from linear equation obtained earlier using fitting procedure. Function of load was formulated using 2nd order polynomial fitting of h_p and load (F) plot. Equation 3.9 was then

used to obtain critical value of surface energy γ^* . Finally ,fracture toughness K_{IC} was then calculated by inserting critical values of γ^* and E^* in equation 3.10.

$$\tilde{E}^* = E_0 e^{-\frac{9(1-\nu)}{4}\varepsilon_f} \quad (3.8)$$

$$\gamma = \int_0^{h_p^*} \frac{F(h_p)}{A_p(h_p)} dh_p \quad (3.9)$$

$$K_{IC} = \sqrt{2E\gamma} \quad (3.10)$$

3.3.7 Scratch Testing

Linear Micro scratch tester (MCTX-S/N:01-04300) was used for scratch testing the samples with a rockwell indenter. Friction coefficient was measured for horizontally printed,vertically printed and wrought samples of Ti-6Al-4V. Preloading force was set to 0.1N. Penetration force was 1N at a speed of 0.1N/s. Scratch was done for a length of 1mm at speed of 0.5 mm/min. Scratched sample was later analyzed under optical and scanning electron microscope. Other recorded parameters include Absolute penetration (μm),Scratching force-X (N),Displacements (mm) and Axial force-Z(N) Progressive load scratch testing was performed using CSM micro tester equipped with diamond tip rockwell indenter(I-176). Load was progressively increased until failure of the coating was achieved. Critical load to achieve delamination and fracture were observed and are recorded as L_c . Acoustic emission signals were analyzed to identify L_c .

3.3.8 FTIR

Fourier Transform Infra-Red spectroscopy was performed using Vertex 70v from Bruker. Standard testing conditions were used. Background was recorded first with a blank sample and then subtracted from the sample results inside the machine software for clear peak identification. One sample for each group was analyzed and powder sample was measured for comparison.

CHAPTER 4

CHARACTERIZATION AND ASSESSMENT

The focus of this chapter is to characterize and analyze the 3D printed and polished samples using Analytical techniques like sessile drop experiment, Optical Microscopy, Profilometry, SEM ,EDS ,XRD and Scratch Hardness. These analytical techniques will be used to investigate properties of the samples like wetting state, surface energy, surface topology, roughness, microstructure, composition, phases and hardness.

4.1 Ti-6Al-4V Characterization Results

This section contains the results of characterization of the samples. As received printed samples are divided into two groups. First group is X-oriented samples and second group is z-oriented samples. Other sample groups include polished samples from x & z orientation group and powder sample for comparison with the printed sample.

4.1.1 Wetting State & Surface Energy

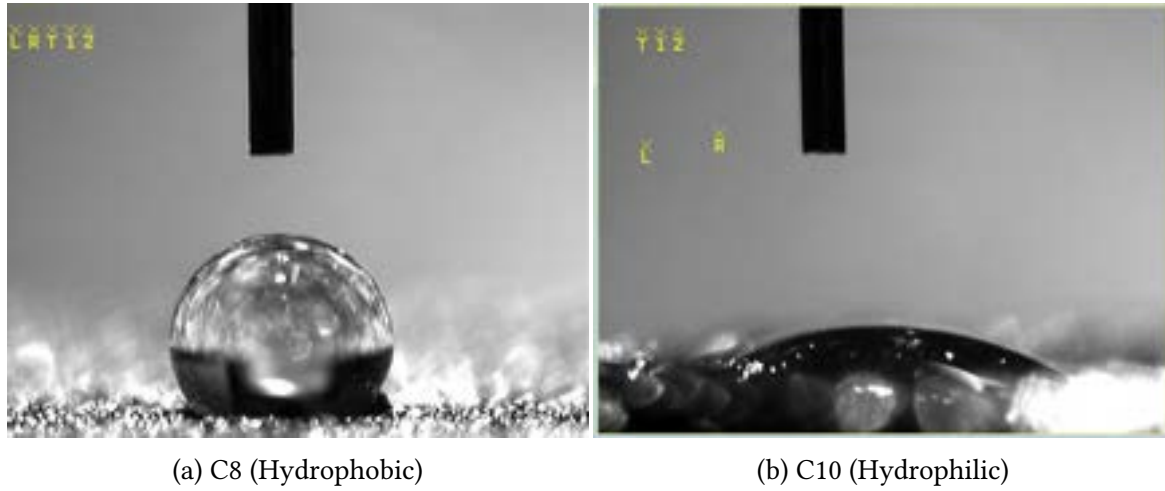


Figure 4.1: Water Contact Angle C8(X), C10(Z)

Wetting state was quantified using sessile drop experiment. Water was used to observe the wettability of the material. 3D printed surfaces showed both hydrophobic and hydrophilic behaviors. X-orientation samples mostly exhibited hydrophobic behavior and Z-orientation samples showed hydrophilic behavior. Figure 4.20 shows the wetting state for sample C8 and C10. C8 has water contact angle of 130 and C10 30 degrees. Difference in such tremendous different wetting states of the same material can be attributed to the surface topology of the two samples. C8 belongs to the group of samples with X- orienta-

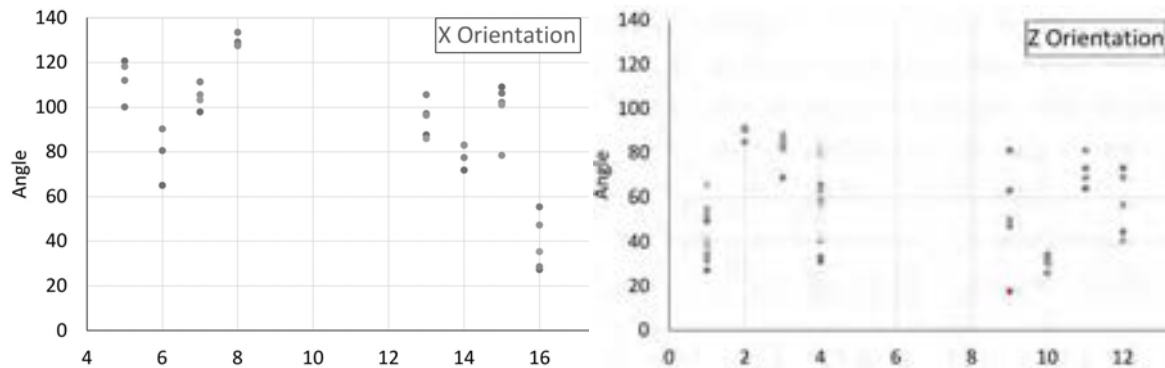


Figure 4.2: Water Contact Angle X & Z Orientation

tion as the top side and C10 belongs to sample group with Z-orientation as the top side. C16 deviates from the herd behavior and behaves hydrophilically giving an angle of 38 degrees despite belonging to the X group. The reason for this deviation is the abundance of porosity and lack of fusion defects on the top surface of C16. C16 behaves similar to a sponge absorbing the drops at first few tries. Red dot shown in measurements of C9 Figure 4.2 refers to a discarded value of the reading. The readings of this type were discarded due to reasons like adhesive forces with the edge of the sample causing the droplet to spread further than the actual value. C2,C3 ,C7,C8 ,C10 and C15 showed consistent behaviors with very small variation in the readings suggesting a uniform topology distribution on the surface.

Owen Wendt model given in Equation 3.1 can be solved for Polar and Dispersive components of surface energy of the solid using two liquids. Resultant equations are given as Equation 4.1 & Equation 4.2.

$$\gamma_s^p = \left(\frac{\gamma_{l_2} \sqrt{\gamma_{l_1}^d} (1 + \cos\theta_g) - \gamma_{l_1} \sqrt{\gamma_{l_2}^d} (1 + \cos\theta_w)}{2 \left(\sqrt{\gamma_{l_2}^p \gamma_{l_1}^d} - \sqrt{\gamma_{l_1}^p \gamma_{l_2}^d} \right)} \right)^2 \quad (4.1)$$

$$\gamma_s^d = \left(\frac{\gamma_{l_1} \sqrt{\gamma_{l_2}^p} (1 + \cos\theta_w) - \gamma_{l_2} \sqrt{\gamma_{l_1}^p} (1 + \cos\theta_g)}{2 \left(\sqrt{\gamma_{l_2}^p \gamma_{l_1}^d} - \sqrt{\gamma_{l_1}^p \gamma_{l_2}^d} \right)} \right)^2 \quad (4.2)$$

We can then put the values for polar and dispersive components of water and Ethylene Glycol given in Table 3.7 and obtain simplified form in which surface energy is only dependent on contact angle of water and glycol. Two equations can then be solved for values of θ from 0° to 180° using Matlab with a step size of 6° . Two components of surface energy can then be added to obtain total surface energy. Resultant surface energy is then

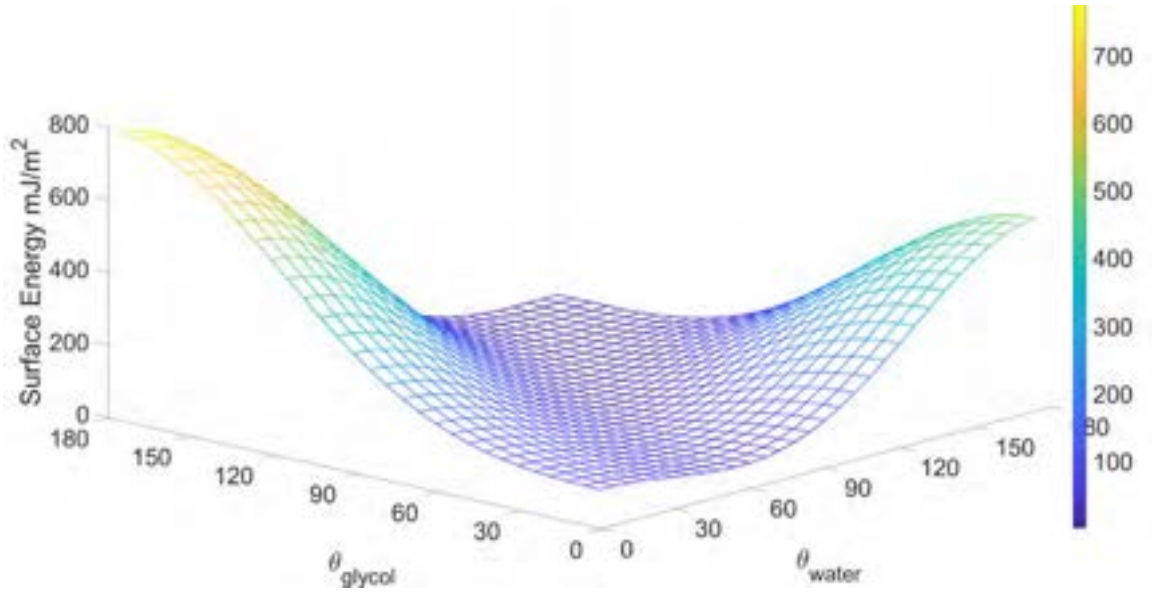
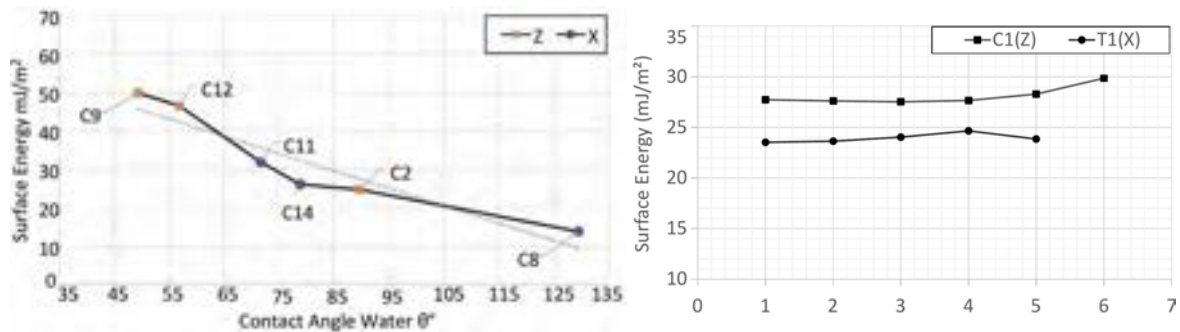


Figure 4.3: Surface Energy Plot for Owen-Wendt Model using water & glycol

plotted against θ_w and θ_g to obtain a surface plot as given in Figure 4.3.

Surface energy of the as the as received samples calculated by Owen-Wendt model is given in Figure 4.4a. The trend line shows a decrease in surface energy as the contact angle decreases. This is true for cases of contact angle of glycol higher than 60° but is opposite for contact angle of glycol less than 50° as evident from the plot of Owen-Wendt Model. Surface Energy of as received samples is from 15 mJ/m^2 to 50 mJ/m^2 . Z-orientation as received samples occupy the higher spots of surface energy as they have lower water



(a) Contact Angle Vs Surface energy of As-Received Samples

(b) Surface energy of Polished Samples

Figure 4.4: Surface Energy of Ti-6Al-4V

contact angles. There are certain deviations like in the case of C2. This deviation can be attributed to the dominated nature of roughness and surface topology in contribution to surface energy. Another reason can be the presence of satellite powder particles attached to the surface. Surface topology is the major cause for these large deviations in surface energy as the variation in surface energy of polished samples is just $3.8mJ/m^2$. Surface Energy of Z-oriented and X-oriented polished samples is $27.8mJ/m^2$ and $23.9mJ/m^2$ respectively.

Surface topology of the as received samples C7(X-oriented) and C10(Z-oriented) is given in Figure 4.5 . X Oriented samples show the partially molten powder particles attached to the surface. These unmolten powder particles act as micro pillars for the water giving the surface lotus effect. This is the primary reason for higher water contact angle for the case of X-oriented samples. On the other hand Z-oriented samples have meltpool stepping on the surface leaving tracks on molten pool due to rapid solidification. Further

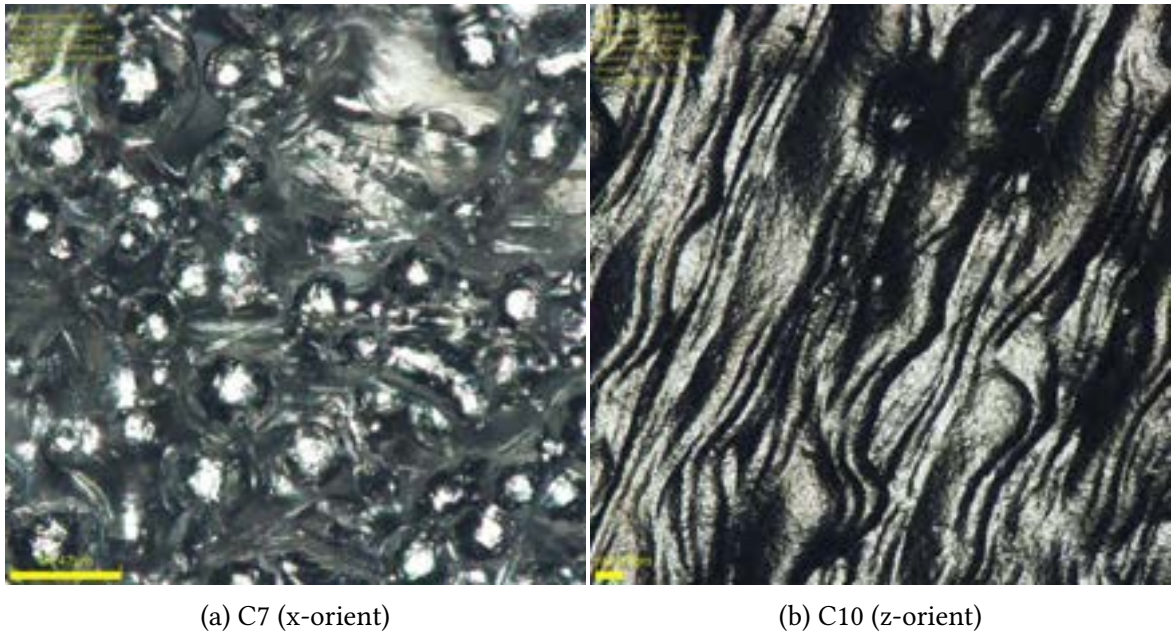


Figure 4.5: Surface Structure of C7 and C10 using Optical Microscope

investigation of the surface topology including melt pools and stepping will be done in Section 4.2.3 using SEM micrographs.

4.1.2 Roughness

Roughness of the samples was measured using both optical Profilometer and Confocal Microscope. Values of roughness are given in Table 4.1. Line roughness for both horizontal and vertical direction was recorded using confocal microscope. X-oriented samples show 5-9 times the roughness(R_a) of z-oriented samples while measuring with confocal microscope and 5-13 times for Optical Profilometer. Roughness profile for C4 is given in 4.6. Green line shows the waviness, blue line represents roughness and red line is observed resultant value. Vertical and horizontal roughness profiles of T9(X-oriented) sample are given in Figure 4.7. T9 shows micro and nano-sized pillars comprising of unmolten powder particles sintered to the surface. These spherical particles act as pillars to hold air pockets below the water droplet making sessile drop act in Cassie-Baxter regime. These trapped air pockets give lotus leaf its hydrophobic properties. X-oriented samples show hydrophobic behavior (Figure 4.2) despite having similar surface energy (Figure 4.4). This suggests the presence of air pockets making droplets act in Cassie Baxter regime.

Figure 4.8 shows 2d images of 3 X-oriented and 3 Z-oriented samples. Within the sample group the roughness and topology are similar and across the group it varies drastically. Figure 4.9 shows 3D graphs on all 6 samples,% of acquired data points is also similar for both cases. Table 4.1 shows the recorded values of roughness. Optical profilometer shows higher topology difference between the X & Z oriented samples when compared with confocal microscope due to higher resolution.

Table 4.1: Roughness Values from Optical Profilometer and Confocal Microscope

		Rp(μm)	Rv(μm)	Ra(μm)	Rt(μm)	Sa(μm)	Equipment
C4(Z)	Horizontal	0.816	0.913	0.55	5.427	5.884	Confocal Microscope
	Vertical	0.951	1.018	0.61	4.222	–	Confocal Microscope
T9(X)	Horizontal	7.268	6.8	3.086	47.702	26.598	Confocal Microscope
	Vertical	9.782	11.049	4.942	45.796	–	Confocal Microscope
	Data Points	Rp(μm)	Rv(μm)	Ra(μm)	Rt(μm)		Equipment
C4(Z)	36.85%	14.431	-8.797	0.491	23.228		Profilomter
C10(Z)	49.17%	16.521	-22.882	0.451	39.404		Profilomter
C12(Z)	56.12%	17.963	-12.569	0.573	30.532		Profilomter
C16(X)	16.92%	29.859	-39.648	2.867	69.507		Profilomter
T12(X)	14.93%	42.016	-67.632	3.649	109.648		Profilomter
C8(X)	14.35%	58.96	-97.526	6.233	156.486		Profilomter

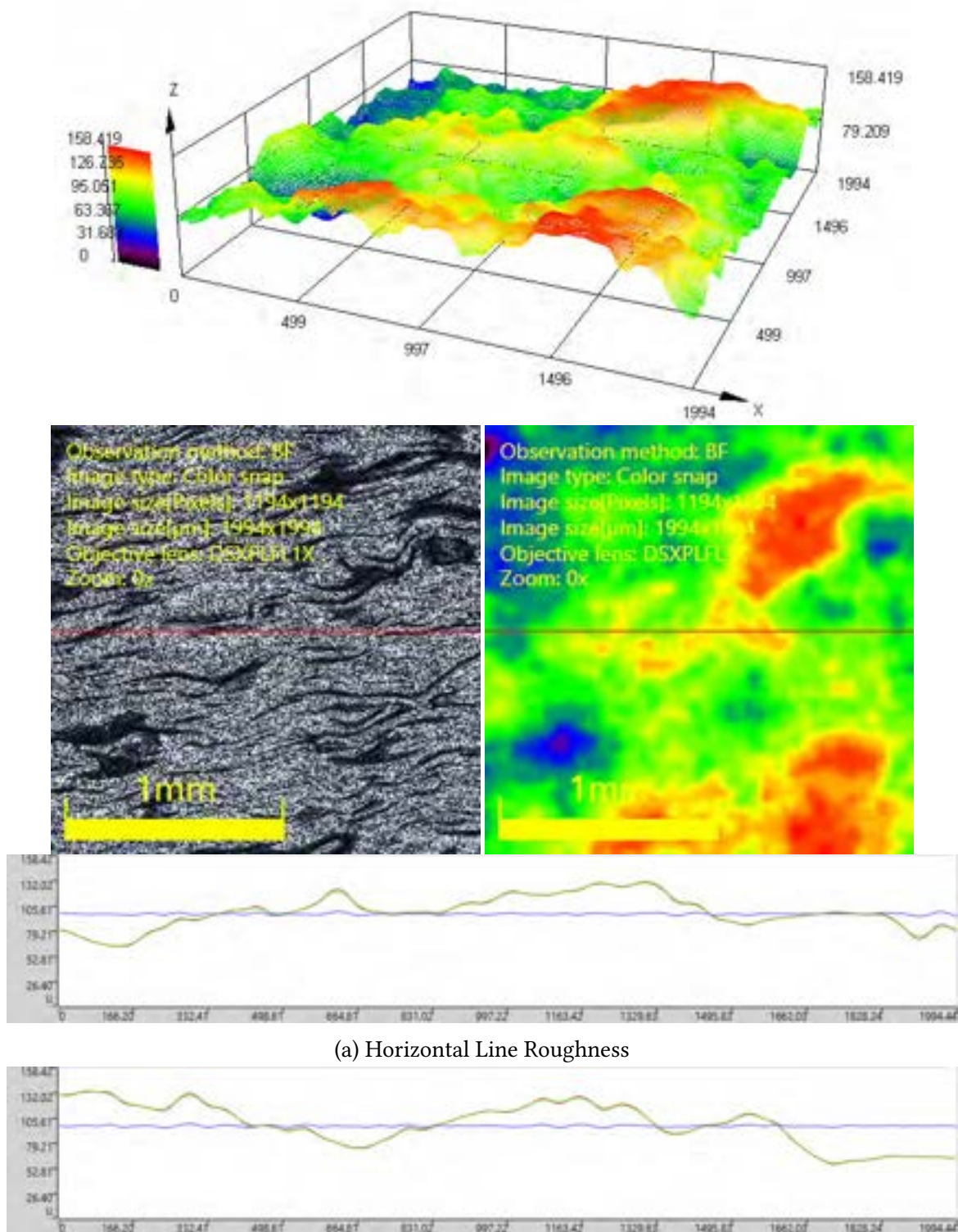


Figure 4.6: Roughness C4(Z-orient)

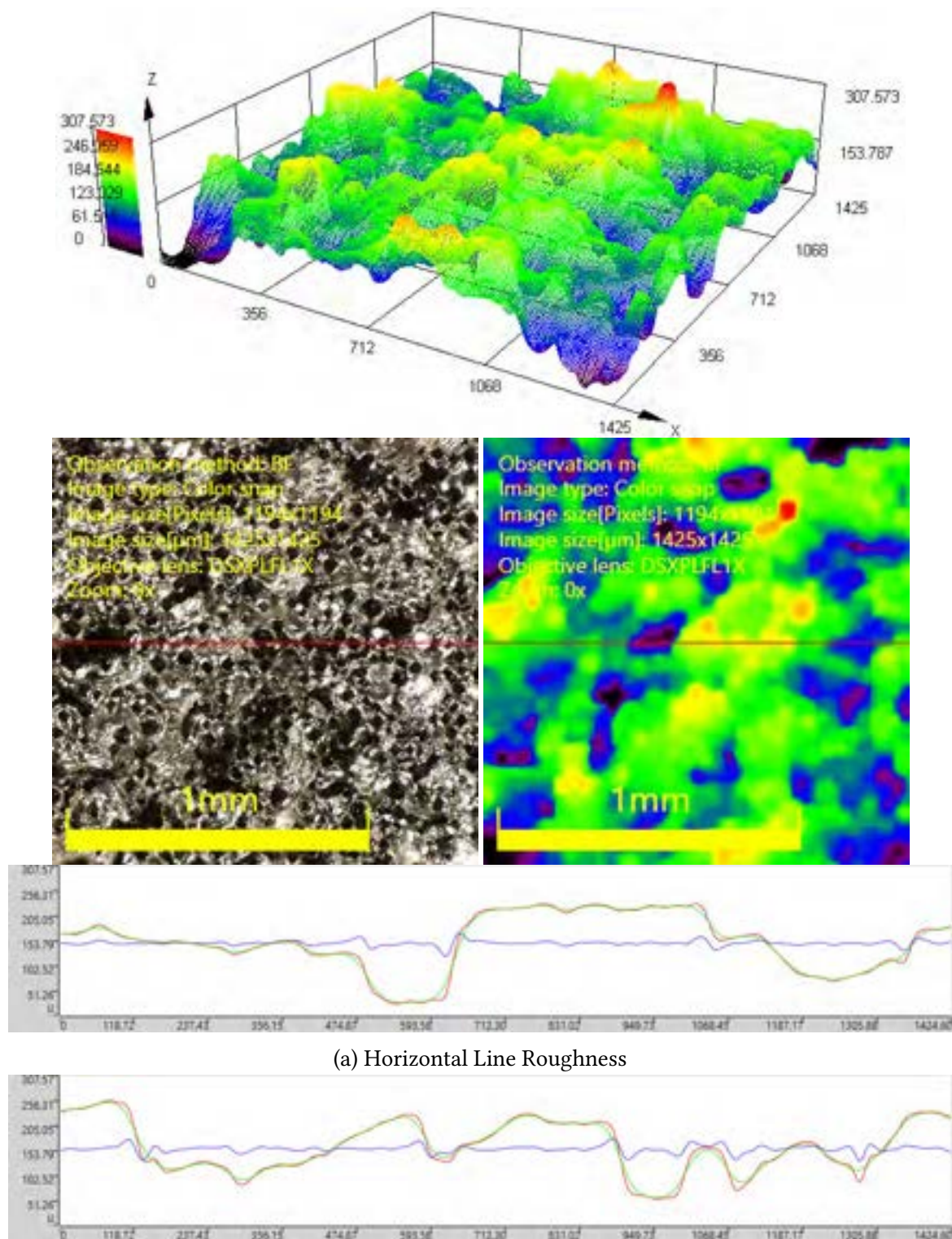


Figure 4.7: Roughness T9(X-orient)

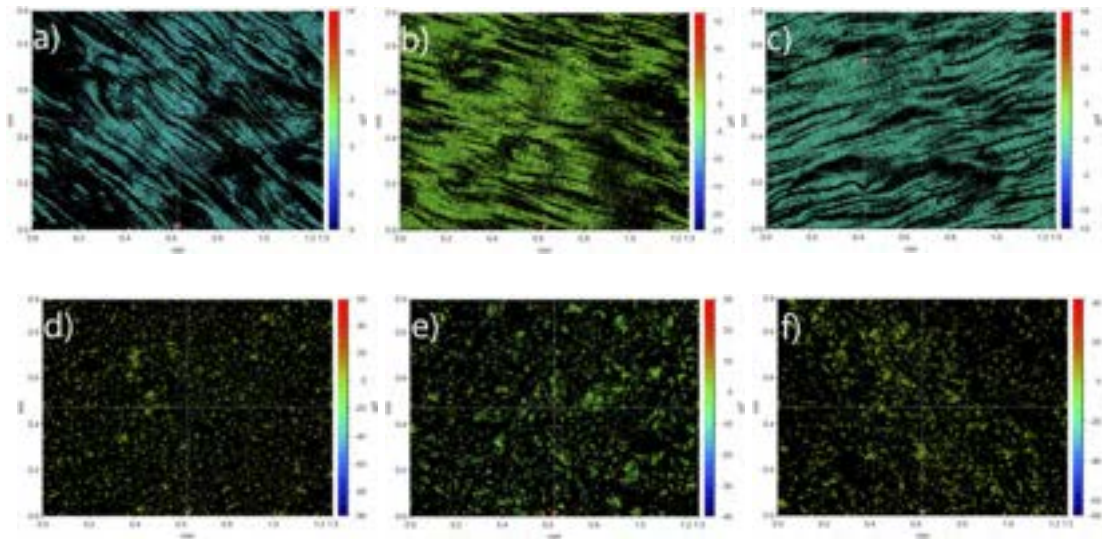


Figure 4.8: Hardness Ti-6Al-4V 3D Printed Vs Wrought Samples (a)C4 (b)C10 (c)C12 (d)C8 (e)C16 and (f)T12

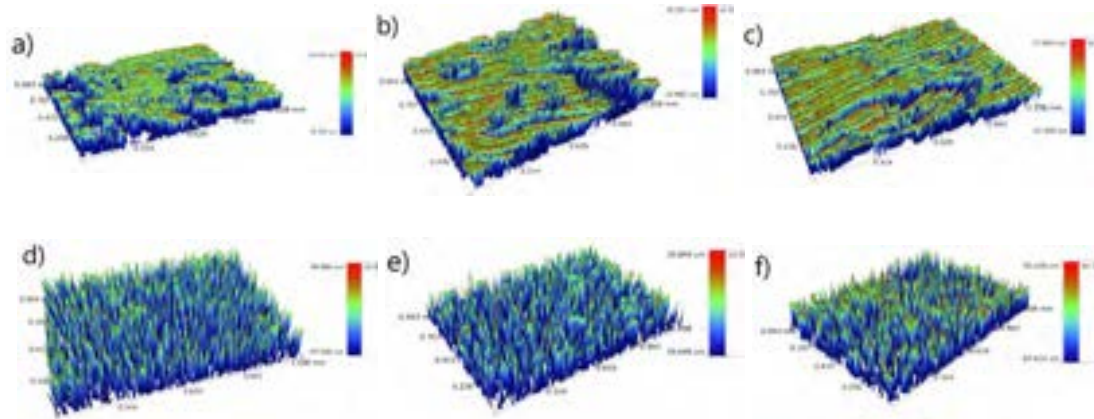
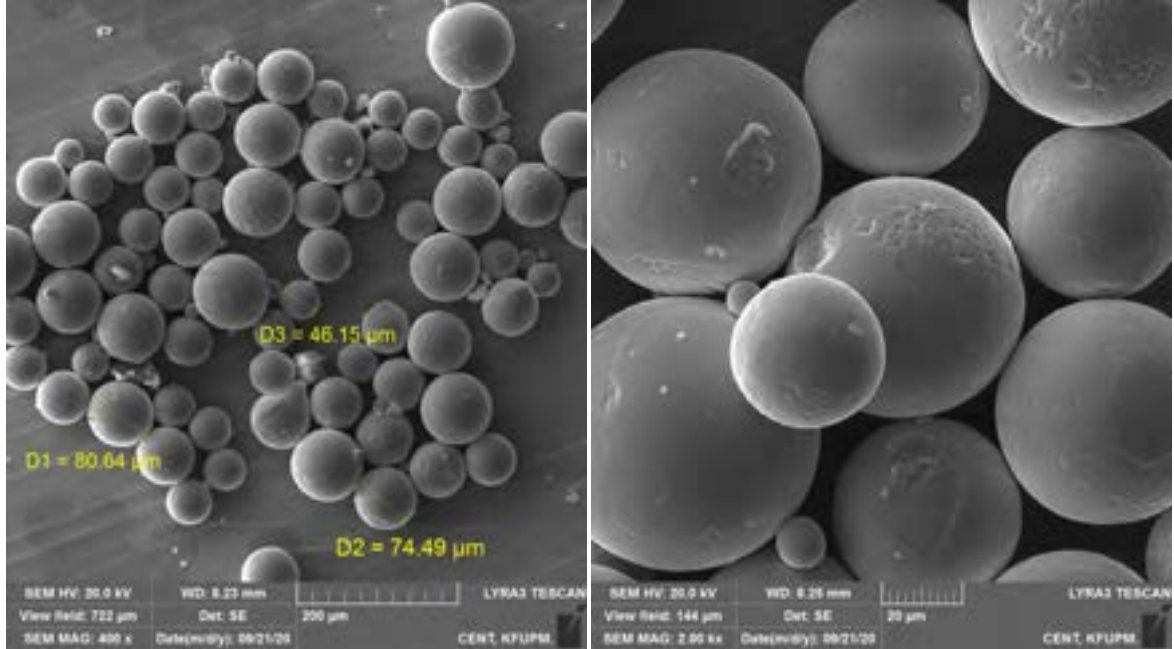


Figure 4.9: Roughness measured using Optical Profilometer (a)C4 (b)C10 (c)C12 (d)C8 (e)C16 and (f)T12

4.1.3 SEM

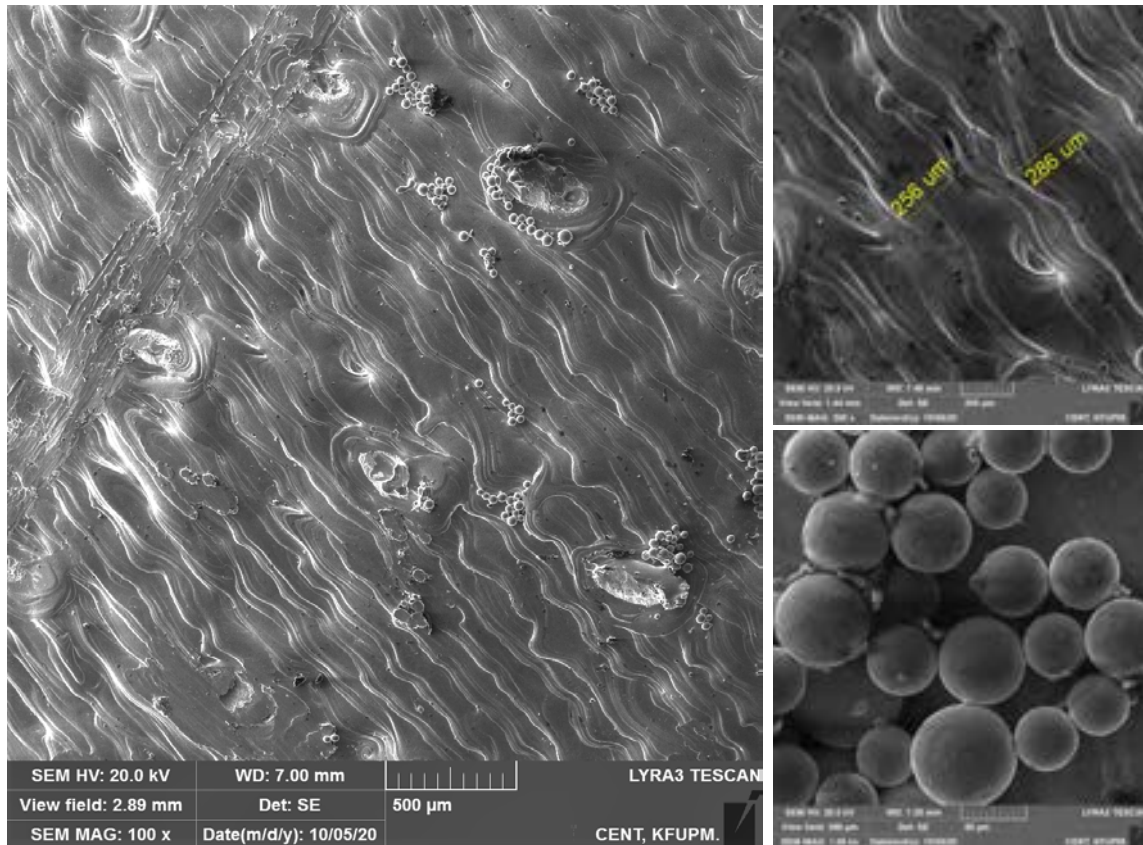


(a) Powder size distribution

(b) Satellite particles and fusion defects

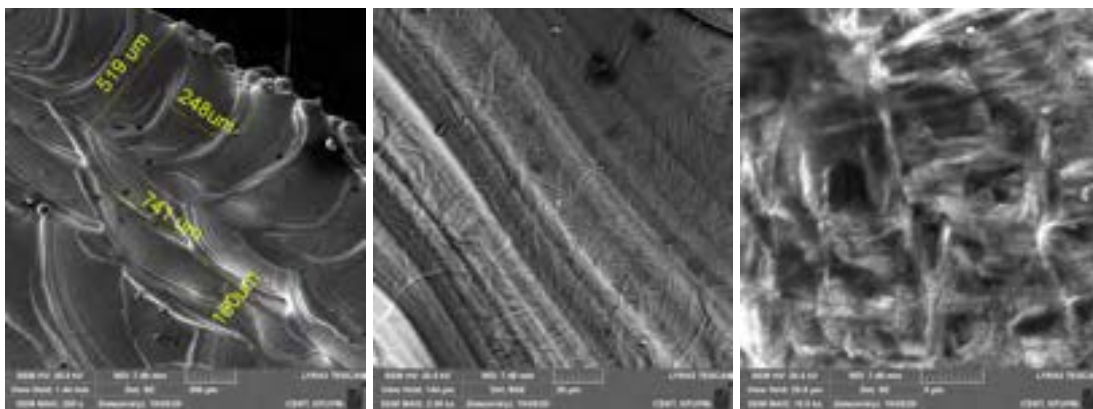
Figure 4.10: Ti-6Al-4V Powder used for printing

Figure 4.10a shows the distribution of Ti-6Al-4V powder size used for printing. Powder shows variation in the diameter with particles as big as 80.64 μm diameter to as small as 46.15 μm diameter. The majority of particles lie within 46-60 μm range. This is fine as EBM printing ranges from 45 μm to 106 μm [3]. Figure 4.10 shows the defects in atomized powder. Some powder particles have satellite particles attached to the surface and have lack of fusion defects. There is also chipping of some particles but most of the particles are spherical and show a skewed normal distribution towards the lower size.



(a) Meltpool Layer with defects

(b) Layer Stepping & Unmolten Powder



(c) Perpendicular scanning direction melt pools

(d) Acicular α phase needles inside meltpool(BSE)

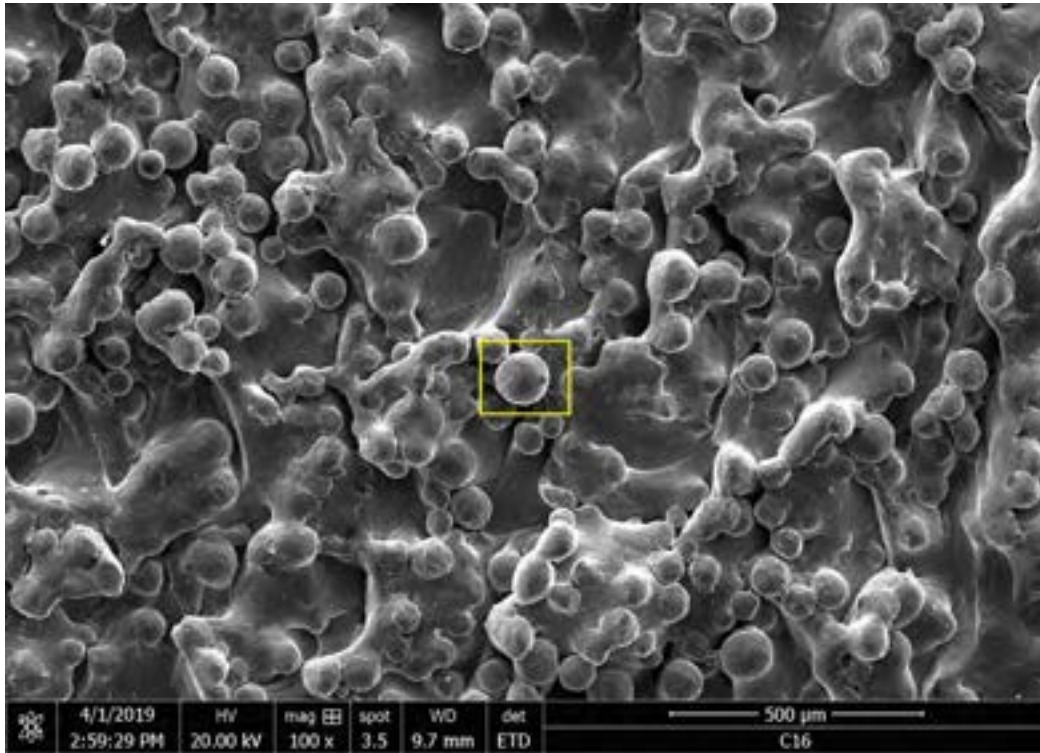
(e) Widmanstatten pattern of α needles

Figure 4.11: SEM micrographs of as printed S30(z-orient) with meltpool stepping

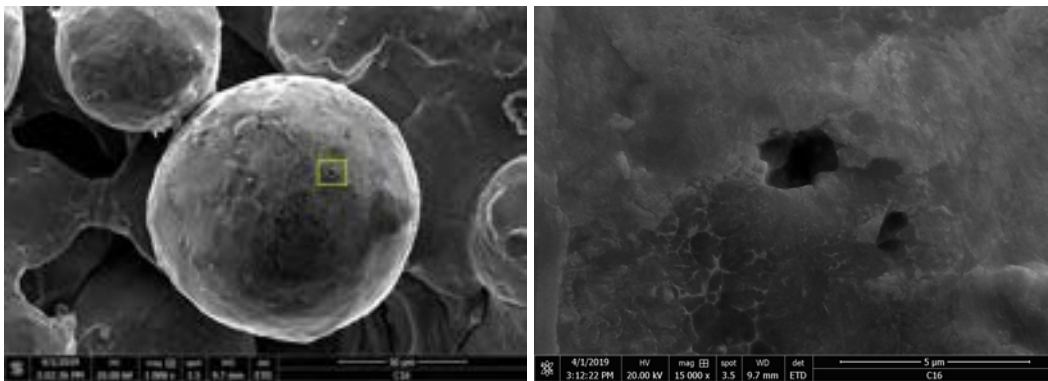
SEM micrographs of S30 are given in Figure 4.11. S30 is z-oriented sample and shows meltpool layers in the top surface. Meltpool layers are shown in Figure 4.57a. We can

observe several defects in the printed part. Figure 4.57e shows the layer stepping. This layer stepping is caused by the rapid movement of the Electron beam and solidification of the molten layers. Layer stepping is also dependent on the angle of the top surface with the build plate as gravity can affect and change the shape and size of the stepping. Figure 4.11d is back scattered micrograph which shows the presence of α phase acicular needles near the surface of the printed sample. Further magnification in Figure 4.11e reveals Widmanstätten basket weave like pattern of the α phase needles. Meltpool directions can be observed in Figure 4.11c. There are two sets of meltpools perpendicularly aligned to each other. This change in direction of the meltpool is due to scanning direction of the Electron beam. Shape is similar to melt beads in welding. Smaller meltpools are due to the scanning of edge with a length of $519\mu\text{m}$ and a width of $248\mu\text{m}$ and bigger meltpools are the result of surface scanning strategy with a length of $741\mu\text{m}$ and width of $160\mu\text{m}$. If we suppose the meltpools to be ellipses and calculate the area of smaller beads and bigger pools the difference comes to be around 8% suggesting a consistency in overall meltpool area. Meltpools cease to exist towards the center of sample instead the shape changes to layer like structure with wavy patterns. Width of layers is from $256\mu\text{m}$ to $286\mu\text{m}$. Top right corner of Figure 4.11c shows the unmolten powder particles attached to x-orientation of the sample. Figure 4.57e reveals the presence of unmolten powder on the surface due to partial melting or poor cleaning of the printed part. Small spherical satellite particles also appear between the meltpools.

Investigation of C16 micrographs reveals a different structure consisting of spherical powder particles as shown in Figure 4.12. Powder particles adjacent to the melt layer have fused to the surface forming a sheet of spherical micro pillars along the surface. We



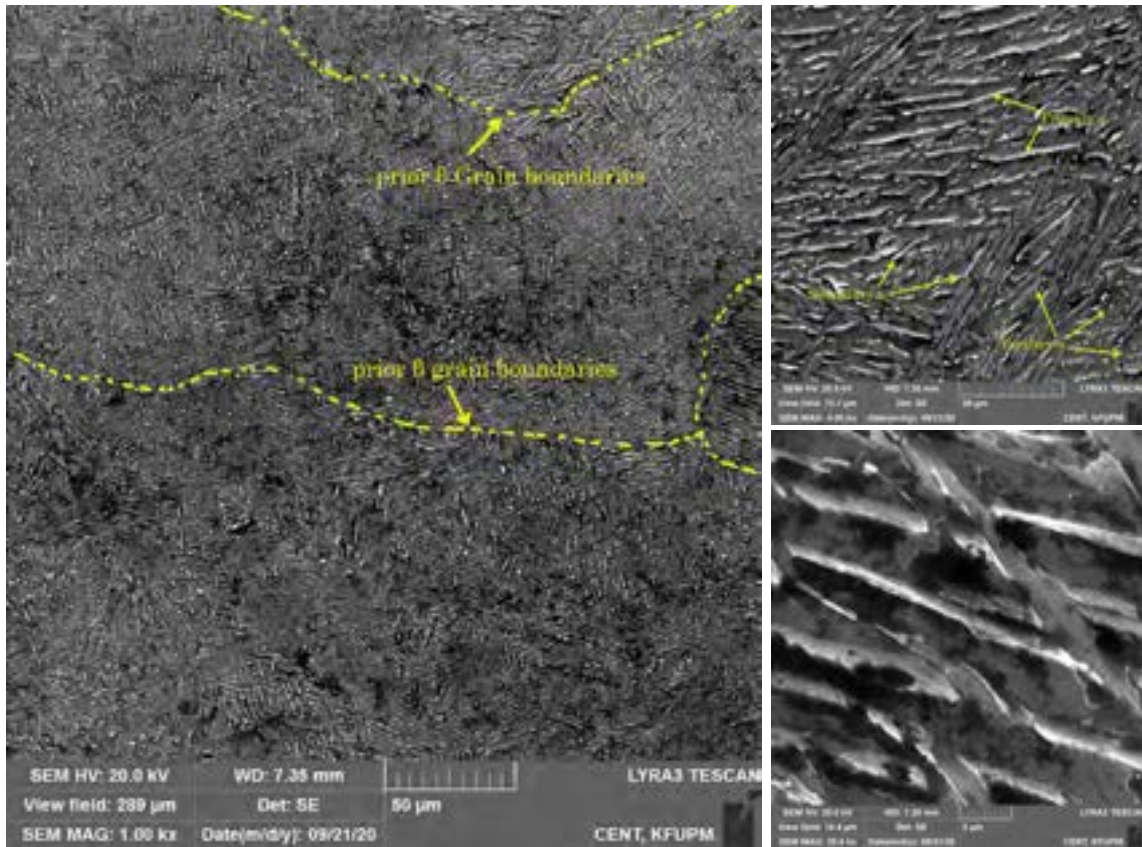
(a) Powder Sintered to molten layer (Macro-500 μ m)



(b) Satellite particles attached to molten (c) Pore in satellite powder particle (Micro-layer (Meso-50 μ m) 5 μ m)

Figure 4.12: SEM micrographs of as printed C16(x-orient) with unmolten powder

can clearly observe the spherical shape of particles but some particles have fused with neighboring powder to form agglomerates. Phenomena looks similar to Ostwald ripening in the solid solutions but doesn't form big spherical particles due to premature cooling of the particles and gravity at the macro scale.



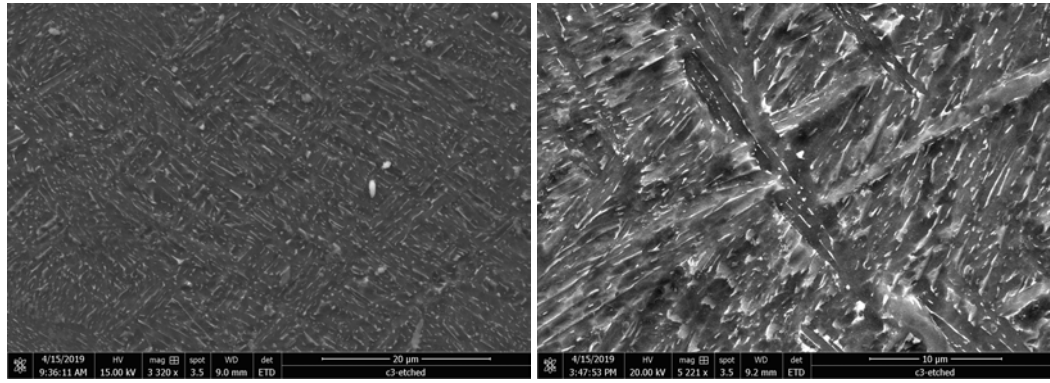
(a) α needles within β grains

(b) Laths of α

Figure 4.13: SEM micrographs of etched C5

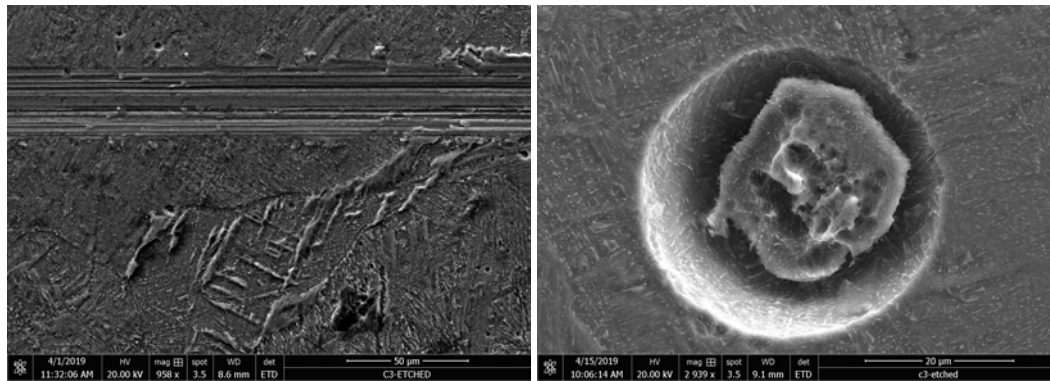
Figure 4.56g shows magnified micrograph of the partially molten powder particle attached to surface. Few of the molten powder spheres have satellite particles attached to them and some have pores on their surface. Figure 4.56h shows one of pores in the powder particle.

Investigation of polished C5 after etching reveals the microstructure of the material as shown in Figure 4.13. Widmanstatten structure of α needles is observed within the β grains. Identifying the grain boundaries is difficult as α needles sometimes overlap the β grains. Further magnification in Figure 4.13b shows a hierarchical structure of α laths. Primary α laths are around $18\text{-}22\mu\text{m}$ and secondary α is around $5.5\text{-}6.5\mu\text{m}$. Tertiary



(a) Microstructure of etched C3

(b) α laths in β grain



(c) Scratch on etched C3

(d) Lack of fusion defect

Figure 4.14: SEM of etched C3 with scratch

alpha is around $0.9\text{--}1.5\mu\text{m}$. This hierarchy of structure is due to repeated heating cooling of molten layers. In 3D printing material is deposited in a layer by layer fashion which results in repeated thermal cycles due to heating and cooling of subsequent layers. Cooling rate has primary influence on the grain boundaries resulting in columnar grains in build direction due to preferential cooling in that direction.

Z oriented C3 sample was also analyzed using SEM after etching. Microstructure was similar to C5(x-orient) with needles of α within β grains but structure was more dominant with smaller size needles when compared to C5. Figure A.2f shows the α laths distribution. Figure A.1h shows the scratch done while scratch testing and deformed α laths protruding

out of the surface. Figure 4.14d shows lack of fusion defect due to presence of trapped air within the sample. These defect sites can be sources of crack origination during failure of the material.

4.1.4 EDS

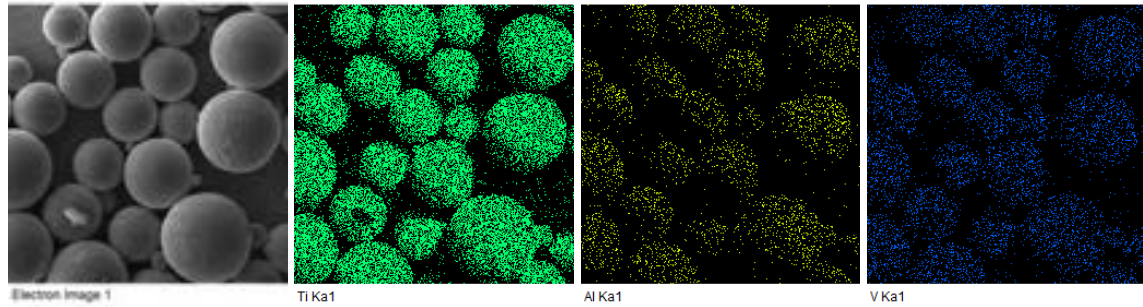


Figure 4.15: EDS of Powder Ti-6Al-4V with mapping

Table 4.2: Elemental composition of Powder Ti-6Al-4V Figure 4.15

Element	Ti	Al	V
Weight %	88.32	7.01	4.67

EDS analysis was done to obtain the elemental composition of the material. Figure 4.15 shows the elemental mapping of Ti-6Al-4V powder. Distribution is uniform for all three elements. Dark spots are due to limitation of machine as the take off angle for eds detector is 35^0 so the valleys within the powder appear dark. One dark spot on the spherical powder in Ti mapping is due to the impurity entering the sample while preparation. Ti-6Al-4V is an α - β alloy. Aluminum acts as an α stabilizer and raises the β transition temperature. Moreover low density of aluminum decreases the weight of the alloy. Higher concentration of aluminum in the powder suggests presence of more α and slightly brittle behavior.

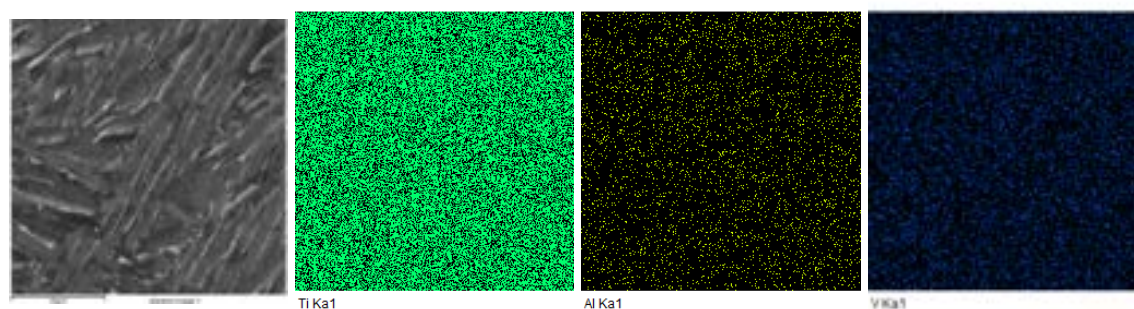
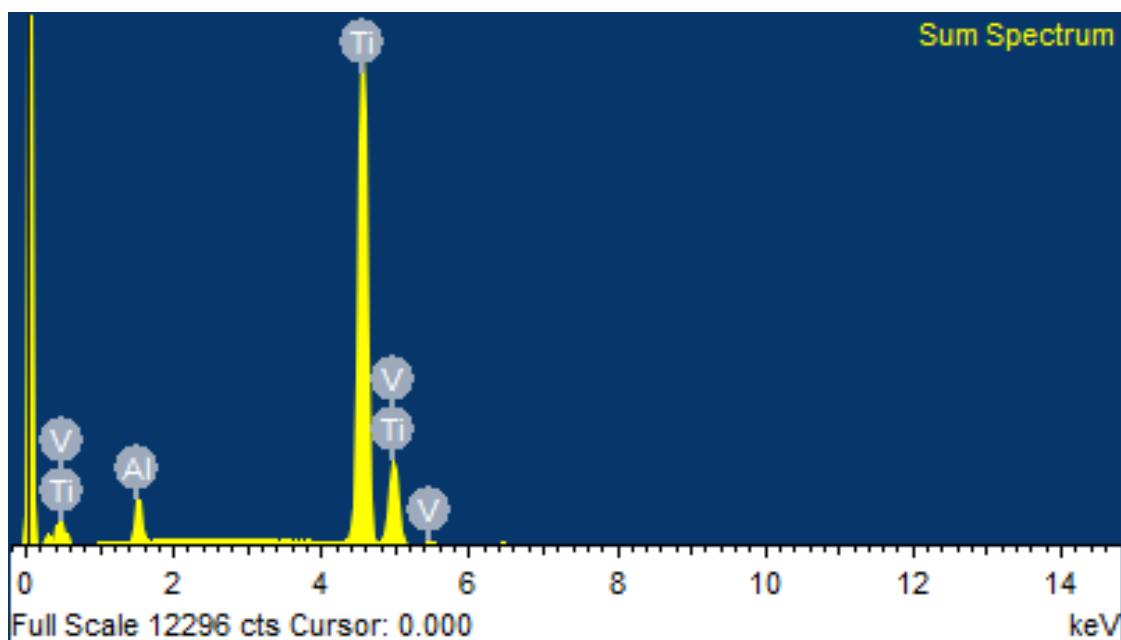


Figure 4.16: EDS of etched C5 with mapping

Table 4.3: Elemental composition of Figure 4.16

Element	Ti	Al	V
Weight %	91.11	4.98	3.91

C5 etched sample was also analyzed using EDS as shown in Figure 4.16. Mapping of the elements reveals no visible difference in the sample. Sample appears to have uniform distribution with slight hints of α in mapping of Aluminum and Vanadium. None the less difference is small enough to quantify any real results.

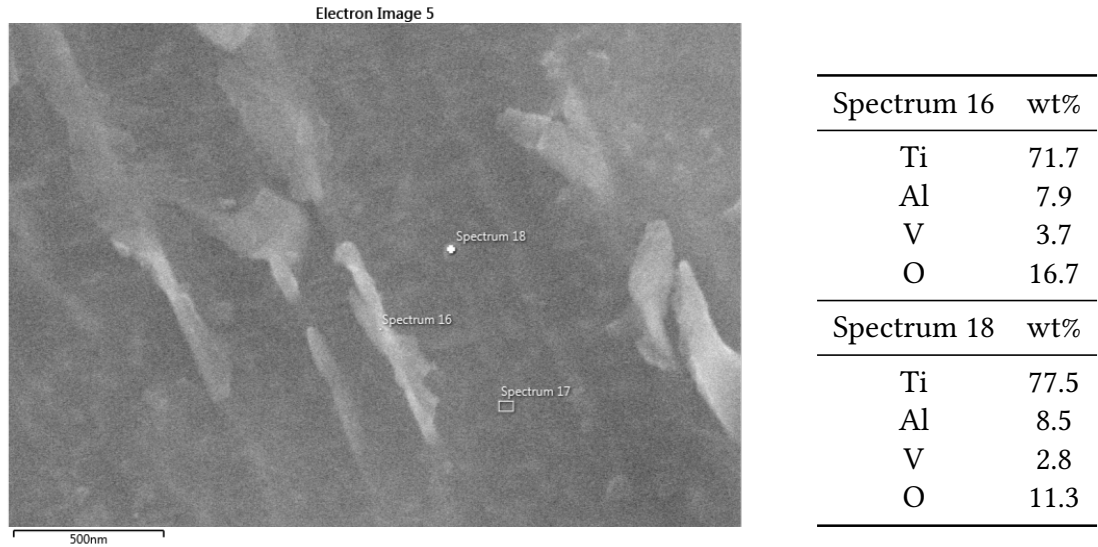


Figure 4.17: EDS of C3 microstructure containing α and β phases

Elemental mapping didn't show any difference between the phases so to analyze and quantify the phase difference point analysis was done on the magnified image of two phases. Figure 4.17 shows the result of analysis. Spectrum 16 is a point EDS on α lath protruding out of the surface and spectrum 18 is placed on substrate β phase. α shows 5.4% higher oxygen content. Oxygen also acts as α stabilizer in Ti-alloys. Although aluminum content is slightly less than Spectrum 18 still when observed in conjunction with SEM micrograph of the region of interest it reveals the presence of α phase. Analyzing phases using EDS in this way can be difficult as EDS works on bulk sample reason being a technique utilizing back scattered electrons(BSE). BS electrons are generated from below the surface and can cover few 100 nm region below the surface.

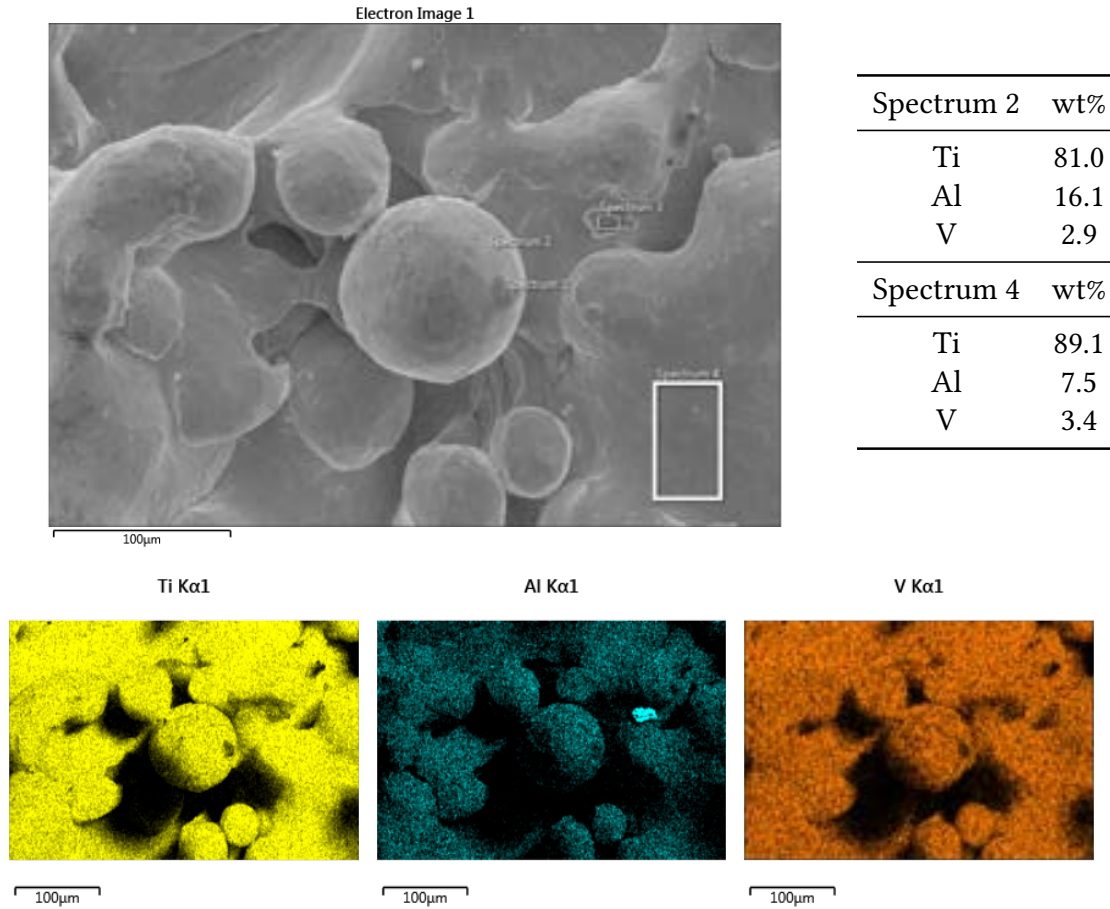


Figure 4.18: EDS and mapping of printed C16 surface

Figure 4.18 shows the elemental mapping of printed sample C16. Distribution appears to be uniform with 1 point of impurity particle. Upon point analysis of the surface at spectrum 2 it reveals 16.1% Aluminum content. Higher aluminum means the presence of α as aluminum is α stabilizer. Spectrum 4 is an area analysis showing 7.9% aluminum which is same as spectrum 16 in Figure 4.17. But as there is no oxygen here so this is β phase which is also evident from microstructure. Point analysis shows presence of α in certain spots and area analysis shows presence of β in the bulk.

4.1.5 XRD

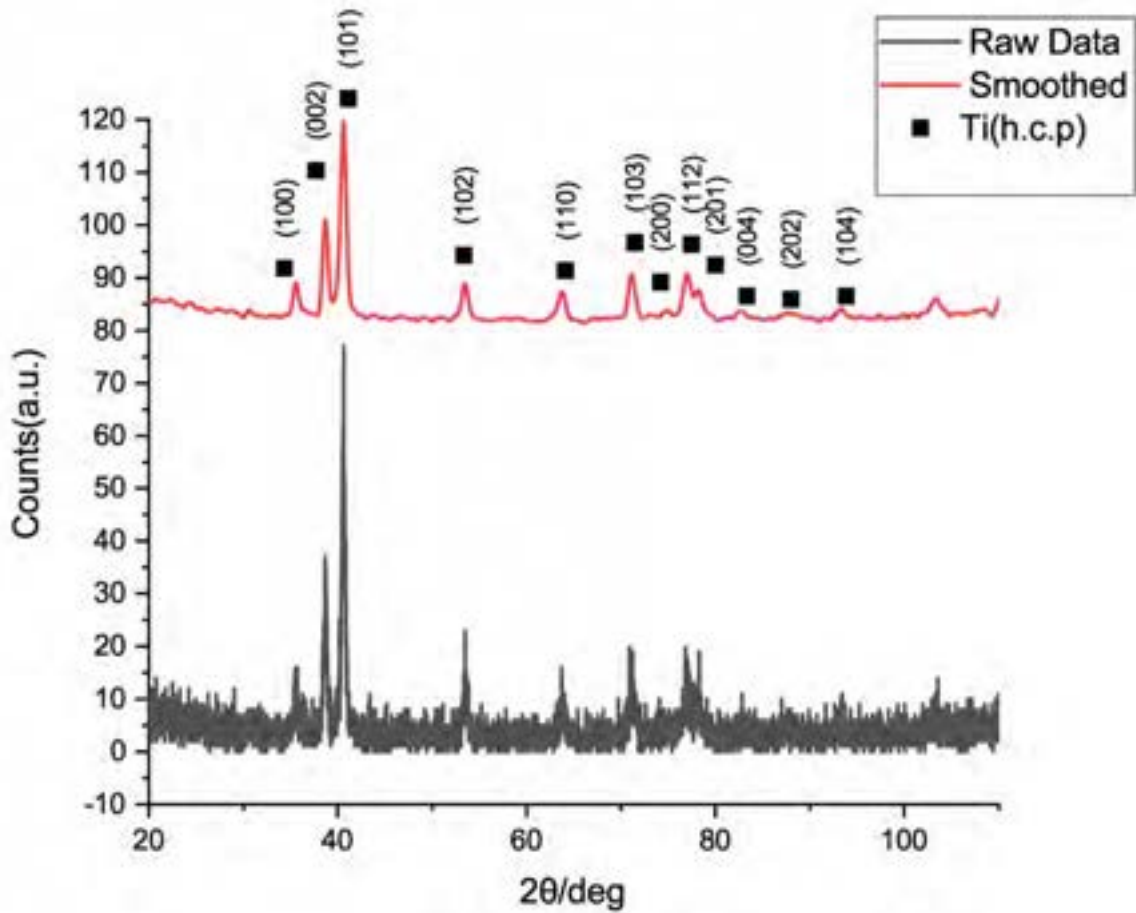


Figure 4.19: XRD-C7 with smoothing

Plot for XRD peak of C7 is given in Figure 4.19. Data contains a lot of noise from the background. Origin was used to clean the data and smooth the peaks. Peaks were matched and identified using the Ti-phases given in literature [113] [99] [121] [122]. Their results are already shown in Subsection 2.5. Peaks matched for Ti-6Al-4V containing Ti hexagonal closely packed structure. Both α & α' phase have HCP structure and their lattice parameters have very small differences which cannot be quantified using X-ray diffraction.

Combined XRD graphs for 8 samples is given in Figure 4.20a. Data and peaks of all

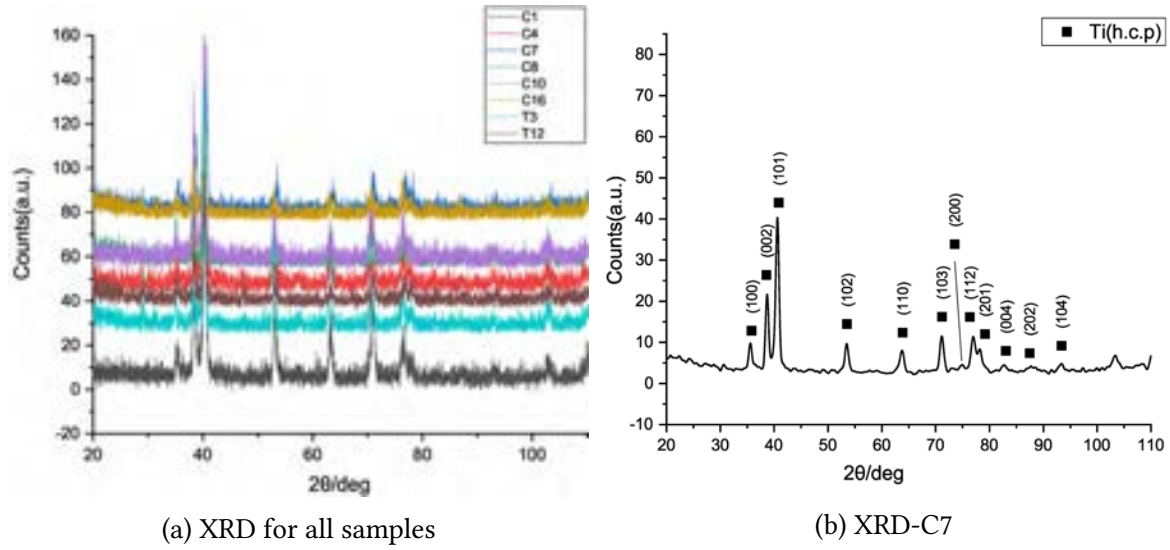


Figure 4.20: Combined graph of all samples and labeled graph.

8 samples overlap each other. This means there is no phase change or major variation between the samples. C1,C4,C8 & C10 are printed in Z orientation and other samples belong to X orientation. Both groups show same phase with no deviation suggesting similar phase concentration. This is also evident from SEM micrographs. Figure 4.20b shows one of the samples C7 along with labeled peaks for Ti(h. c. p.).

4.1.6 Vickers Hardness

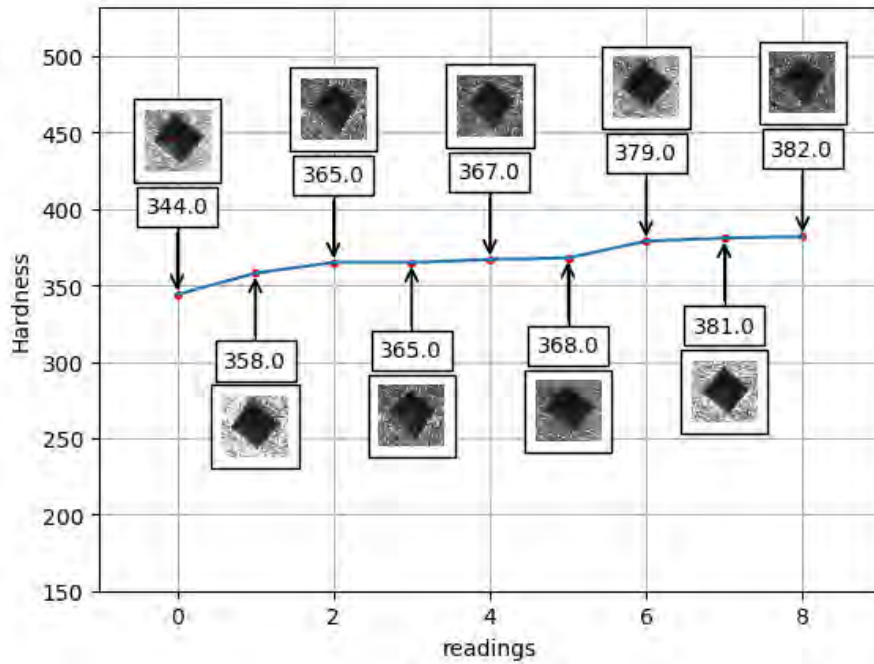


Figure 4.21: Hardness C3

Vickers hardness was calculated for three printed samples two samples C5 and S4 were X-oriented and one sample was z-oriented. Z-oriented sample had 367HV which was larger than X oriented samples C5 and S4 having 350HV and 352 HV respectively. The slight variation can be attributed to columnar grains aligned across the build direction. Z-oriented samples had same HV as wrought Ti-6Al-4V as demonstrated in Figure 4.22 and 4.23. C3 sample shows two regions of varying hardness as shown in Figure 4.45. One region has 380Hv and other 365 HV . This difference in HV suggests grains have different microhardness. α phase has higher hardness and its distribution can vary the microhardness. Moreover printed samples have Widmanstatten structure and wrought Ti-6Al-4V has a bimodal structure. This difference in structure gives 3D printing samples higher hardness due to fine phase distribution nature of Widmanstatten structure.

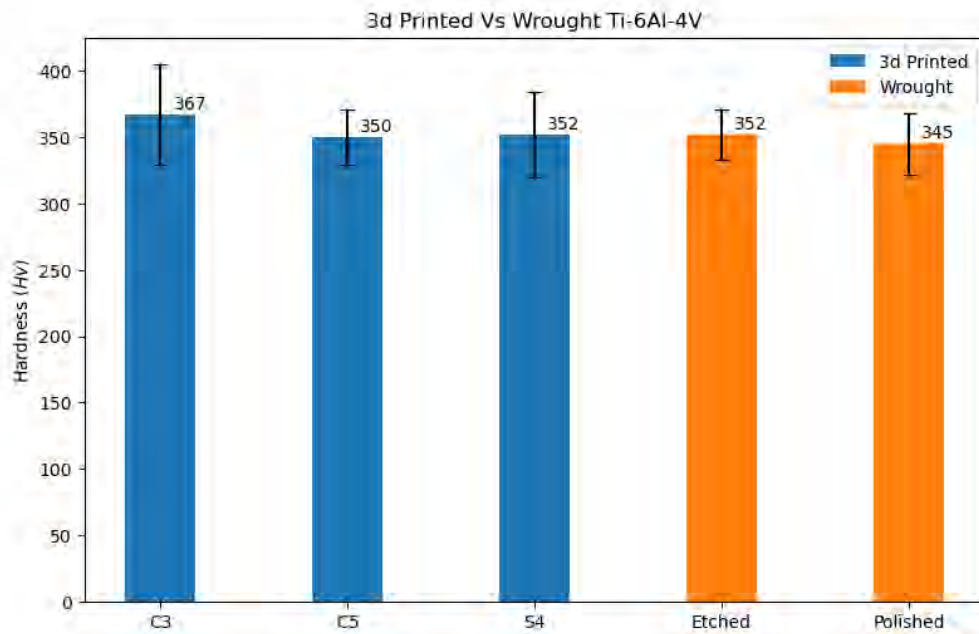


Figure 4.22: Hardness 3D printed Vs Wrought

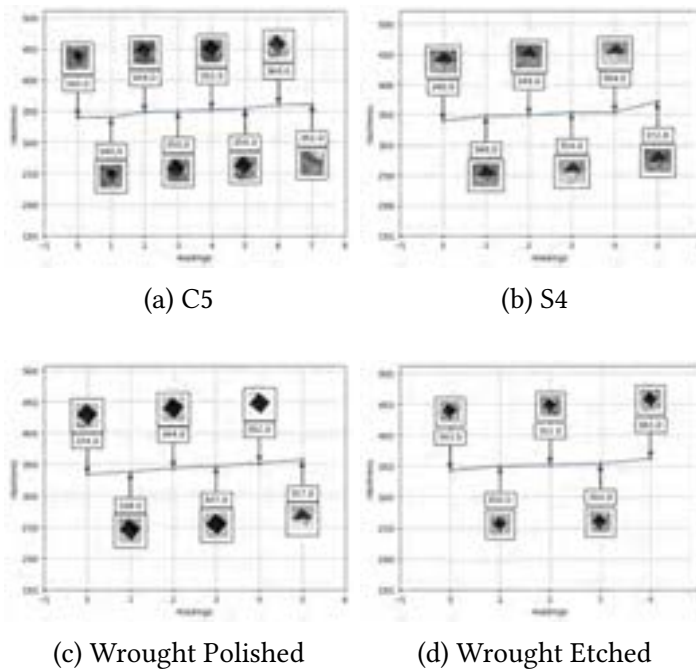


Figure 4.23: Hardness Ti-6Al-4V 3D Printed Vs Wrought Samples

4.1.7 Scratch Hardness

Table 4.4: Scratch Hardness EBM Ti-6AL-4V vs Wrought

Sample	d1 (μm)	d2(μm)	d3(μm)	Scratch Hardness Number
C3	25.85	22.00	24.44	43.01
Ti-6Al-4V etched	25.16	22.54		43.92
Ti-6Al-4V Polished	24.44	25.14		40.63

Scratch hardness of 3D printed Ti-6Al-4V is given in Table 4.4 against scratch hardness of regular wrought Ti-6Al-4V. The difference between the two samples is negligible. On the other hand friction coefficient behavior is different from both etched and polished Ti-6Al-4V. Figure 4.24 shows that friction coefficient for wrought sample keeps on increasing

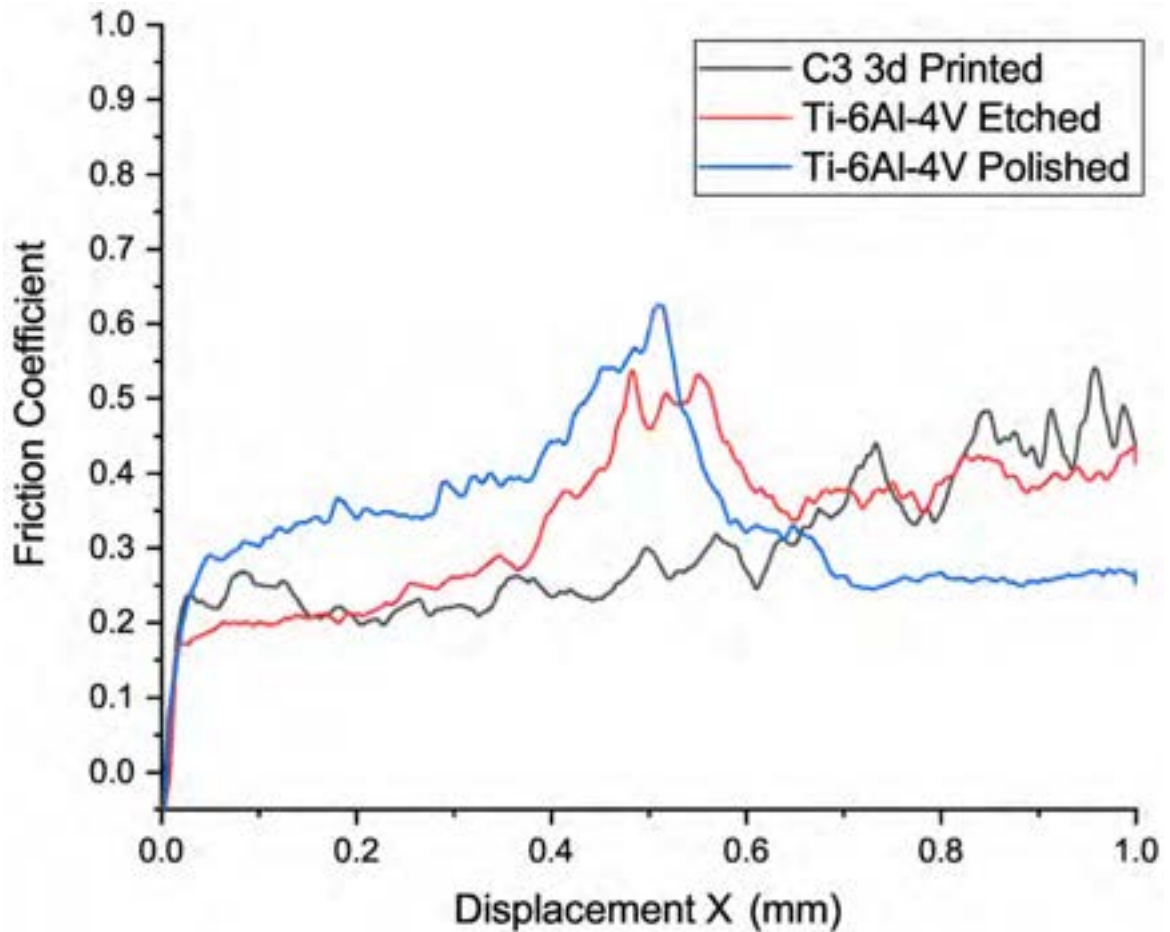


Figure 4.24: Friction Coefficient vs Displacement

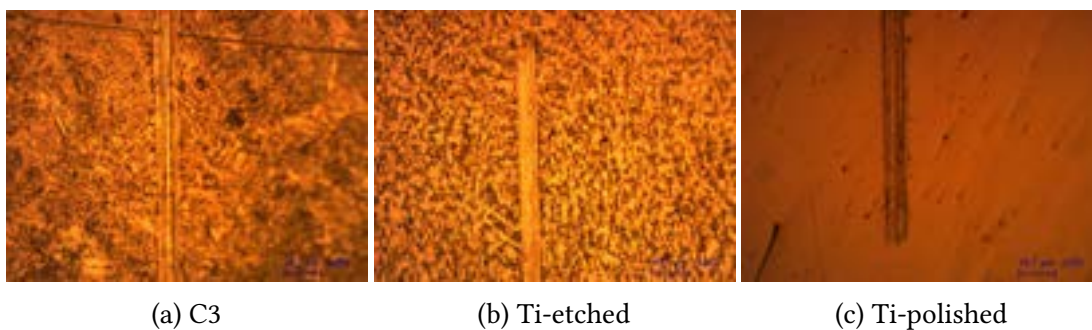


Figure 4.25: Optical microscope images of scratches

until 0.5 mm then decreases suddenly due to removal of the buildup material in-front of the indenter. Coefficient of friction for polished sample at 1mm is less than that of etched sample. Coefficient of friction for C3 keeps on increasing which suggests a constant build up of residual in front of the scratch indenter until the end of scratch. This is also evident from SEM micrograph of the scratch region given in Figure 4.29. Optical Images for other scratches are given in Figure 4.25.

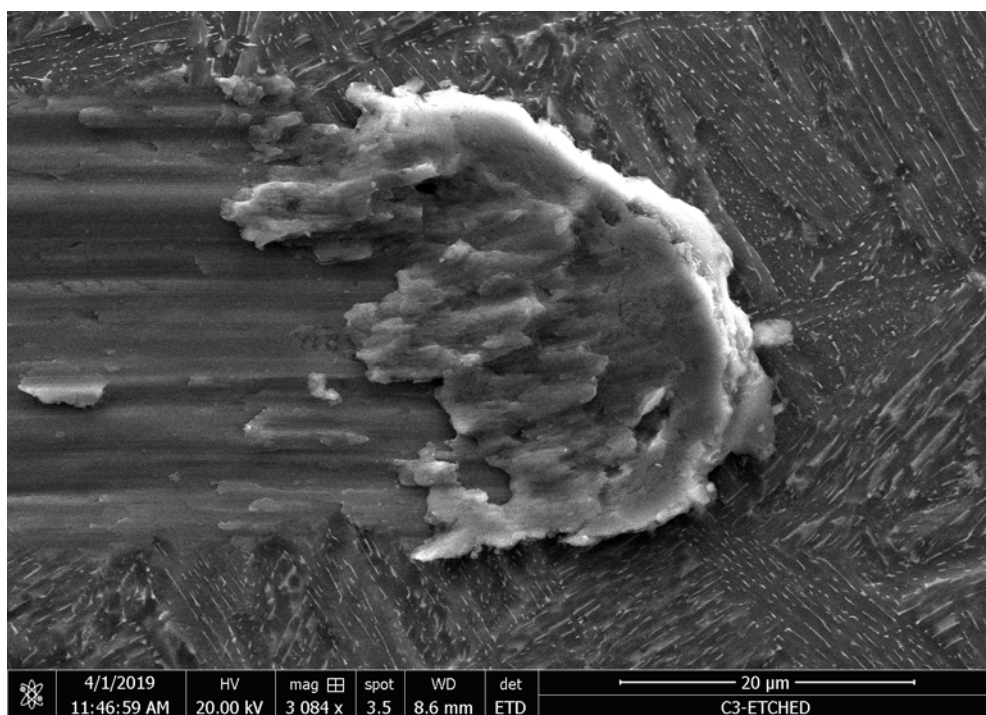
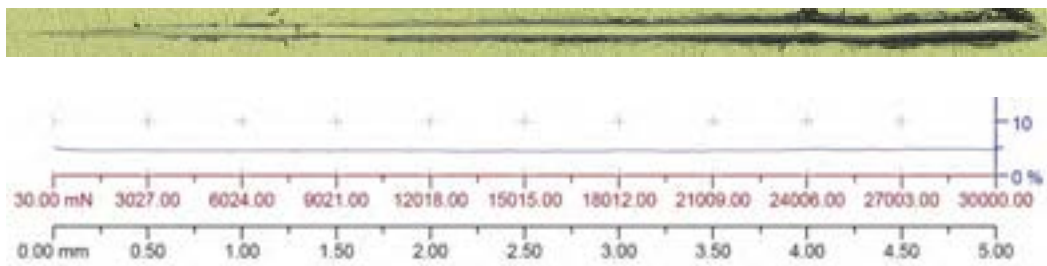


Figure 4.26: SEM micrograph of C3 residual accumulation

Progressive load scratch was also performed to analyze fracture behavior at higher loads. 30 mN initial load was applied which was steadily increased at a speed of 5N/s to 30 N . Scratch length of 5mm was used with a speed of 5mm / min. A Rockwell diamond indenter with tip radius of 100 μm was utilized. Acoustic emission graph showed no sudden peaks suggesting no large crack formation under these loads. Coefficient of friction had a periodic behavior with regions of increasing slope and then sudden drops. This can be a result of build up in front of indenter which is removed periodically after certain lengths.



(a) Acoustic Emission

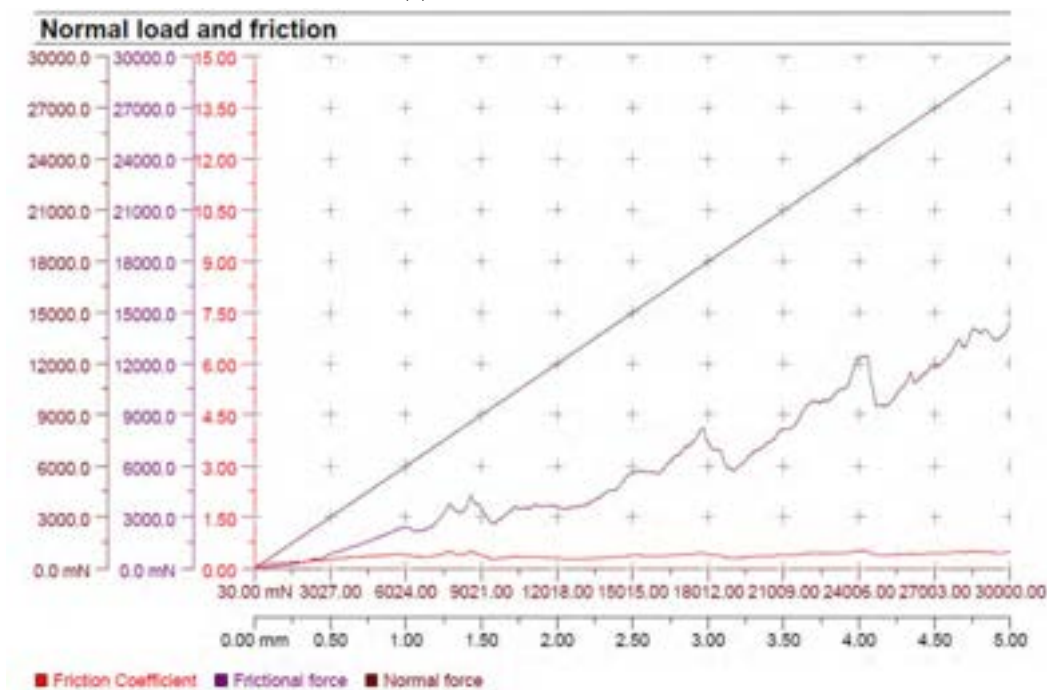


Figure 4.27: Progressive load scratch test on Ti-6Al-4V substrate

4.1.8 Fracture toughness

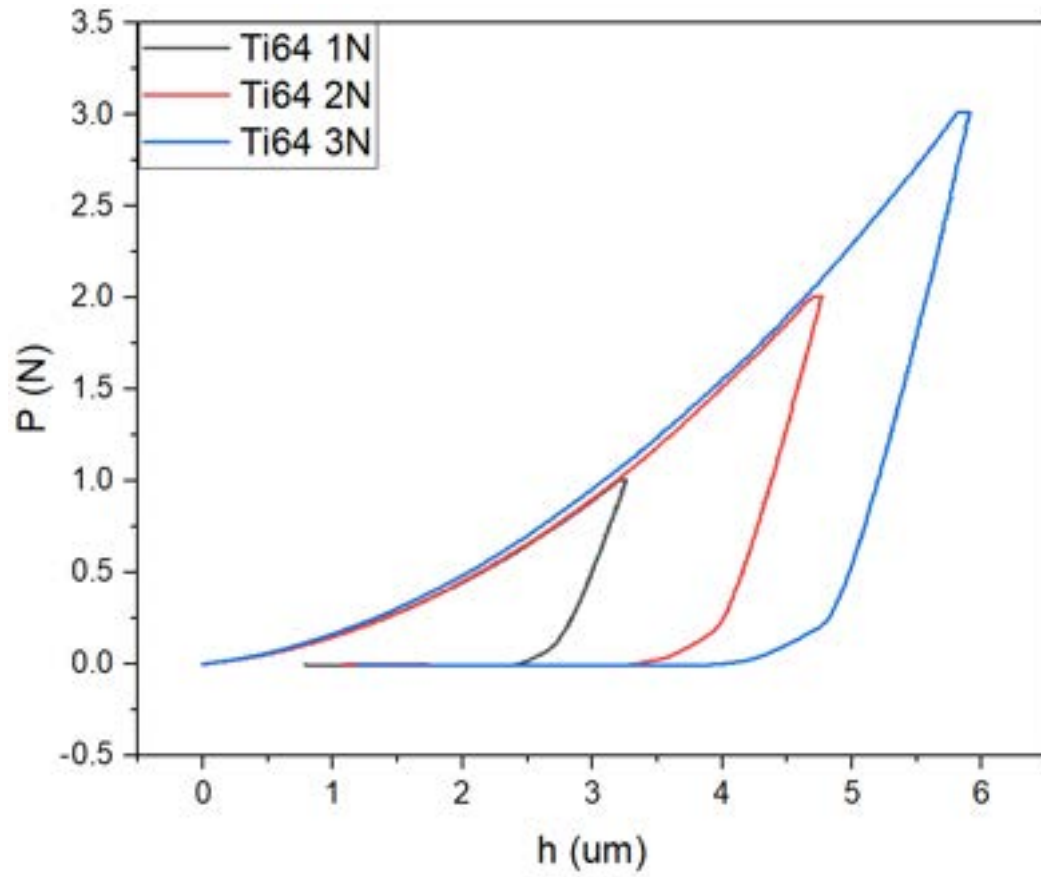
Table 4.5: Properties obtained from loading unloading curve for Ti-6Al-4V

	Ti64				
	1N	2N	3N	Average	
HIT	4832.85	4595.07	4641.187	4689.702	MPa
HV	456.153	433.7097	438.063	442.6419	
EIT	124.8847	115.75	104.978	115.2042	GPa
E*	137.236	127.1977	115.3607	126.5981	GPa
Er	122.546	114.495	104.8053	113.9488	GPa
hm	3.258333	4.765	5.899	4.640778	μm
S	2.016	2.733	3.049	2.599333	N/ μm
hc	2.871333	4.185667	5.113667	4.056889	μm
hr	2.760333	4.03	4.911333	3.900556	μm
hp	2.623333	3.873333	4.740667	3.745778	μm
Ap	207.7903	436.9933	650.1777	431.6538	μm^2

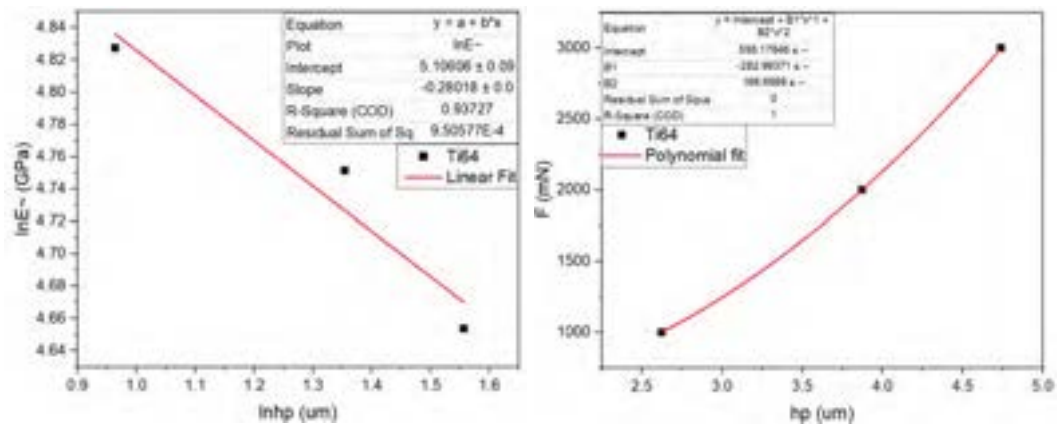
Micro indentation was performed on polished sample of Ti-6Al-4V at 3 different loads 1N, 2N and 3N with a loading rate of 2N/min, 4N/min and 6N/min respectively and dwell time of 10s. Table 4.5 shows the results of various parameters obtained from the loading-unloading curves. This data was used to plot the graphs shown in figure 4.28. Polynomial and quadratic fits from Figure 4.28 were used to calculate critical values of modulus and surface energy. Calculated fracture toughness is given in table 4.6

Table 4.6: Fracture toughness for Ti-6Al-4V

	Ti64			
	E*	h*	Υ^*	K _{ic}
Method	GPa	μm	kJ/m^2	MPa $\text{m}^{1/2}$
ef 6%	104	5.195324	35.9	86.45375
CSM E*	126.59	2.5759	21.5	73.70987



(a) Load vs indentation depth Ti-6Al-4V



(b) Effective modulus vs penetration depth (c) Maximum load vs Penetration depth

Figure 4.28: Plots to calculate fracture toughness of of bulk Ti-6Al-4V

4.1.9 FTIR

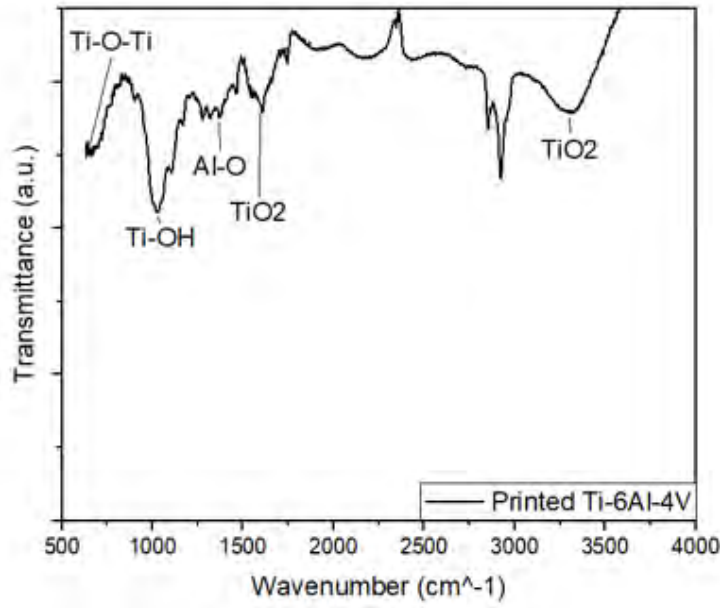


Figure 4.29: FTIR of Ti-6Al-4V

FTIR was used to estimate the ratio of residual stresses in different Ti-6Al-4V samples. Equation 4.3 [149] gives the relation for residual stresses ratio using shift in FTIR peaks [150] [151] [152] where σ is stress and $\Delta\omega$ is the relative shift in FTIR peaks. Highest stress was observed for Z-oriented sample followed by X-oriented sample followed by powder and lastly wrought sample.

$$\frac{\sigma_1}{\sigma_2} = \frac{\frac{\Delta\omega_1}{\omega_1}}{\frac{\Delta\omega_2}{\omega_2}} \quad (4.3)$$

Peaks	$\frac{\sigma_{powder}}{\sigma_{C10}}$	$\frac{\sigma_{powder}}{\sigma_{C8}}$
Ti-O-Ti	5.41	1.44
Al-O	1.57	1.22

Table 4.7: Printed to Powder stress ratio

Peaks	$\frac{\sigma_{wrought}}{\sigma_{C10}}$	$\frac{\sigma_{wrought}}{\sigma_{C8}}$	$\frac{\sigma_{wrought}}{\sigma_{powder}}$
Al-O	3.47	2.70	2.21

Table 4.8: Printed to Wrought stress ratio

4.1.10 Summary

3D printed samples show both hydrophobic and hydrophilic wetting behavior based on printing direction. Gravity and unmolten particles attached to the X direction are major source of roughness. Surface energy of polished samples varies only slightly between X ($23.9\text{mJ}/\text{m}^2$) and Z orientation ($27.8\text{mJ}/\text{m}^2$). Roughness is major factor driving the wetting behavior. Z-axis topology consists of melt tracks that depend on scanning speed and strategy. X-axis topology consists of adjacent powder particles fused onto the surface due to partial melting. These fused particles are the source of secondary roughness as shown in Figure 4.31. X-axis roughness can increase as much as 5-13 times compared to Z-axis roughness due to these molten particles. Surface Energy decrease with increasing water contact angle and X-oriented samples show lower surface energy than z-oriented samples.

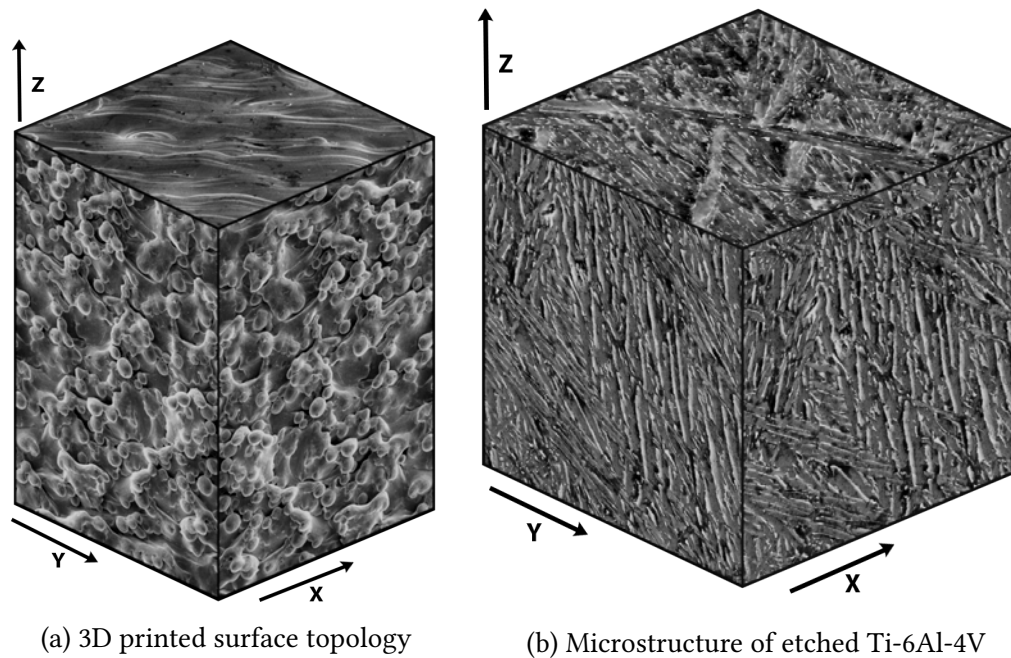
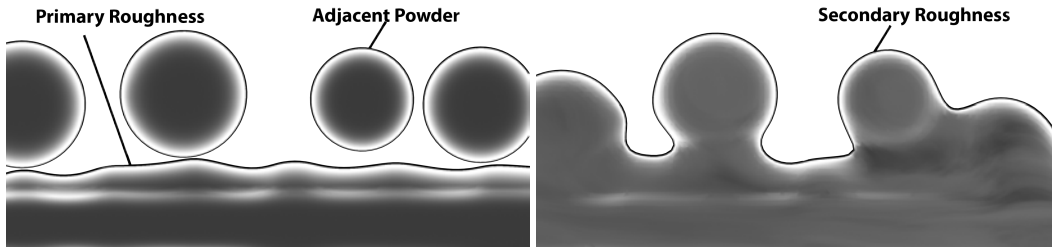


Figure 4.30: SEM micrographs of Ti-6Al-4V

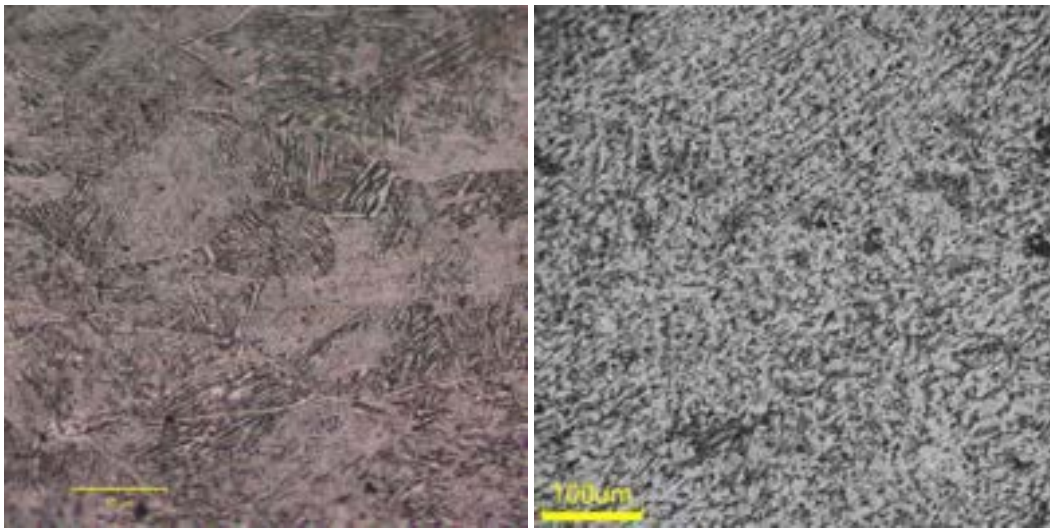


(a) Adjacent Powder particles before fusion (b) Adjacent Powder particles after fusion

Figure 4.31: Illustration of primary and Secondary roughness in X-orientation

Microstructure of 3D printed sample is compared with wrought Ti-6Al-4V sample in Figure 4.32. Regular Ti-6Al-4V has α - β bimodal structure but 3D printed Ti-6Al-4V has Widmanstatten structure of α needles within β grains. The structure shows hierarchy of α needles which is result of repeated heating and cooling cycle while printing subsequent layers. Hardness also increases with decreasing size of α due to increase in dislocation density [111]. Formation of α' is also possible depending on the bed heating temperature or α' can form α - β structure. Laths of α appear to be deformed due to thermal stresses.

Size of powder particle was compared with printed unmolten particles with Z-



(a) Printed Ti-6Al-4V(Widmanstatten)

(b) Wrought-Ti-6Al-4V(Bimodal)

Figure 4.32: Grayscale Optical Micrograph of Ti-6Al-4V microstructure

orientation. Gaussian distribution of the fitted curve is given in Figure 4.33. Origin was used to analyze the distribution. ImajeJ and olympus DSX software were used to analyze the particle size. Details of the procedure are given in appendix. Printed particles have mean diameter of $55\mu\text{m}$ and powder has mean diameter equal to $60\mu\text{m}$. The 8.3% decrease in size is due to partial melting of the powder particles. Hardness of the printed sample is larger than wrought sample as fine needle like structure has higher density of dislocation. This can increase the hardness but decrease the ductility of the sample. Needles comprise of α phase which has higher concentration of aluminum. Ti alloy has brittle behavior at aluminum concentrations higher than 8% [153]. Scratch hardness number for printed samples is similar to wrought samples. Coefficient of friction keeps increasing for printed sample until the end of scratch(1mm) but for wrought sample highest peak is

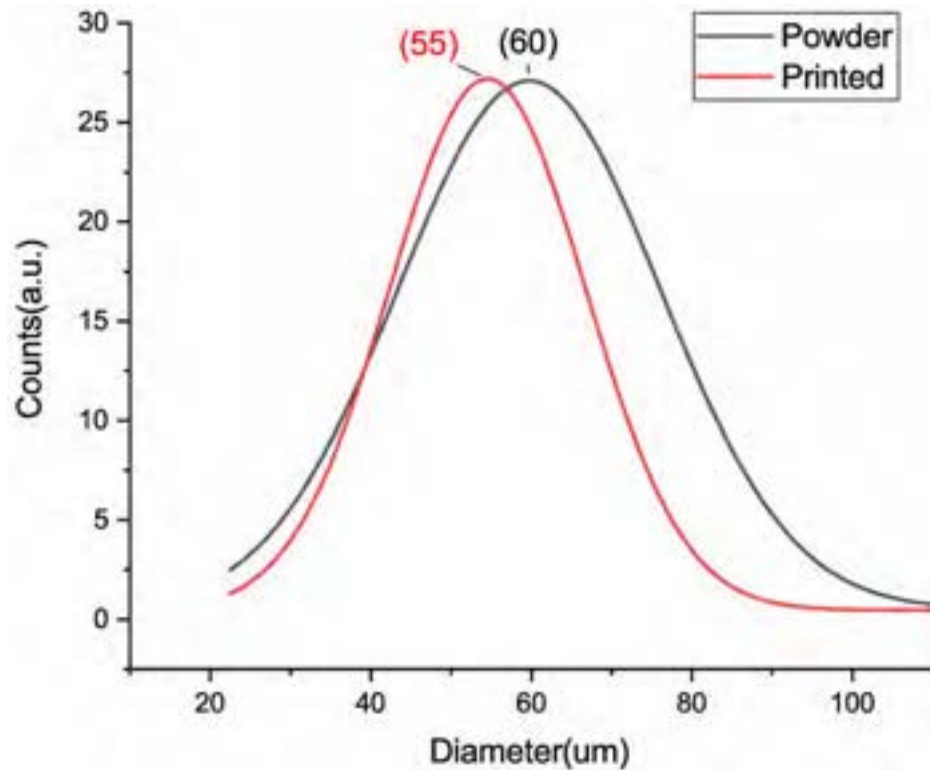


Figure 4.33: Size distribution powder vs Printed sample

at 0.5mm. This suggests a steady buildup for printed sample. XRD analysis shows Ti(H. C. P) as the dominant phase. Both α and α' have hexagonal closed packed structure and lattice constant is similar [154]. Difference is small enough to be indistinguishable for an XRD measurement. SEM structure show α laths and needles within β phase in the form of basket weave pattern. This structure is referred to as Widmanstatten structure. Optical micrographs show presence of irregular grains and some columnar grains along the build direction.

4.2 Stainless Steel 316L Characterization Results

4.2.1 Wetting State

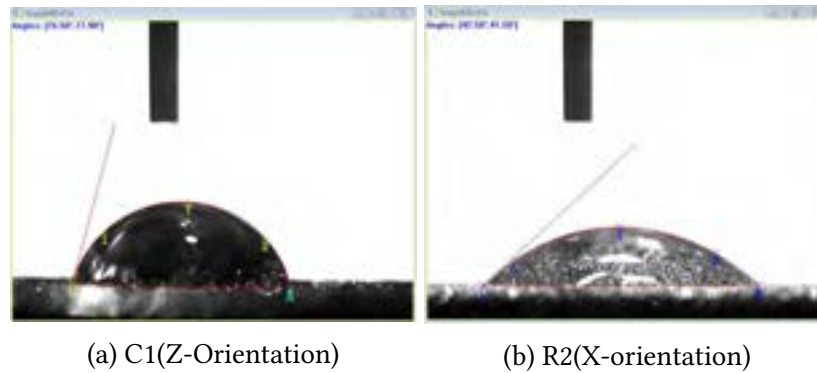


Figure 4.34: Water Contact Angle Steel 316L C1, R2

Wetting state of the as received Steel316L samples was quantified using water in sessile drop experiment. Both X and Z orientation samples showed hydrophilic behavior. Figure 4.34 demonstrates the wetting states of both orientation. The variation of average contact angle is from 63° to 69°. R2 belonging to X group shows lower angle 42.2°. This deviation from trend is due to printed holes in the center. This is consistent with C16 Ti-6Al-4V sample showing hydrophilic behavior due to presence of pores. Chart 4.46 shows the comparison between the four samples. When compared with EBMed Ti-6Al-4V samples X-oriented SLMed Steel316L samples don't show hydrophobic behavior. SLMed samples have much lower roughness in X orientation when compared to X-oriented EBMed Ti-6Al-4V. Number of molten particles attached to the surface is quite lower when compared to the Ti64 samples. Electron beam has much higher energy than laser beam so it results in higher attachment of unmolten powder particles. Lower spherical powder density and smaller size of microscopic pillars under the drop cannot hold same amount of air pockets under



Figure 4.35: Contact angle a)Water b)Glycol for polished SS316L

the water droplet so it enters Wenzel state in which hydrophilic behavior of hydrophilic material increases based on the roughness. Contact angle is highly dependent on the ratio of surface in contact with liquid to total surface. These results suggest that water droplets on X oriented Ti-6Al-4V samples are in Cassie-Baxter state and hence are supported on air pockets. These air pockets give the samples hydrophobic behavior despite having the same crystal and micro structure. Contact angle of polished sample is shown in Figure 4.35. Average water contact angle was recorded to be $98.3^{\circ} \pm 1.3$ and average glycol contact angle was found to be $70.95^{\circ} \pm 2.55$. Surface energy was calculated using the Owens-Wendt model as discussed earlier and had a value of 26.7 mJ/m^2 .

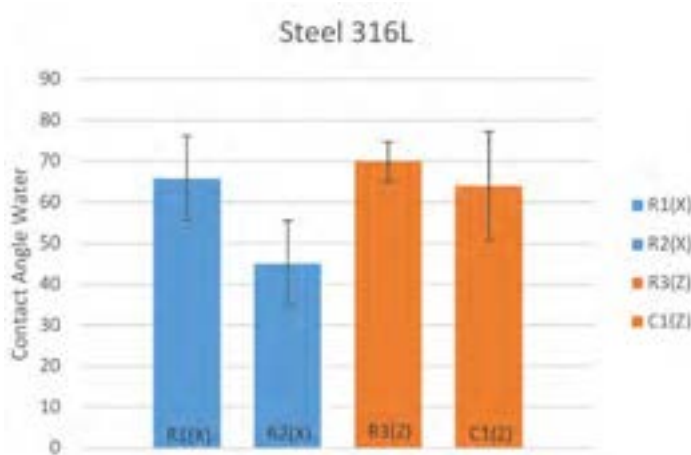


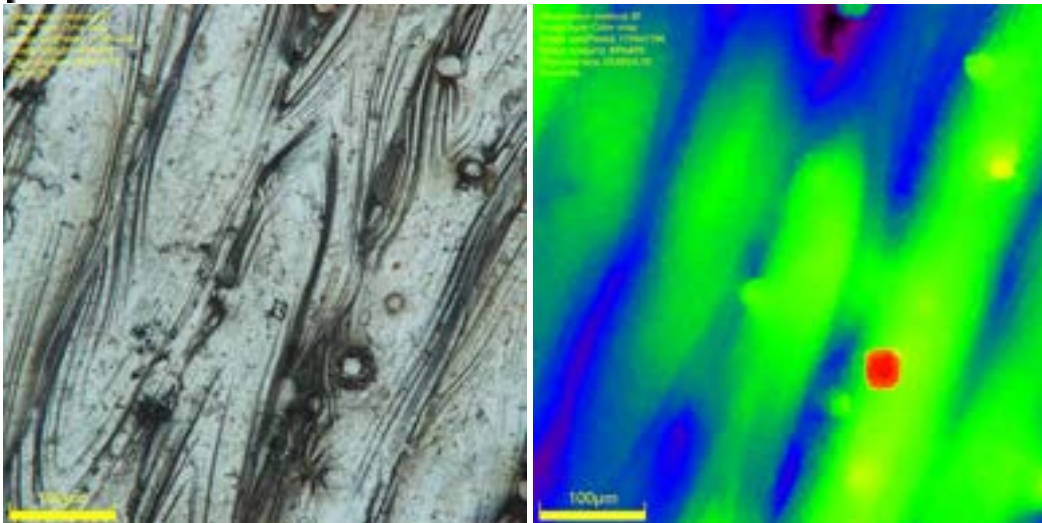
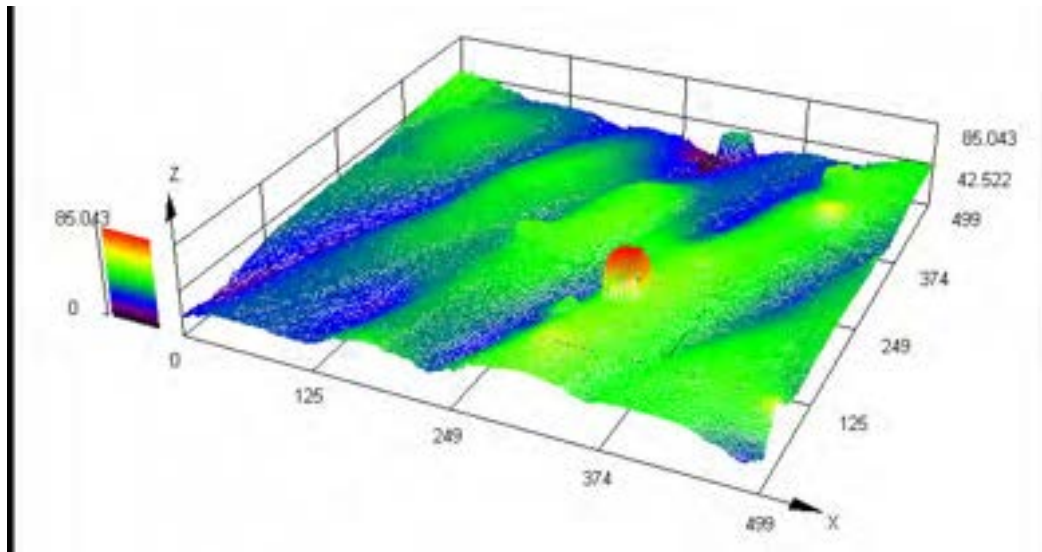
Figure 4.36: Water Contact Angle Steel 316L X & Z Orientation

4.2.2 Roughness

Confocal microscope was used to measure the roughness of as received samples. One sample was chosen from each group printed in different orientations. Line roughness was measured in both vertical and horizontal direction. X Oriented samples has 0.3-3.5 times the roughness of Z oriented samples. This behavior is consistent with the Ti-6Al-4V samples as discussed in section 4.1.2. Roughness profile and 3D topography of height are given in Figure 4.37 and Figure 4.38 for samples printed in Z and X orientations respectively. Side by side comparisons of the Optical micrographs and height profiles are given in Figure 4.39. X-oriented samples show microscopic quasi-spherical particles attached to the surface. These are formed by partial fusion of the surrounding metal powders. Density and size of the particles are less when compared to EBMed Ti-6Al-4V as EBM has higher energy density and larger powder size. By analyzing the results and comparing them to Ti-6Al-4V it can be realized that despite having smaller size of starting powder particles roughness(R_a) of Steel316L is 1.53 times that of Ti-6AL-4V. This anomaly can be attributed to the higher energy of Electron beam which will create higher temperature of the melt zone resulting in lower roughness due to longer times for cooling. Also higher thermal conductivity of Steel 316L will result in faster solidification in the vicinity of solid part.

Table 4.9: Roughness Values of as Received Steel 316L from Confocal Microscope

Printing	Roughness	Rp(μm)	Rv(μm)	Ra(μm)	Rt(μm)	Equipment
Z	Horizontal	1.843	3.582	1.153	7.887	Confocal Microscope
	Vertical	1.302	1.547	0.631	5.77	Confocal Microscope
X	Horizontal	4.245	4.747	1.811	16.649	Confocal Microscope
	Vertical	4.531	5.611	2.119	15.992	Confocal Microscope

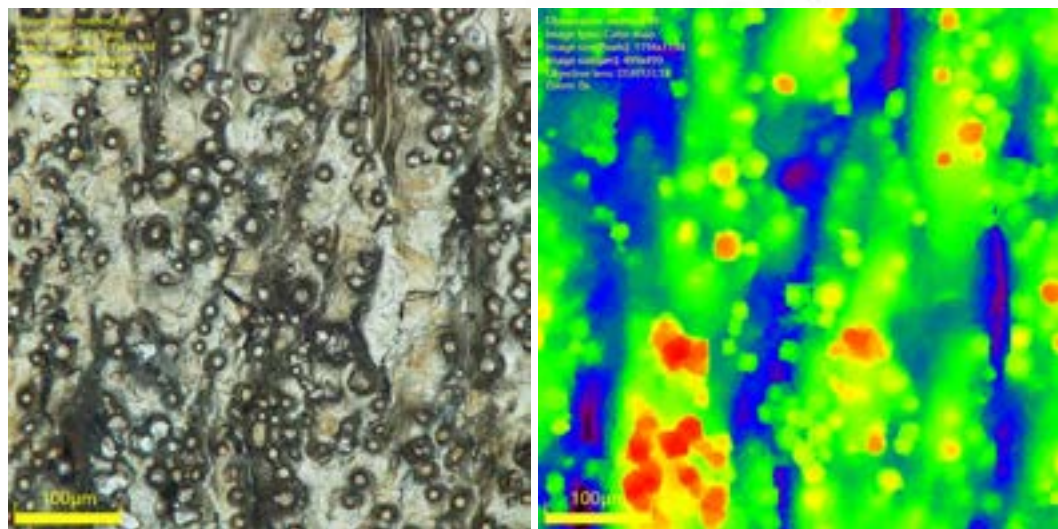
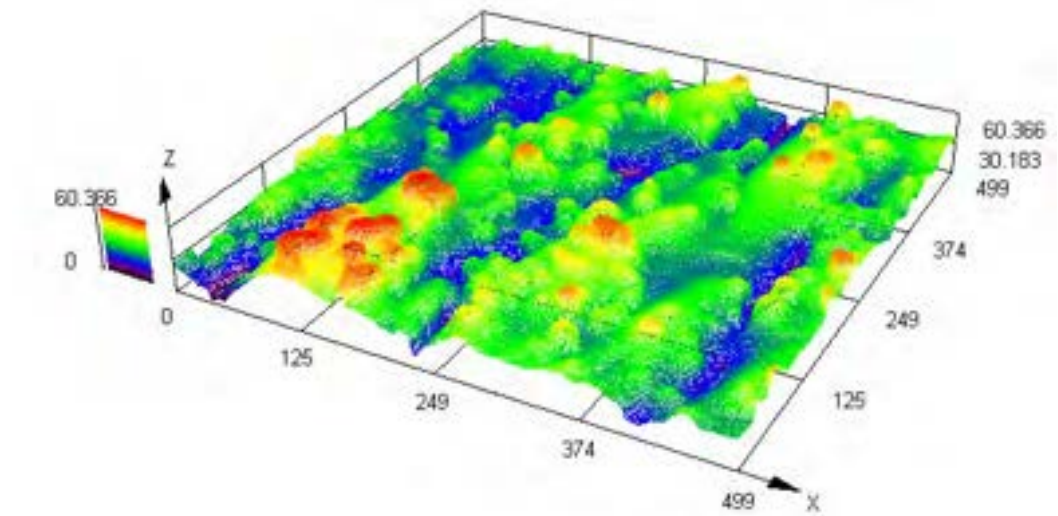


(a) Horizontal Line Roughness



(b) Vertical Line Roughness

Figure 4.37: Steel 316L roughness (Z-orient)



(a) Horizontal Line Roughness



(b) Vertical Line Roughness

Figure 4.38: Steel 316L Roughness (X-orient)

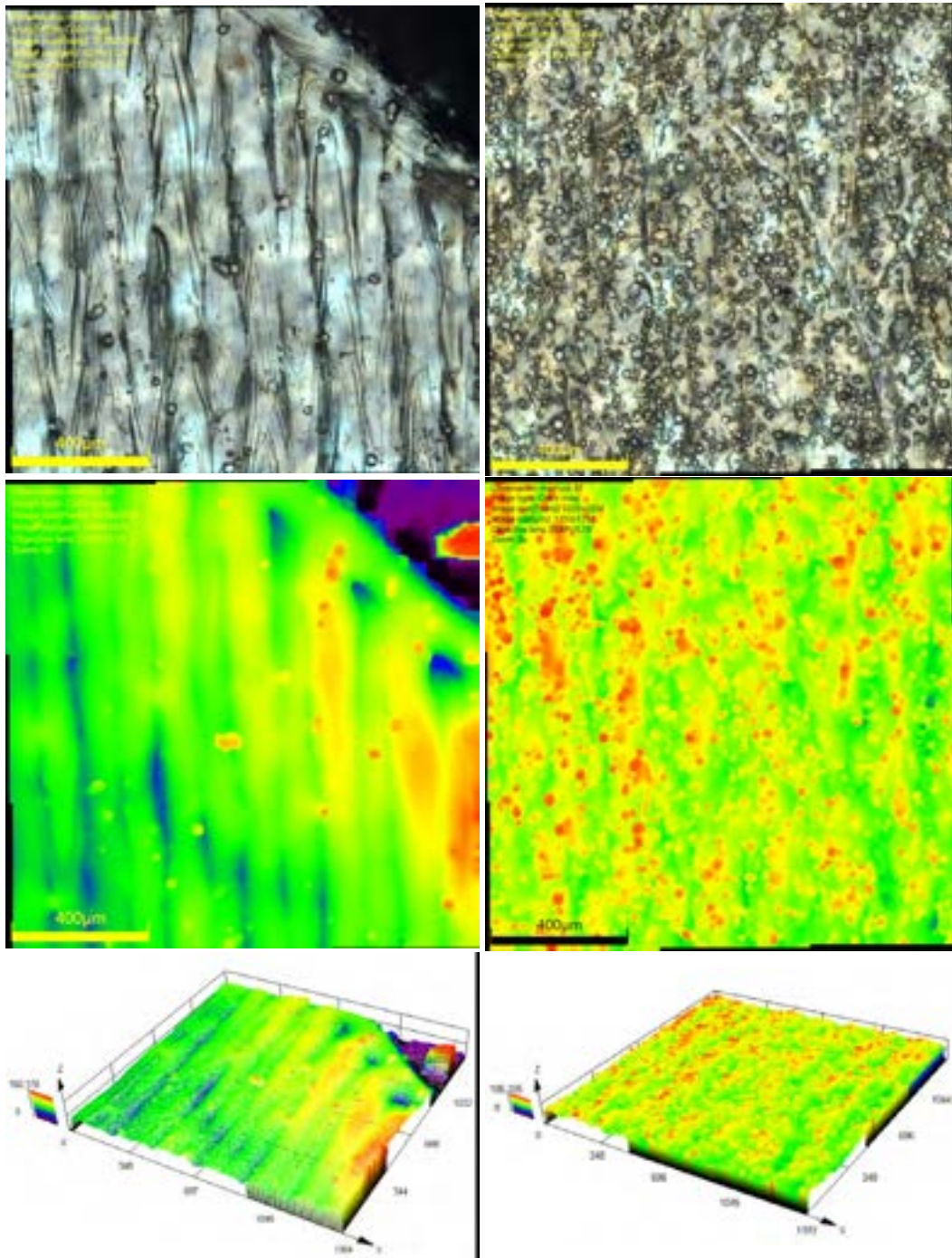
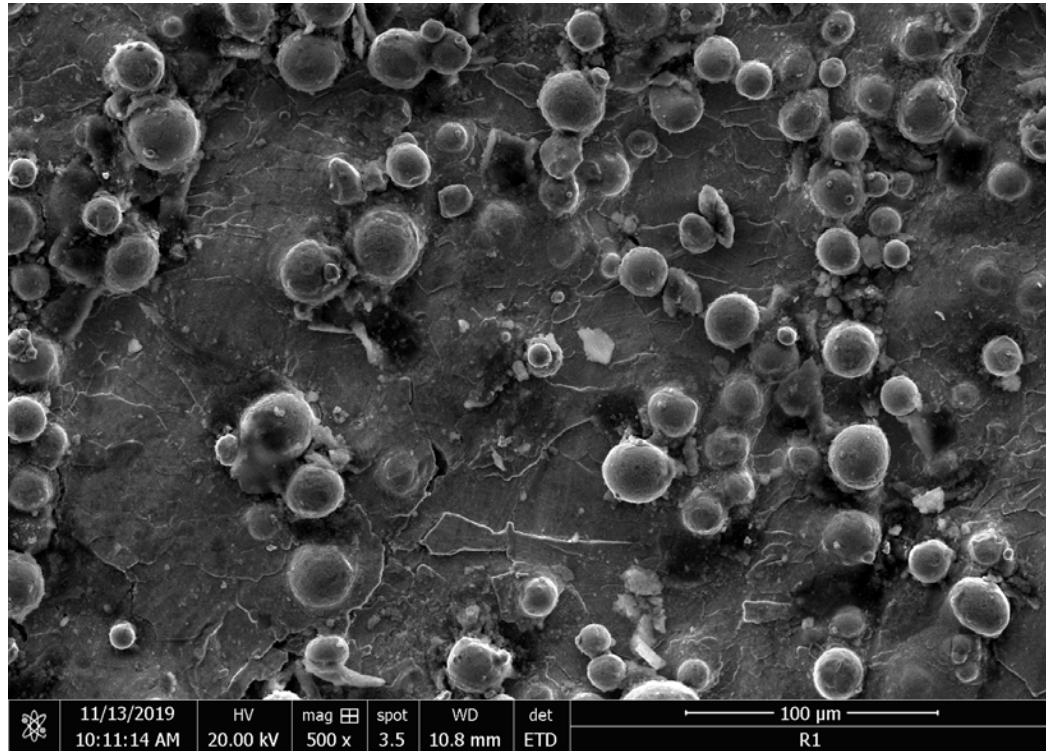
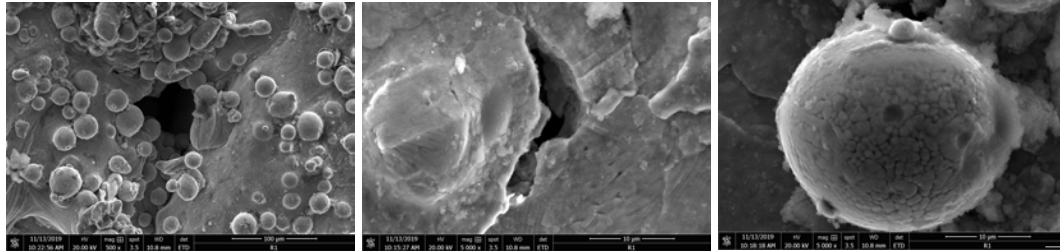


Figure 4.39: Optical Micrographs ,Height profiles and 3D Micrographs respectively of Steel 316L Z(Left) and X(Right) orientation

4.2.3 SEM



(a) Unmolten particles fused to X-oriented side



(b) Printed hole

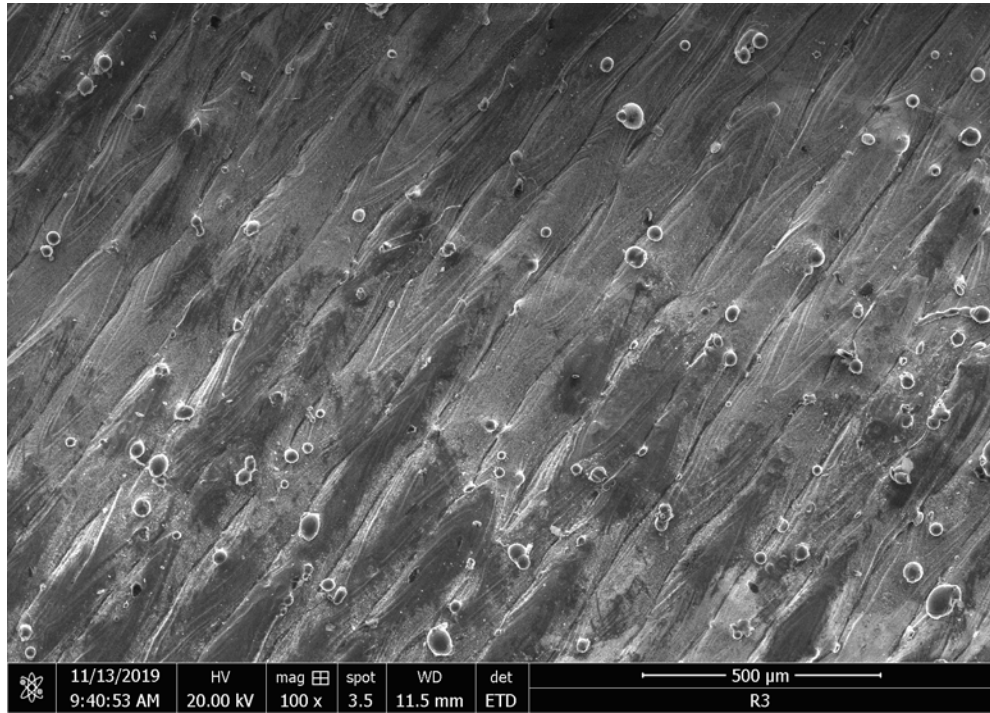
(c) Lack of fusion

(d) Grain boundaries on Unmolten particle

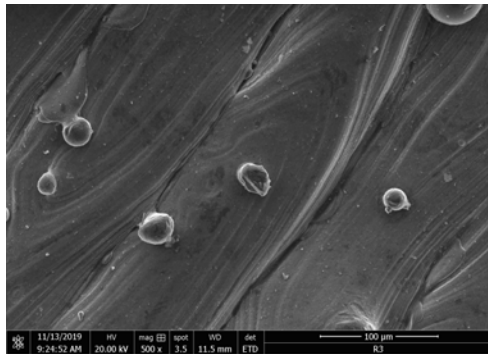
Figure 4.40: SEM micrographs of as printed Steel 316 L R1(x-orient)

SEM micrographs of as printed Steel316L are given in Figure 4.40. Surface shows quasi-spherical particles spread attached to print layer due to partial melting. Average size of the particles is $18.7 \mu\text{m}$ with particles ranging from $4.5\mu\text{m}$ to $28.3 \mu\text{m}$. Figure 4.40b shows the printed hole. Printing hole perpendicular to the build direction is difficult due to the flow of molten metal into the hole from build of subsequent layers. Lack of fusion is visible in the

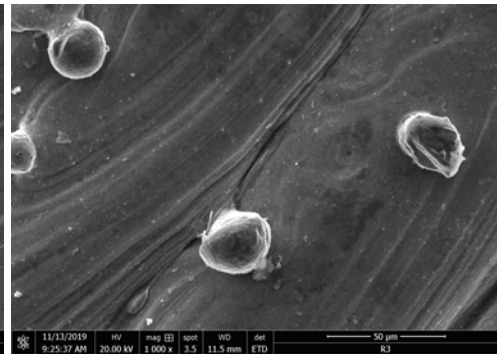
print layer as seen in Figure 4.40c. Figure 4.40d shows dendritic solidification structure in the powder surface. Micrographs of Z-oriented SS 316L are presented in Figure 4.41. Scanning of the layer results in flow-lines parallel to scanning direction. Structure of the flowlines is preserved due to high cooling rate observed in printing. High temperature gradients result in faster solidification and flow lines and stepping of layers can be observed. Average size of the layers is $119.9\ \mu\text{m}$. Z oriented surface also has few unmolten particles attached to it. Some particles have formed agglomerates due to partial melting so average size of the attached particles is $32.9\ \mu\text{m}$ which is larger than the particles of X direction. Agglomerates are made of multiple quasi-spherical powder particles fused together which results in larger average size. Figure 4.56i and Figure 4.55e show a hole printed in build direction. Internal surface of the hole has higher roughness due to attachment of partially molten powder particles similar to x-orientation. Direction of the scan is visible from flow-lines of the melted powder at top of the hole. Texture of the surface is highly dependent on the scanning direction.



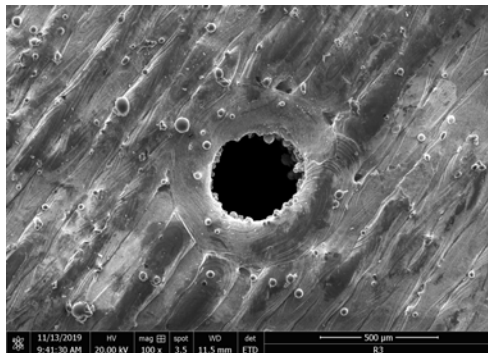
(a) R3 Print Layers



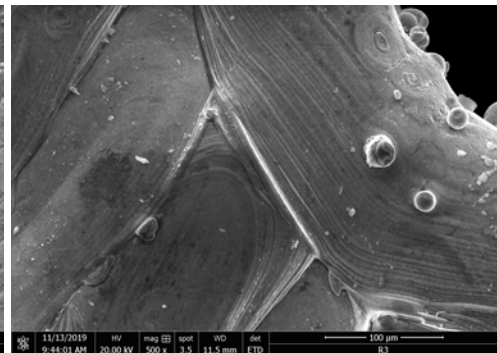
(b) Directional layers



(c) Fused powder Particles

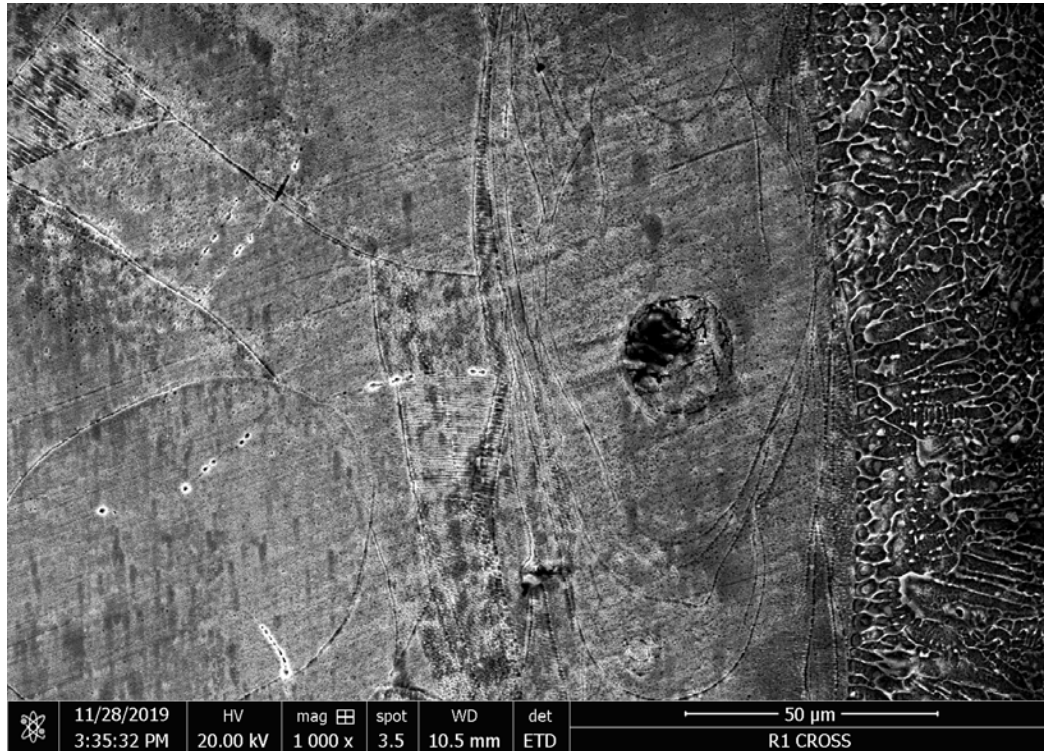


(d) Printed Hole

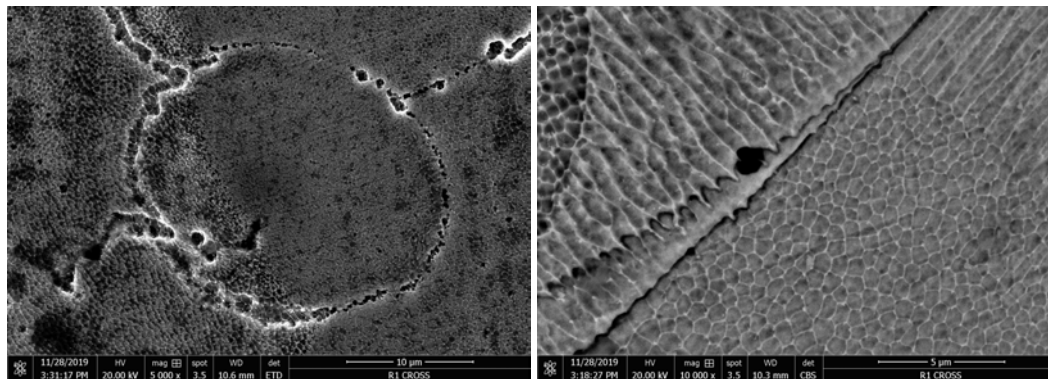


(e) Scan direction layers

Figure 4.41: SEM micrographs of as printed Steel 316L R3(Z-orient)



(a) Top layer vs melt layer grain structure

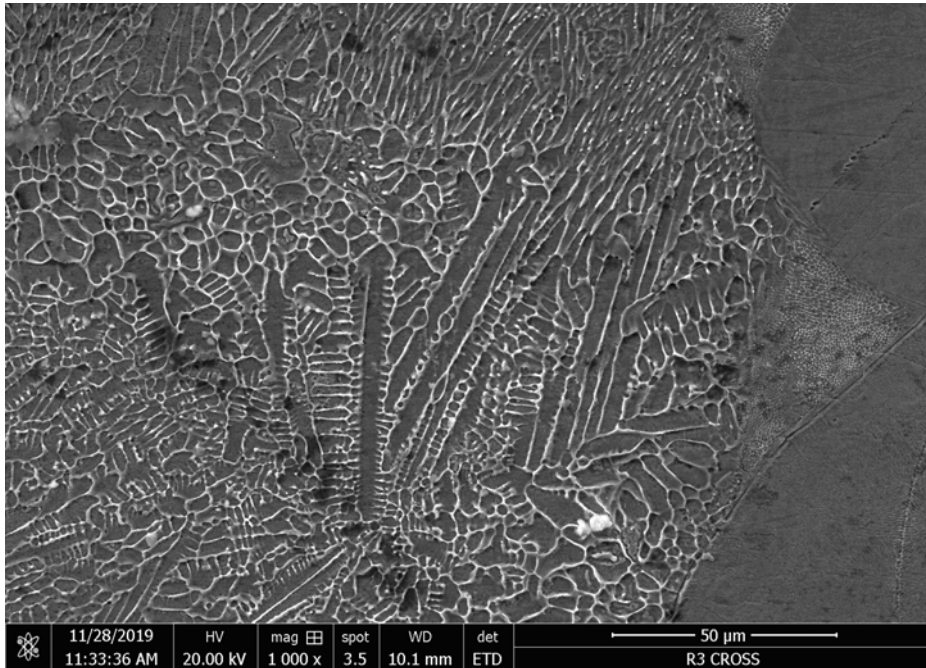


(b) Grain structure extending across fusion (c) Melt pool layers with Equiaxed and elongated cells

Figure 4.42: SEM of etched R1 cross section

Analysis of the top layer cross section was done after grinding, polishing and etching. Figure 4.42 shows the SEM micrographs of the cross section of R1. Top layer shows the structure resulting from the scanning strategy of subsequent layers. Right side of top-layer as shown in Figure 4.42a is the last layer of the part. Microstructure of this layer is different from the bulk material as it is subjected to only a few thermal cycles. Structure

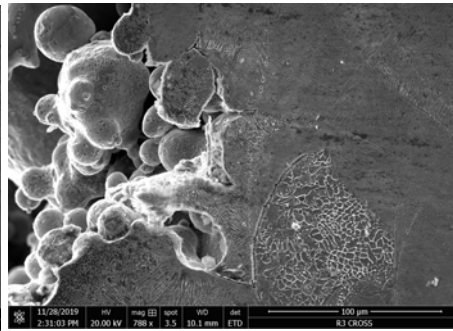
shows transition from equiaxed cellular to elongated cellular and smaller cellular structure. Average size of the equiaxed cells in the top layers is $3\text{ }\mu\text{m}$ with elongated grains ranging from $10\text{ }\mu\text{m}$ to $26\text{ }\mu\text{m}$. Figure 4.42b shows an island defect formed by lack of fusion of melt layers. Cellular structure of inside grains extends across the meltpool defect which is result of eptiaxial growth due to partial melting of successive layers. Growth of structure occurs in the direction of maximum temperature gradient and helps in same alignment as nearby grains. This structural alignment across and within meltpools can be observed in Figure 4.42c. Average size of the equiaxed cells within the bulk of material is $0.6\text{ }\mu\text{m}$ which is 5 times smaller than the top layer and elongated cells have grown across the meltpools with length of around $2.5\text{ }\mu\text{m}$ to $15\text{ }\mu\text{m}$. Figure 4.43 contains the micrographs of the lateral layer cross section. Cross section of the fused melt powder at the top layer shows the transition of dendritic structure of the powder to cellular structure of the printed layer. Partially molten powder has equiaxed grains in range $3.7\text{ }\mu\text{m}$ - $7.5\text{ }\mu\text{m}$ and with large elongated grains with width $3\text{ }\mu\text{m}$ - $4\text{ }\mu\text{m}$ and length $22\text{ }\mu\text{m}$ - $67\text{ }\mu\text{m}$. There is a transition region between the melt layers of the 2nd-last layer and last layer. This transition zone has equiaxed cells of size $0.7\text{ }\mu\text{m}$ to $1.3\text{ }\mu\text{m}$. Bulk of the sample subjected to multiple cycles has equiaxed structure of size $0.6\text{ }\mu\text{m}$ - $2.1\text{ }\mu\text{m}$ with few zones of elongated grains with average length of $6.9\text{ }\mu\text{m}$ ranging from $3.8\text{ }\mu\text{m}$ to $10.4\text{ }\mu\text{m}$.



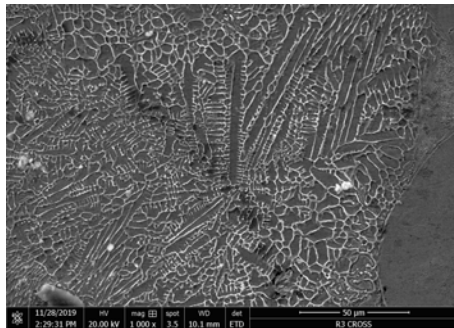
(a) Effect of repeated heating and cooling cycle on grain structure of lateral layer



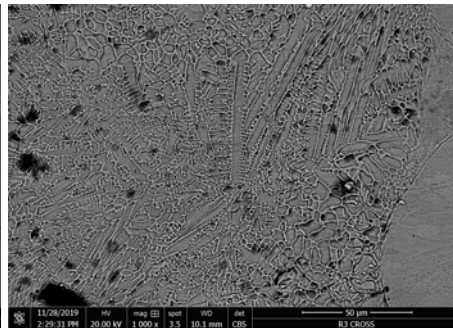
(b) Top layer structure



(c) Decreasing grain size and X direction fused powder



(d) SE micrograph of top layer



(e) BSE micrograph of top layer

Figure 4.43: SEM micrographs of as steel 316L R3 Cross Section

4.2.4 XRD

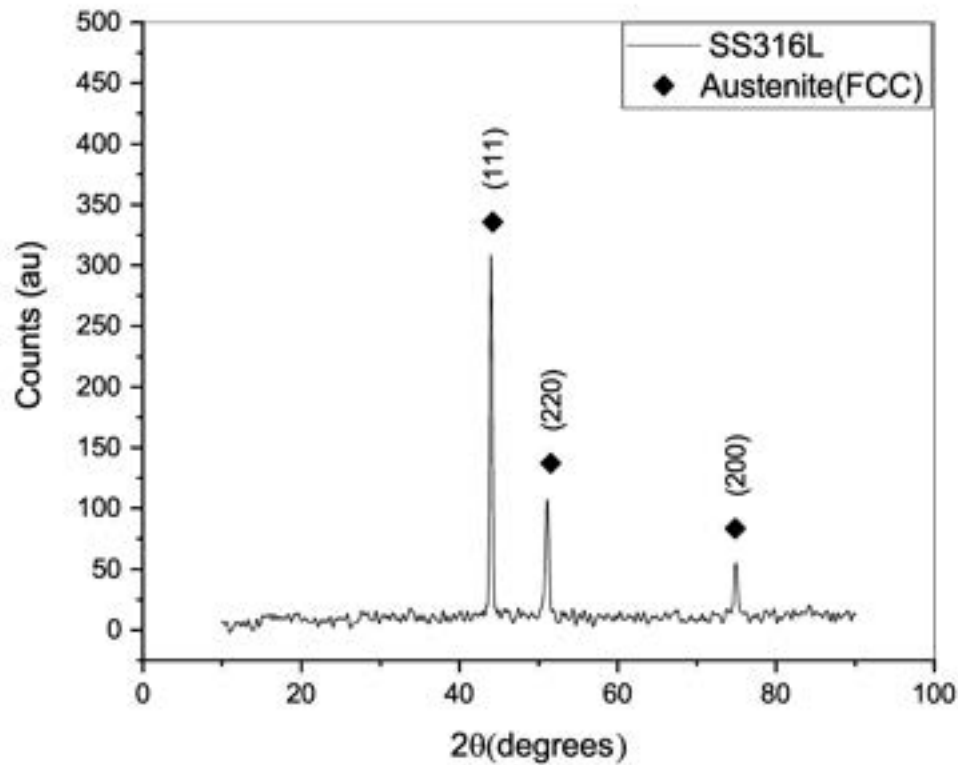


Figure 4.44: XRD SS316L with smoothing

XRD spectra for 3D printed SS 316L is shown in Figure 4.44. Indexing of the reflections was done using literature [124]. Analysis revealed the presence of FCC phase. SS316L is austenitic steel and austenite has FCC structure. This is in agreement with the literature. Analysis was not performed for samples in multiple orientations as Ti-6Al-4V investigation didn't show any variation based on sample orientation. This is also justified by the SEM analysis of cross section of both X and Z oriented samples. Peaks are usually broader when compared to starting metal powder due to refining of the structure as a result of rapid cooling while printing [124].

4.2.5 Vickers Hardness

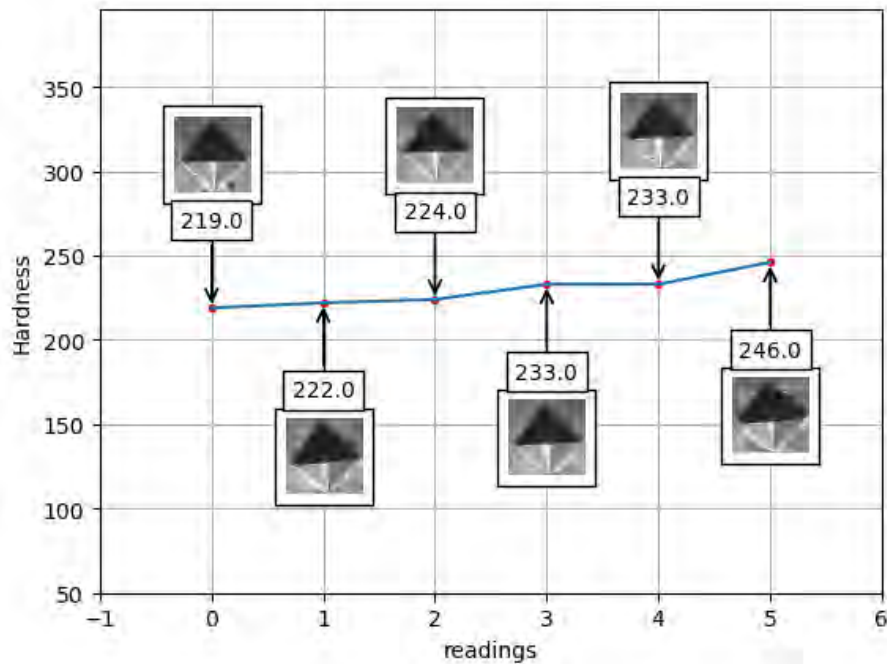
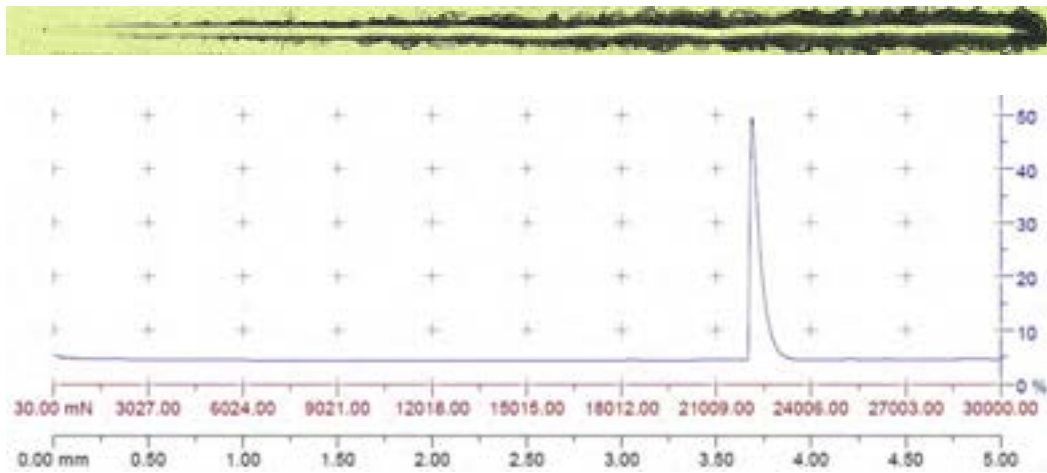


Figure 4.45: Hardness C3

Vickers hardness was calculated for SS316L after polishing. Vickers hardness value of the 3D printed SS 316L was found to be 226 ± 5.77 HV which is larger than 200HV value of cast SS 316L [155]. The increase in hardness is typical behavior for 3D printed materials [155] [156]. Traditional SS316L has an equiaxed structure of heterogeneous lamella [157] but 3D printed SS316L consists of fine subgrain cellular structure. High cooling rates and repeated thermal cycles result in this fine subgrain pattern which increases the hardness of 3D printed SS 316L. Materials with higher dislocation density have higher hardness due to the hindrance of dislocation motion.

4.2.6 Scratch



(a) Acoustic Emission

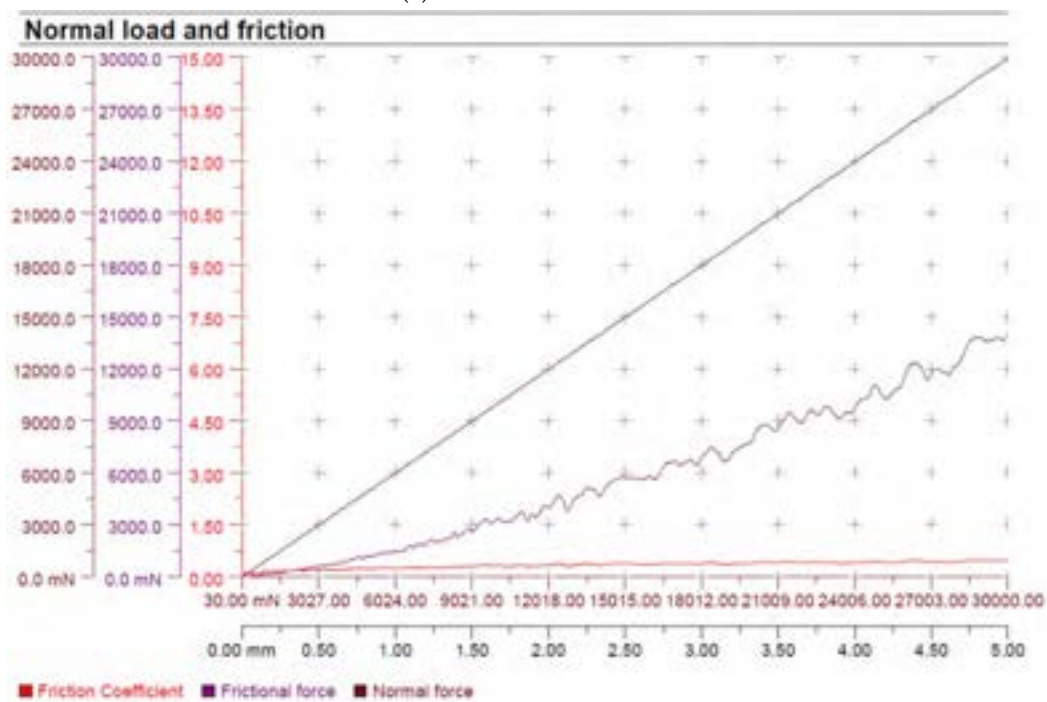


Figure 4.46: Progressive load scratch on Polished Steel316 L substrate

Progressive load scratch was performed with same conditions as mentioned in section 4.1.7. Load was steadily increased to 30N and scratch length of 5mm was used with a Rockwell indented of tip $100\text{ }\mu\text{m}$. In acoustic emission graph there is a sharp peak at scratch

length of 3.75 mm and load of 22.5 N. Acoustic emission jumps to 50% suggesting formation of a crack. There was no crack formation for Ti-6Al-4V under these loading conditions suggesting higher fracture toughness than SS 316L. Crack formed at the critical load is shown in Figure 4.47. Micrograph shows crack perpendicular to the scratch direction. This crack is different from semi circular cracks formed due to conformal and tensile mode of failure in coating.

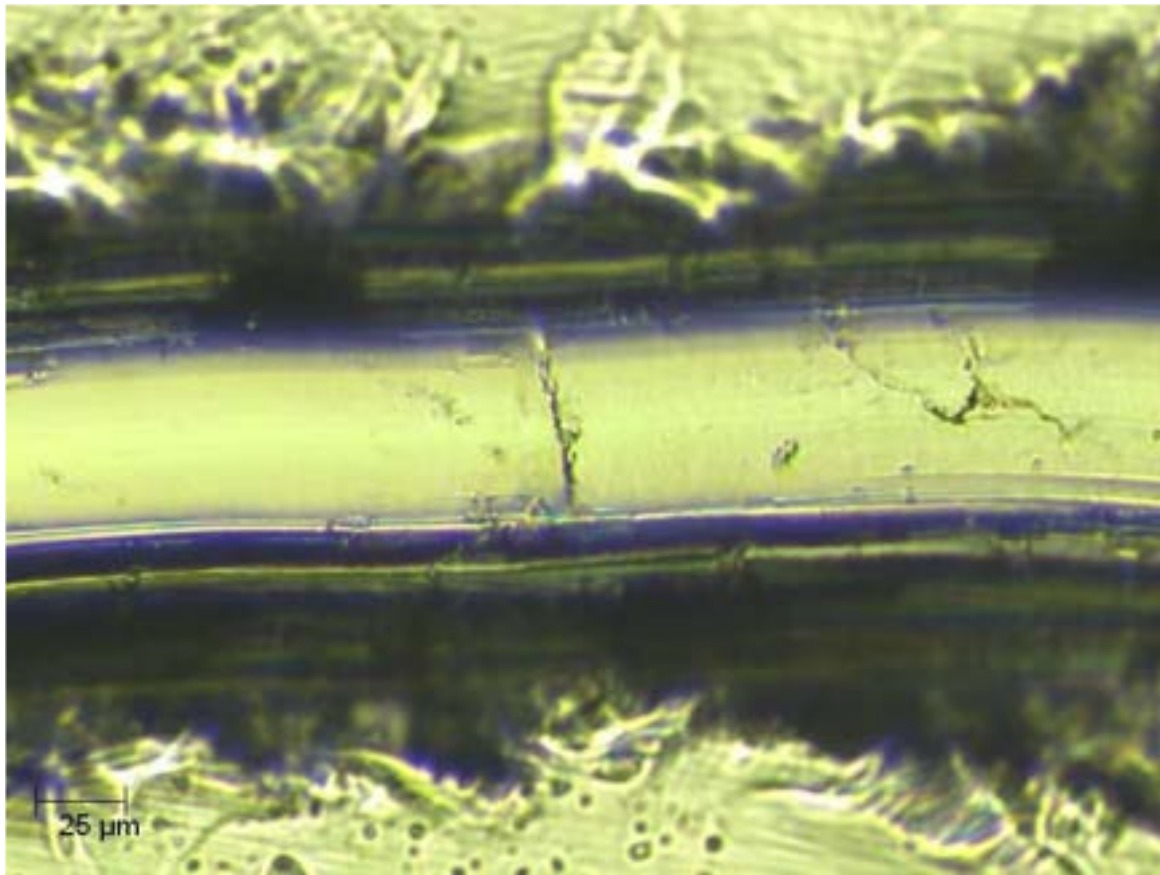


Figure 4.47: Crack formed at critical load

4.2.7 Fracture toughness

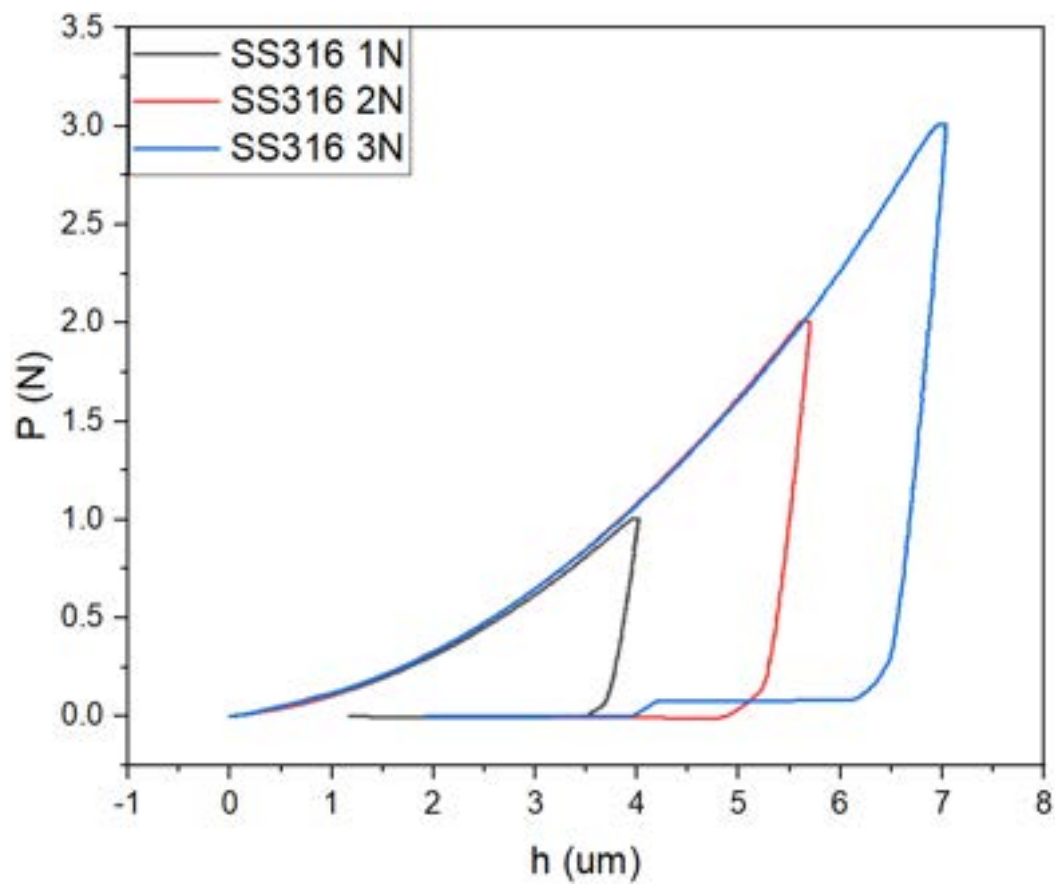
Table 4.10: Properties obtained from loading unloading curve for SS316L

	SS316				
	1N	2N	3N	Average	
HIT	2776.493	2777.061	2747.161	2766.905	MPa
HV	262.0617	262.1153	259.2933	261.1568	
EIT	187.2447	179.6897	170.0103	178.9816	GPa
E*	205.7637	197.461	186.8243	196.683	GPa
Er	174.38	168.3673	160.648	167.7984	GPa
hm	4.011333	5.699667	7.040333	5.583778	μm
S	3.790333	5.171667	6.073333	5.011778	N/ μm
hc	3.806333	5.396667	6.654333	5.285778	μm
hr	3.745333	5.31	6.544667	5.2	μm
hp	3.669333	5.212333	6.421	5.100889	μm
Ap	362.254	723.0543	1096.432	727.2468	μm^2

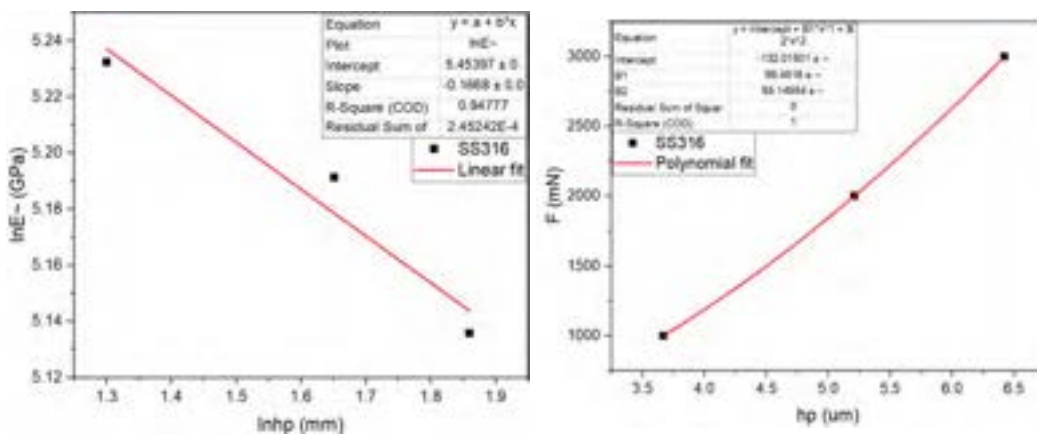
Micro indentation was performed on polished sample of SS316L at 3 different loads 1N,2N and 3N with a loading rate of 2N/min ,4N/min and 6N/min respectively and dwell time of 10s. Table 4.10 shows the results of various parameters obtained from the loading-unloading curves . This data was used to plot the graphs shown in figure 4.48. Polynomial and quadratic fits from Figure 4.48 were used to calculate critical values of modulus and surface energy. Calculated fracture toughness is given in table 4.11

Table 4.11: Fracture toughness for SS316L

	SS316			
	E*	h*	γ^*	Kic
Method	GPa	μm	kJ/m ²	MPa m ^{1/2}
ef 0.007	176.92	5.303	14.5	71.527
CSM E*	196.683	2.8107	6.93	52.22



(a) Load vs indentation depth SS316L



(b) Effective modulus vs penetration depth (c) Maximum load vs Penetration depth

Figure 4.48: Plots to calculate fracture toughness of of bulk SS316L

4.3 TiN coated substrates characterization

4.3.1 Wetting state and surface energy

Contact angles for water and glycol for TiN coated substrates are shown in Figure 4.49. Ti-6Al-4V substrate had a water and glycol contact angle of $72.1^{\circ} \pm 5.2$ and $58^{\circ} \pm 3.2$ respectively. SS316L substrate had a water and glycol contact angle of $69^{\circ} \pm 7.2$ and $52.1^{\circ} \pm 5.5$ respectively. Surface energies of the Ti-6Al-4V and SS316L coated substrates were 31.11 mJ/m^2 and 33.65 mJ/m^2 . Slight variation in surface energy resulted in lower water contact angle for SS316L. Same is the case for substrates with SS316L having 1 mJ/m^2 higher surface energy than Ti-6Al-4V. This will result in better coating adhesion and higher

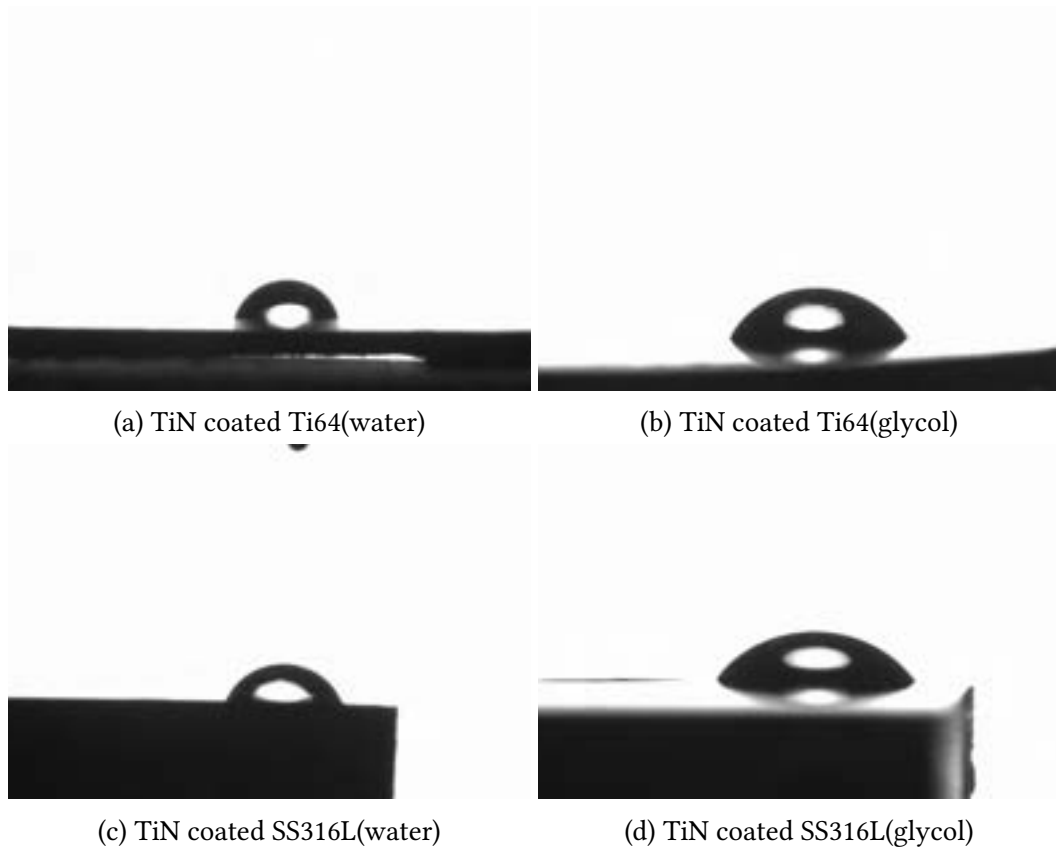


Figure 4.49: Contact angle of PVD coated substrates

critical load for coating failure under scratch testing. Optical micrographs of as received and polished substrates are shown in Figure 4.50. Surface of coated polished substrates is covered with several defects these can be further observed under SEM to study the morphology. Z oriented Ti-6Al-4V as received substrate shows chipping which is result of poor adhesion of the coating to the substrate.

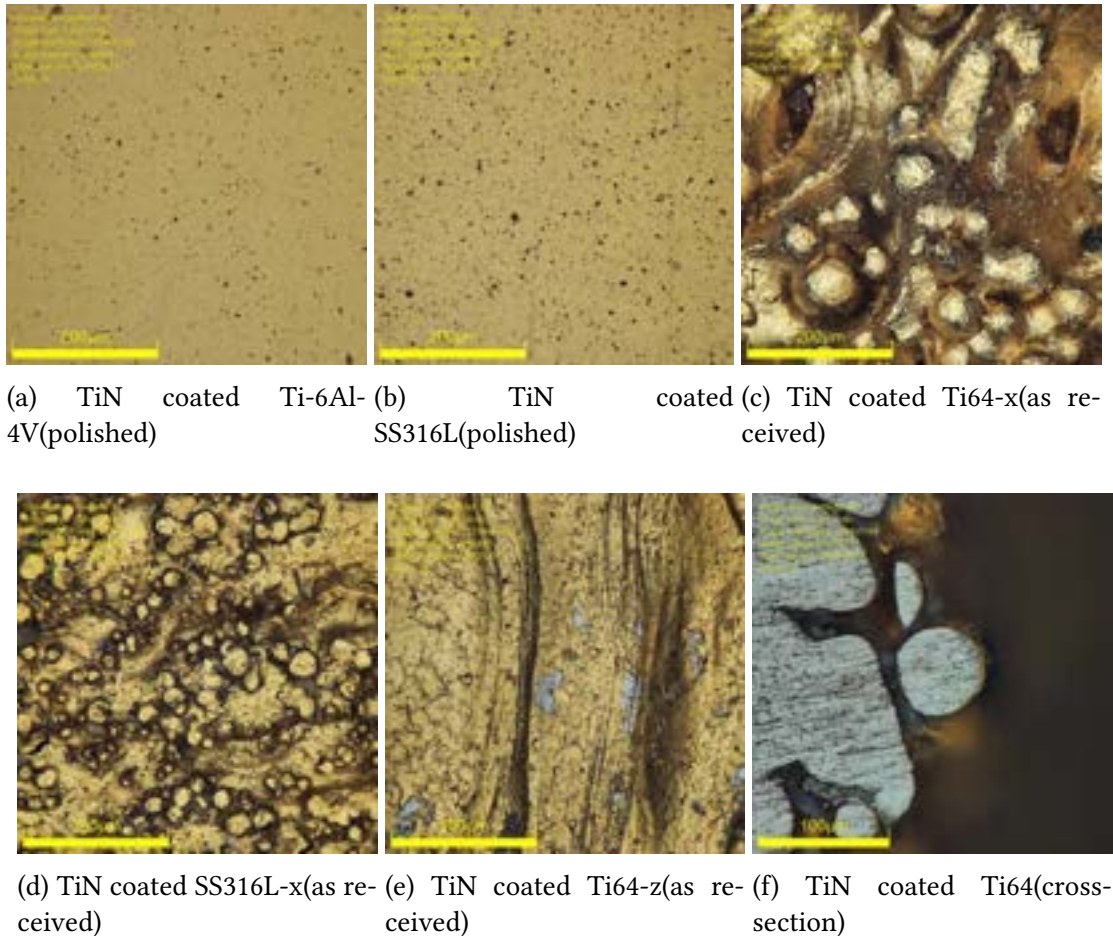
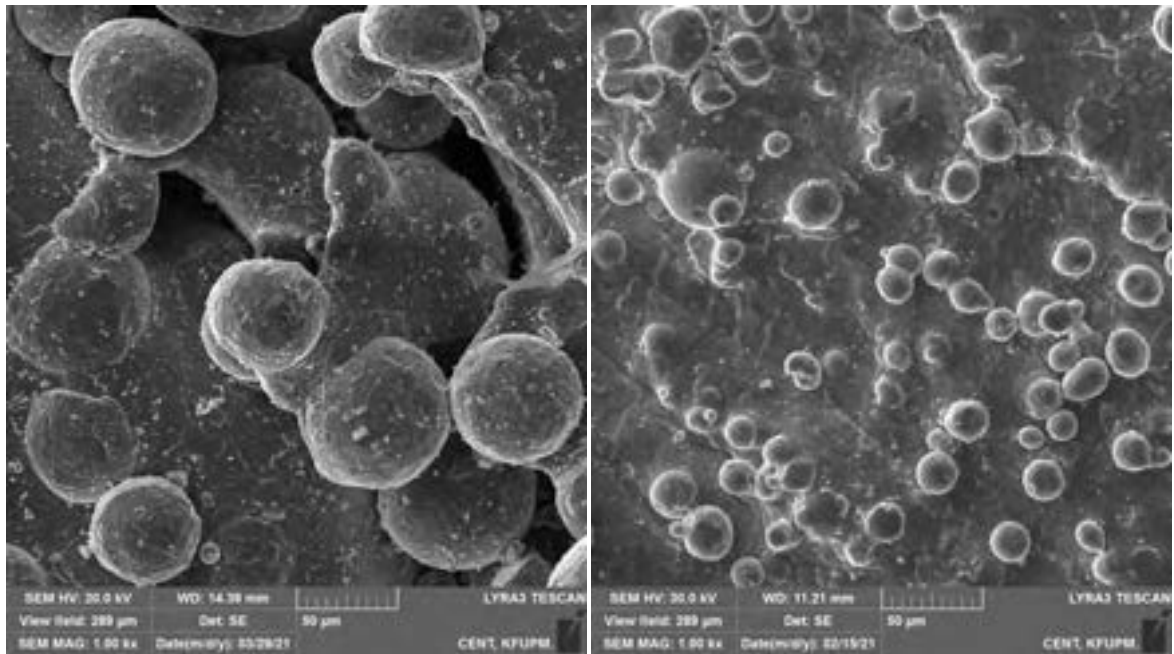


Figure 4.50: Optical micrographs of PVD coated substrates

4.3.2 SEM



(a) TiN Coated Ti-6Al-4V

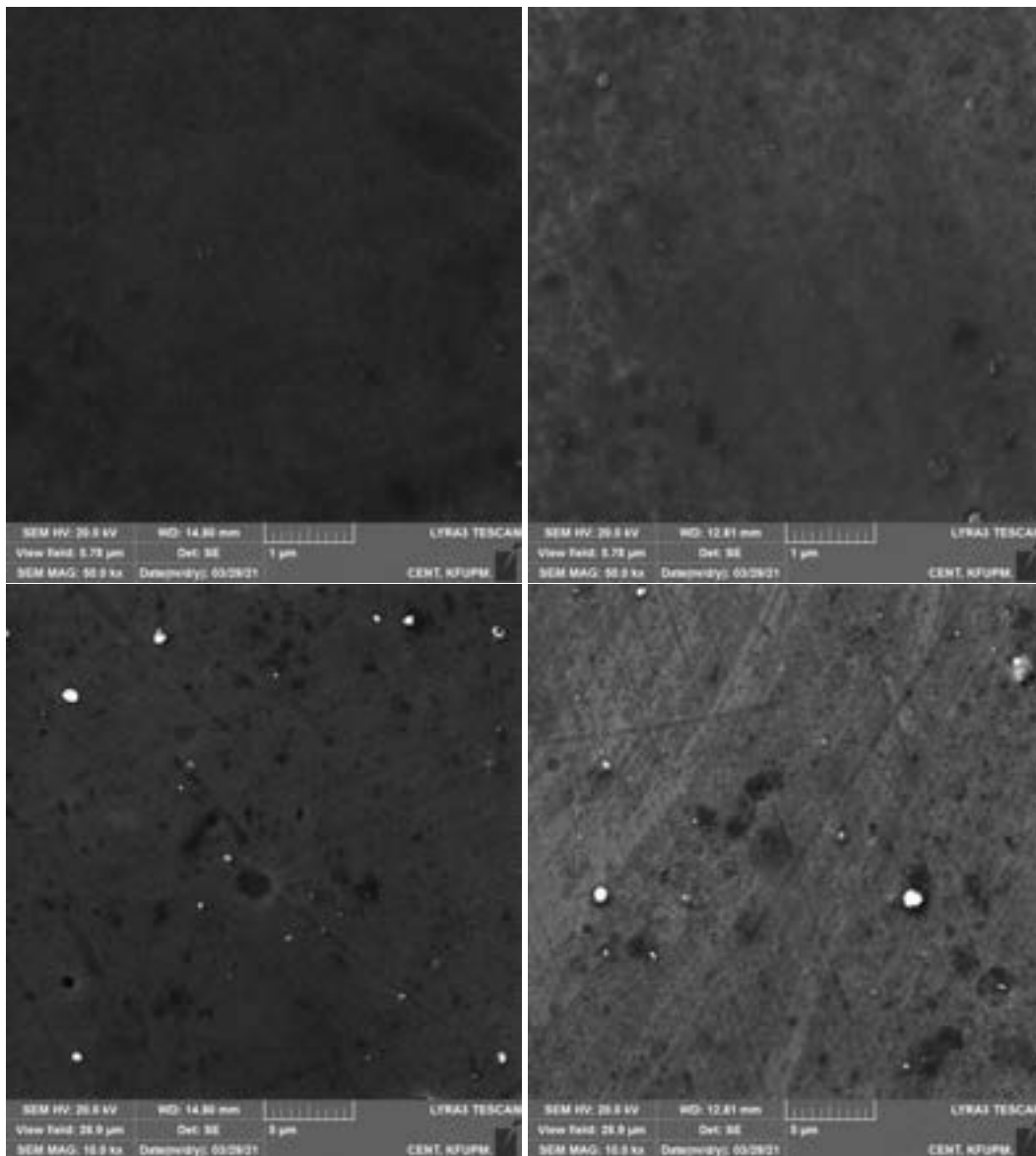
(b) TiN coated SS316L

Figure 4.51: Micrographs of as received samples after TiN coating

As received samples were analyzed under SEM after coating with TiN. Figure 4.51 shows the surface of TiN-SS316L and TiN-Ti-6Al-4V. Surface shows several defects in the form of craters and protrusions. Cathodic arc evaporation process has typically large number of defects due to airborne meltpool particles coming from the ionized regions of cathode. This is typically why other coating techniques are preferred for optical applications. Figure 4.52 shows the surface of the polished samples after coating at higher magnification the defects are not visible as shown in two micrographs at top of Figure 4.52. When we increase the view field to greater than $14 \mu\text{m}$ the defects become visible. Defects are in the form of protrusions, craters and sinkholes. There are some regions with no coating due to flakes of foreign particles or large underlying defects.

Coating surfaces have inherent imperfections and defects. Conical or circular protru-

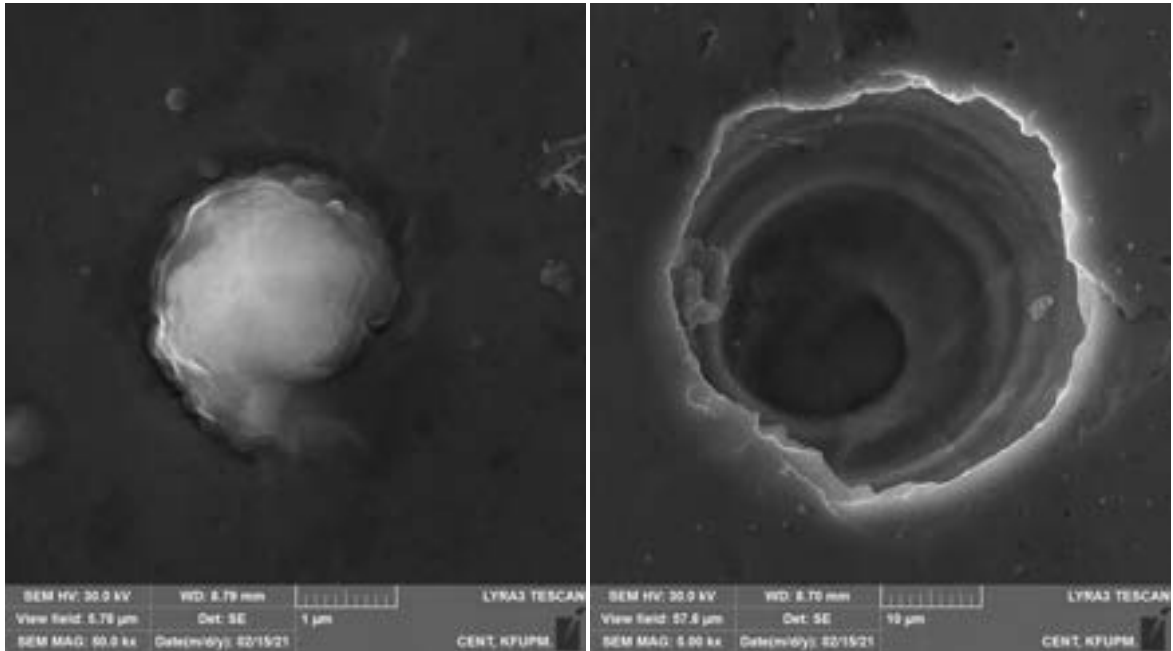
sions, pinholes, pores and voids are formed during coating deposition. Defects usually vary in size and shape but their texture and morphology can explain the process of their formation. Flakes are formed due to the presence of foreign particles on the substrate surface. Voids or pores from the substrate surface can give rise to sinkhole, pinholes and craters. Protruding particles may rise due to impurities or agglomeration of carbides.



(a) TiN coated Ti-6Al-4V

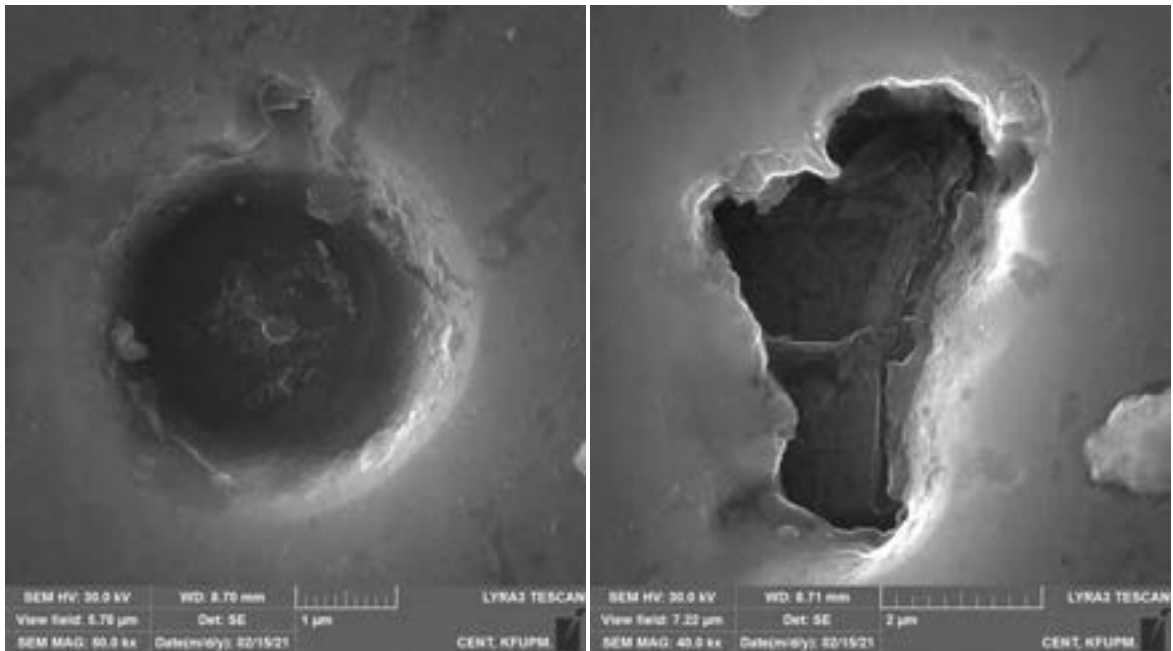
(b) TiN coated SS 316L

Figure 4.52: TiN coating after polishing of Ti-6Al-4V & SS 316L



(a) Quasi circular protrusion morphological feature

(b) Sinkhole defect with no coating



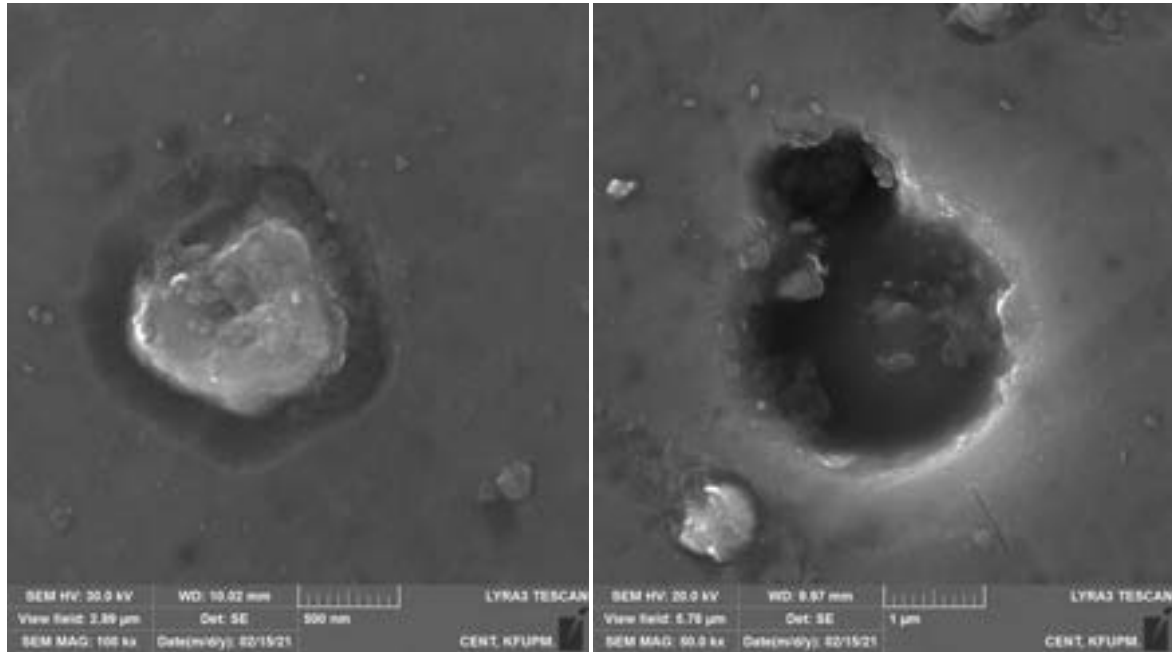
(c) Circular dish like defect

(d) Irregular defect of substrate

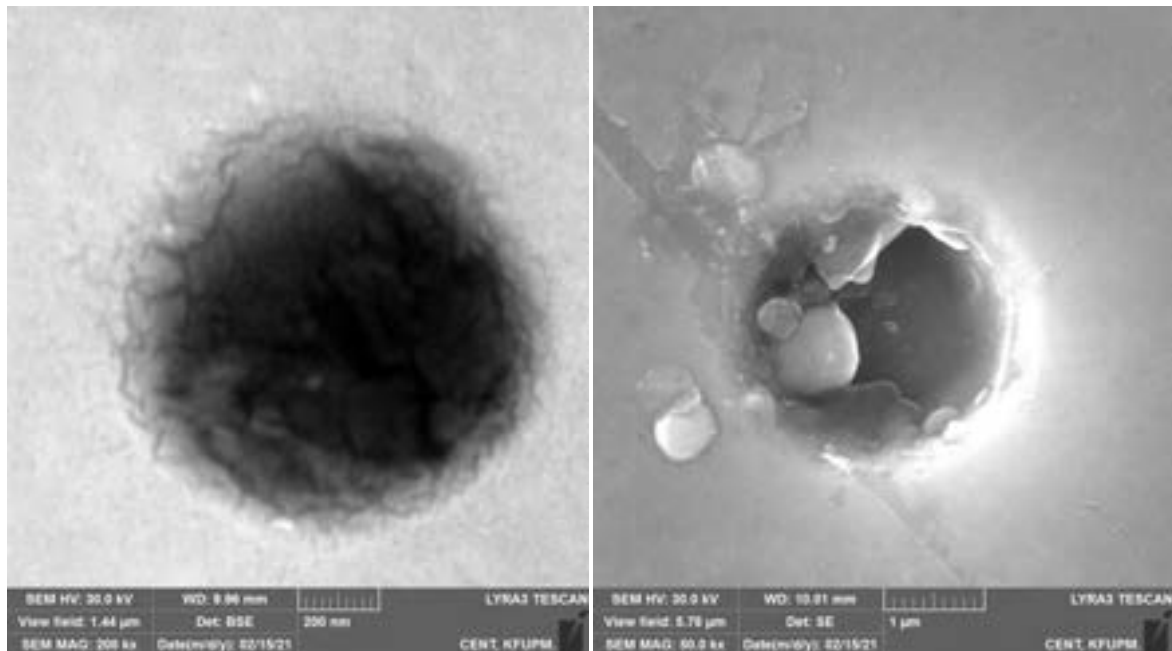
Figure 4.53: Micrographs of defects in TiN coated Ti-6Al-4V

Coating can take different shape depending on its interaction with the surface. Wetting state of the particles decides whether coating forms a complete layer or inclusion. Small

circular defects are formed due to the result of surface energy forcing the melt pool into a circular shape typically ranging 0.5 to 1 μm . Pinhole defects are formed due to sinking of

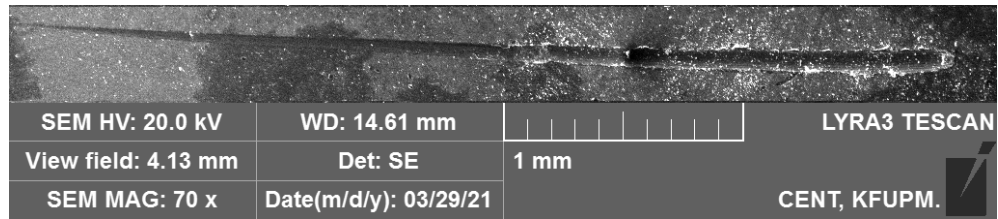


(a) Quasi circular protrusion morphological feature (b) Two defects showing Ostwald ripening and fusion

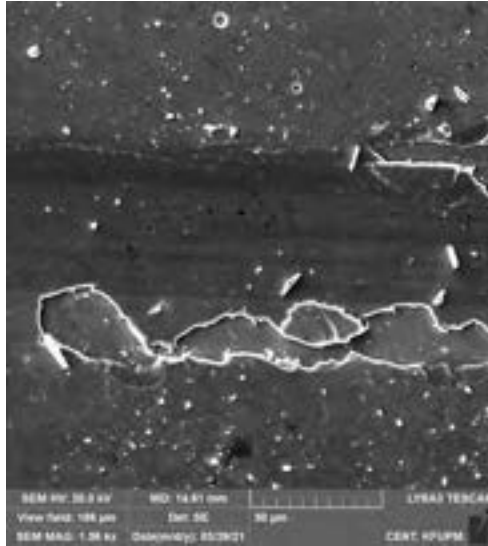


(c) Circular crater with cracking (d) Circular defect with foreign particles coated

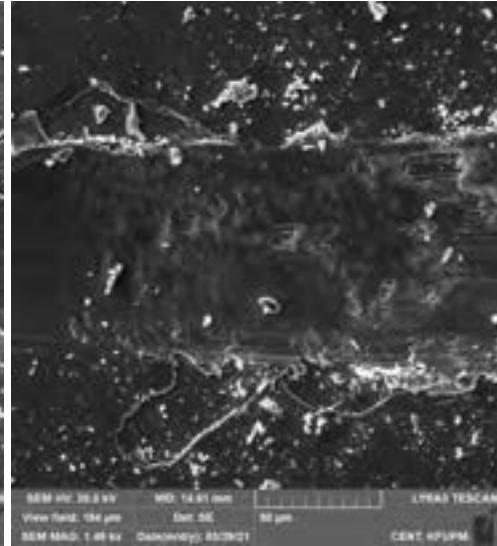
Figure 4.54: Micrographs of defects in TiN coated Steel 316L



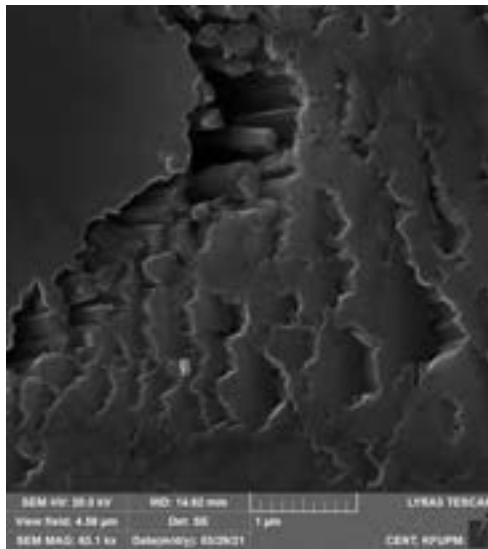
(a) Progressive load scratch and residue



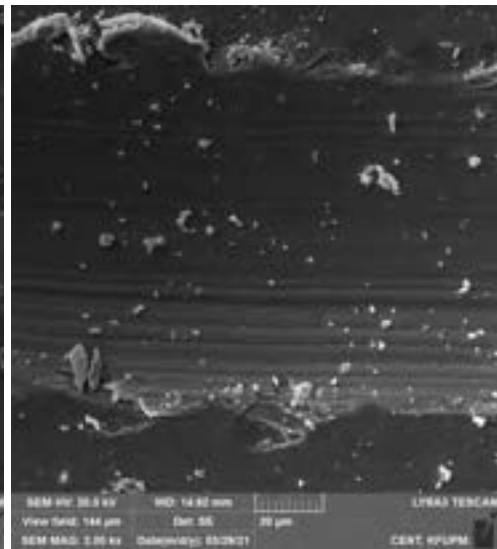
(b) Delamination of coating



(c) Tensile cracking



(d) Microstructure after cracking

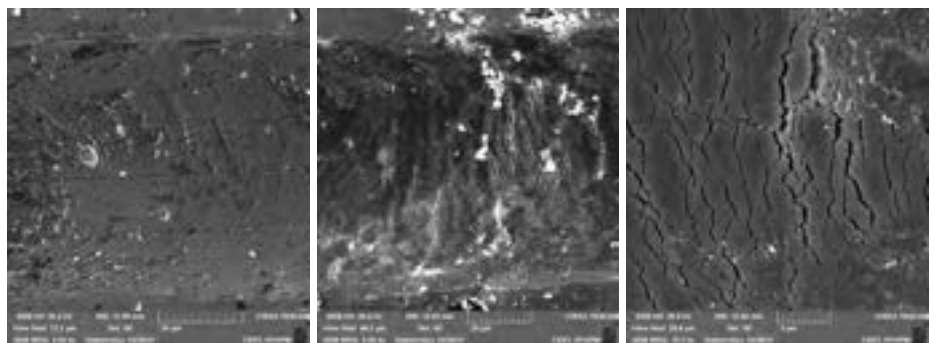
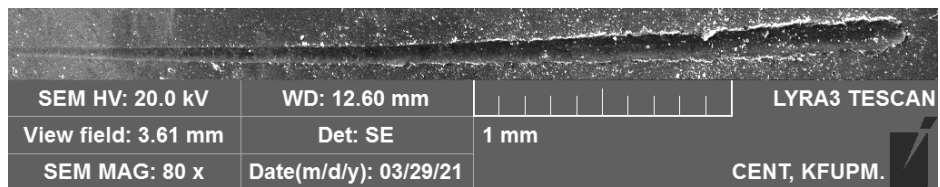


(e) Micro-scratches from build up residue

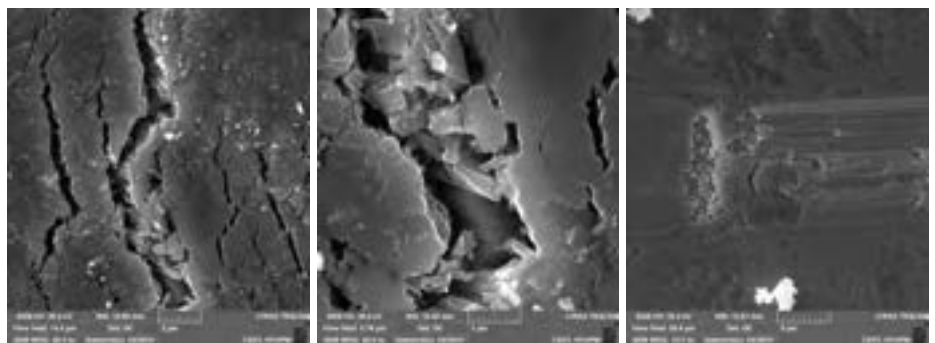
Figure 4.55: Micrographs of progressive scratch on TiN coated Ti-6Al-4V

the molten layer into a void and can be identified from cross-section of the coating layer.

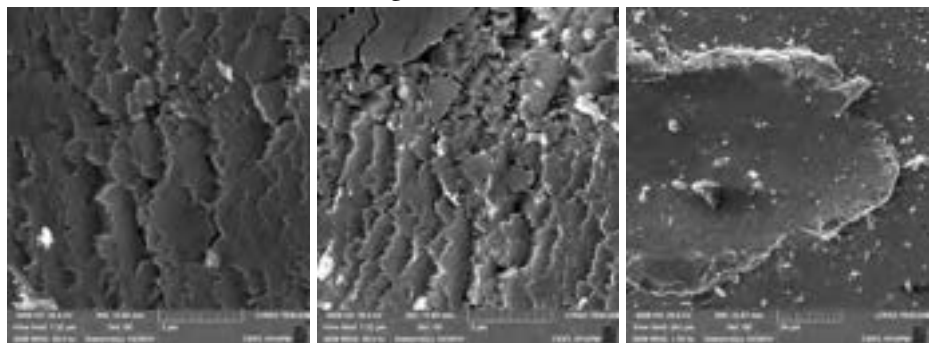
Figure 4.53a shows a quasi circular protrusion defect in Ti-6Al-4V . Coating has covered



(a) Conformal cracking (b) Gradual increase in crack size (c) Mix mode conformal + tensile cracks



(d) Cracked coating (e) Microstructure of coating after failure (f) Delamination and micro-scratches



(g) Equiaxed cracks in scratch direction (h) Increased inclination of cracked structure (i) Residue perpendicular to coating direction

Figure 4.56: Micrographs of progressive scratch on TiN coated SS 316L

the defect due to similar surface energy. On the other hand protrusion defect in SS 316L as shown in Figure 4.54a has a trench of avoided area by the coating due to difference in surface energy. Surface energy affects the adhesive and cohesive forces between the liquid metal and the substrate creating a force governing the resultant coating behavior. Circular crater defect is created due to surface tension of the molten liquid forcing it to be circular having lowest surface free energy. Micro-droplet defects are also formed due to arcing. Impurities present in target cathode and substrate result in increased arcing. These defects are inherent to cathodic arc deposition, one of them is present above the quasi circular pro-trusion in Figure 4.53a approximately 100nm in size. Arcs cause ejection of micro-droplets from meltpools and these growth into defects at the surface of coating. High energy of arcing also results in thermal stresses at the defect locations which can result in delamination of the coating. Micrographs of progressive load scratch test are given in Figures 4.55 and 4.56 for TiN coated Ti-6Al-4V and SS 316L respectively. Scratch shows various modes of failure like conformal and tensile failures. Scratch on steel substrate has also mixed mode of conformal and tensile involving failure both due to bending and compressive/tensile stresses under the load of tip. Ti-6Al-4V scratch has delamination and buildup debris at the end of the scratch. Ti-6Al-4V's scratch ends at a region of micro-scratches from the buildup debris. SS 316L on the other hand starts from conformal mode and then changes to mixed mode of tensile and conformal failure. Cracks also increase in size as load increases. Investigation of failure region reveals the microstructure of the coating grains. These columnar grains start aligning in scratch direction as scratch progresses.

4.3.3 EDS

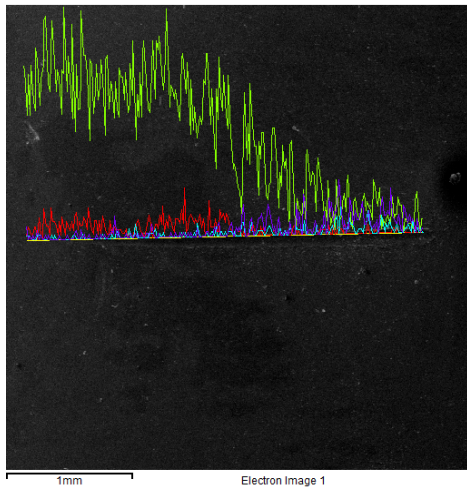
Electron diffraction spectroscopy reveals the elemental composition of the TiN coatings on both the substrates. Ti-6Al-4V shows no weight percentage of substrate elements in the EDS analysis. This means a uniform coating distribution and thicker coating. On the other hand peaks from base substrate come in coated SS 316L. Compositions are given in Table 4.12 and 4.15. Same behavior is observed in the line scans of the scratch after half length as shown in Figure 4.57. Iron and chromium elements from the substrate start showing in the mapping suggesting delamination of coating or thickness becoming less than X-ray interaction zone.

Table 4.12: Elemental composition of TiN coated Ti-6Al-4V

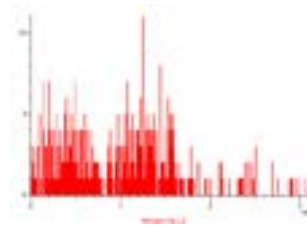
Element	Ti	N
Weight %	74.36	25.64

Table 4.13: Elemental composition of TiN coated SS 316L

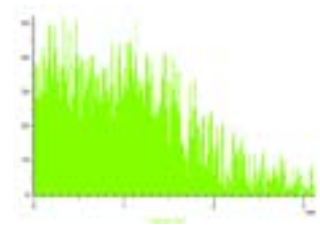
Element	Ti	N	Fe	O	Cr	Ni
Weight %	69.53	20.99	4.82	2.28	1.44	0.95



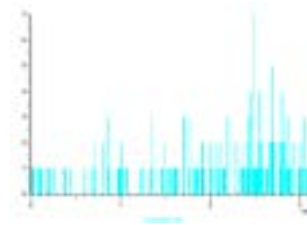
(a) Line Scan of TiN SS316L



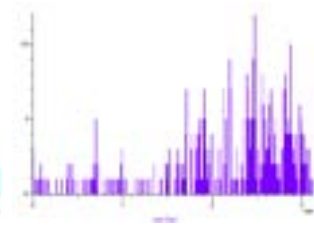
(b) Nitrogen



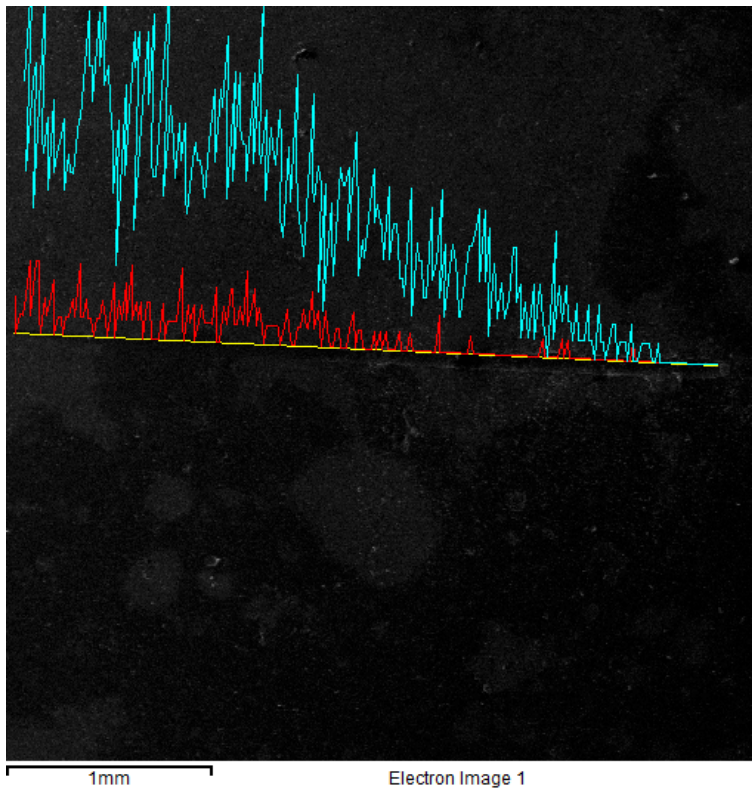
(c) Titanium



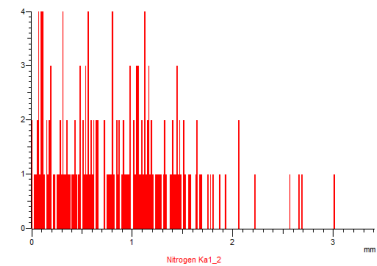
(d) Chromium



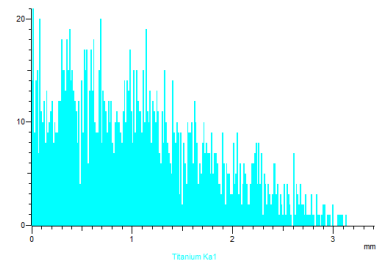
(e) Iron



(a) Line Scan of TiN Ti-6Al-4V



(b) Nitrogen



(c) Titanium

Figure 4.57: Elemental mapping line scan on scratches of TiN coated substrates

4.3.4 XRD

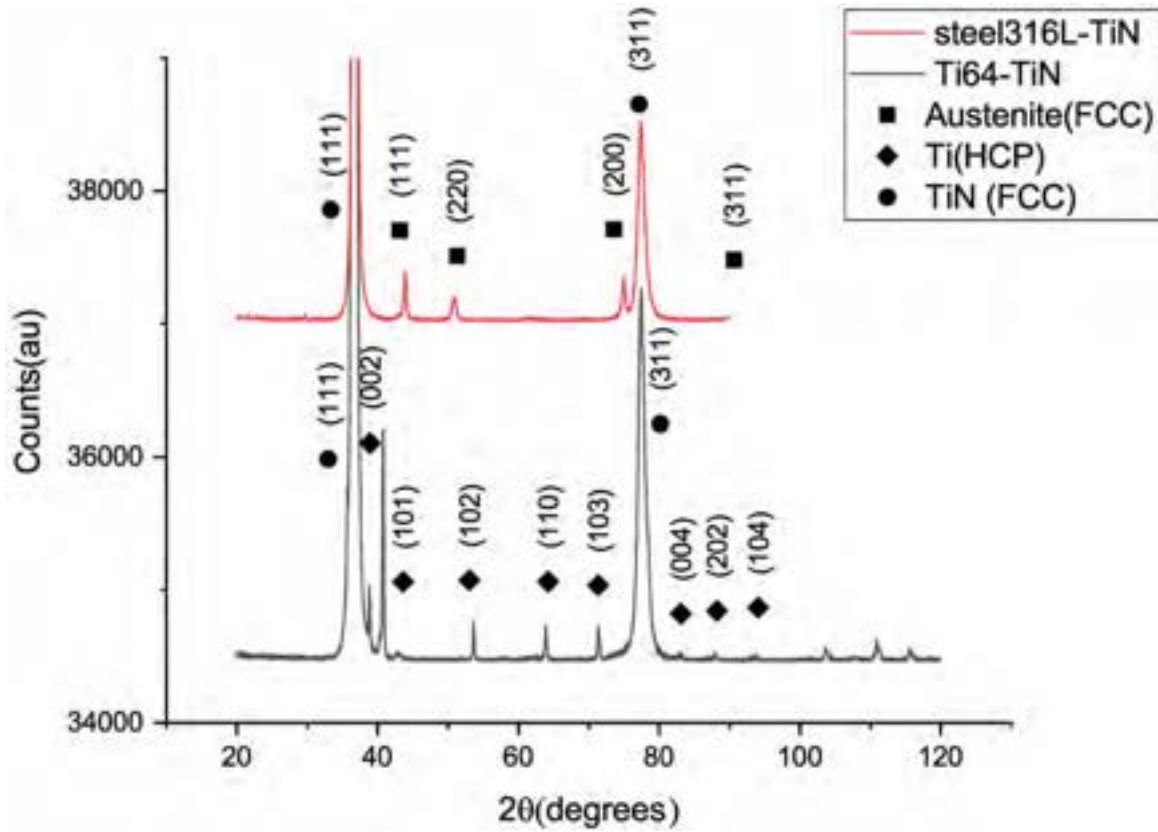


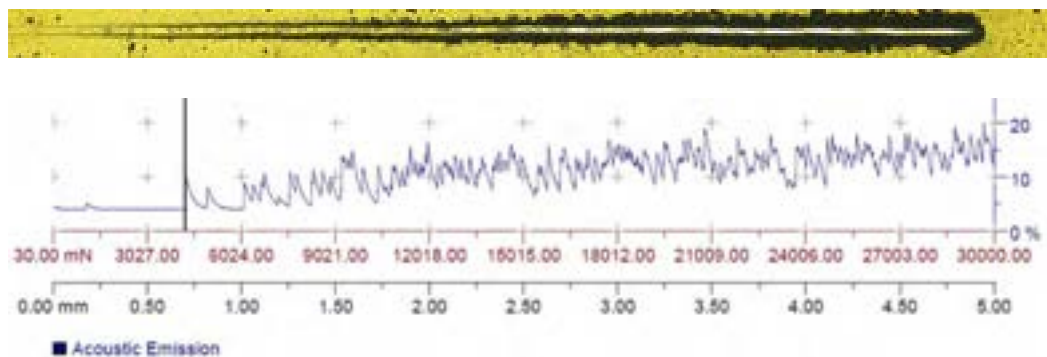
Figure 4.58: XRD for TiN coated Ti-6Al-4V and SS316

XRD spectra for TiN coated Ti-6Al-4V and SS 316L are shown in Figure 4.58. Indexing of the reflections was done using literature and already identified Ti-6Al-4V and SS316L. Analysis revealed mix of peaks from substrate and PVD coating. SS316L graph showed 4 peaks of austenitic FCC steel substrate and 2 peaks for FCC TiN. TiN-Ti-6AL-4V showed 8 peaks of underlying Ti-6Al-4V HCP and 2 peaks for TiN FCC. Substrate peaks are coming due to small thickness of the coating around $1.8 \mu\text{m}$. Two of the highest peaks belong to TiN which is on the surface. Peaks from the substrate are coming due to larger area of interaction of the XRD with the sample than the coating thickness. Width of TiN peaks at half maximum is same for both substrates suggesting similar size for crystallite and no

phase difference between the two samples.

4.3.5" Scratch

Progressive load scratch test was performed to analyze the coating behavior of the two substrates. Results for progressive load scratch are given in Figure 4.60. Critical load for TiN coated Ti64 comes to be 3.4 N. After 3.5 load there are several peaks suggesting coating



(a) Acoustic Emission

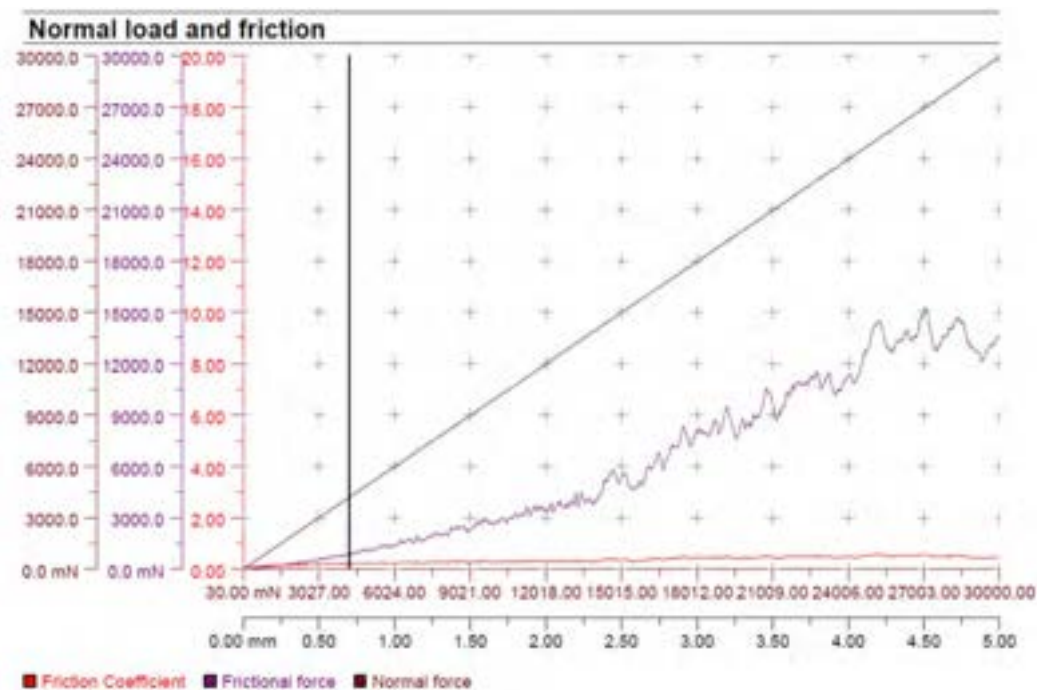
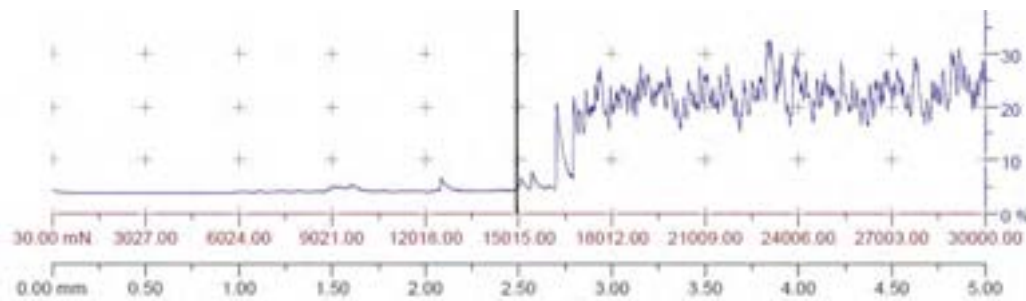


Figure 4.59: Progressive load scratch on Polished Ti-6Al-4V substrate

cracking resulting from bending, compression and tension under the load of the scratch tip. Cracking mode can be observed from the micrographs as presented earlier in section 4.3.2. Two progressive load scratches were performed on each sample. TiN-Ti-6Al-4V had critical load of 4222 and 5774 mN with a mean of 4998mN while TiN-SS316L had much higher critical loads of 7203 and 14957 mN and a mean of 11080mN. SS316L substrate had 2.2 times the critical load of Ti-6Al-4V substrate showing much better adhesion of coating.



(a) Acoustic Emission

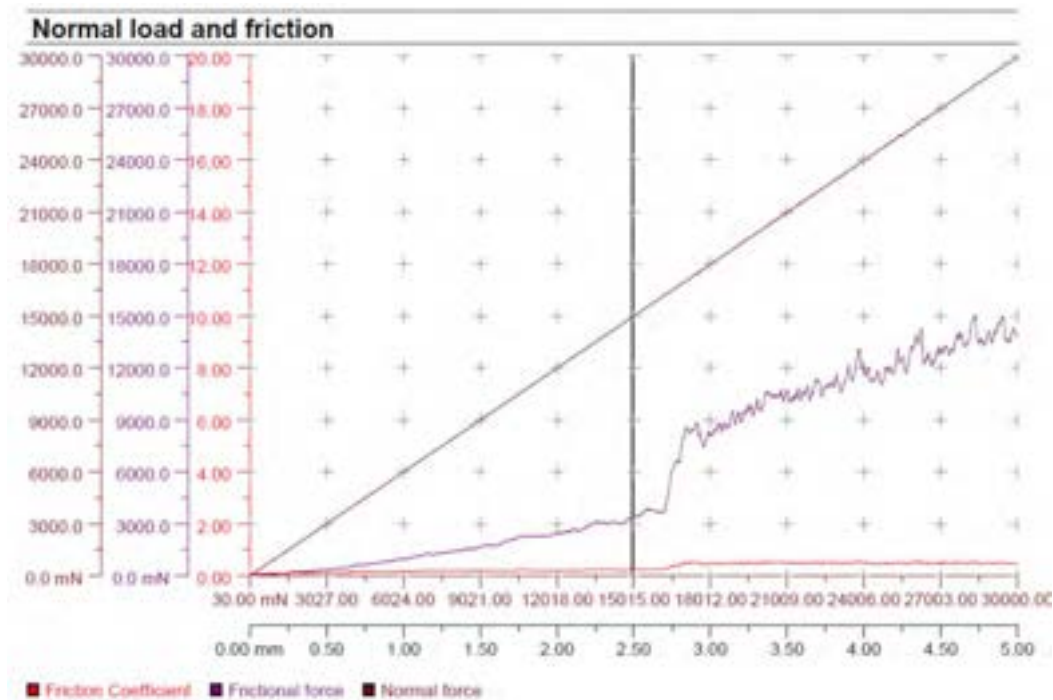


Figure 4.60: Progressive load scratch on Polished Steel316 L substrate

Table 4.14: Results for Progressive load scratch

Sample	Critical Load (mN)	Friction Coefficient
TiN Ti-6Al-4V	4998.5	0.32
TiN SS316L	11080	0.34

4.3.6 Microhardness

Microhardness was performed using a diamond vickers indenter with max load of 0.02N and loading and unloading rate of 0.04N/min. Dwell time was 5 seconds. Instantaneous and reduced modulus were calculated based on loading-unloading curve and theory mentioned in section 2.6

Table 4.15: Elemental composition of TiN coated SS 316L

Sample Units	Hv	E_i GPa	E_* GPa	E_r GPa	h_p μm	A_p μm^2
TiN Ti-6Al-4V	2072	233.3	251.5	210.5	0.027	0.428
TiN SS316L	2144	305.8	333.	288.6	0.012	0.245

CHAPTER 5

CONCLUSION AND FUTURE WORK

Additive manufacturing is an excellent technique to manufacture complex parts with zero waste using layer by layer manufacturing. In this study EBM was used to manufacture sample of Ti-6Al-4V in different directions. Wetting state , surface energy ,topology, microstructure ,phases and hardness of the sample was examined using analytical techniques

5.1 Ti-6Al-4V characterization

- X-oriented samples had hydrophobic behavior and Z-oriented samples had hydrophilic behavior.
- Surface energy of polished X-oriented($27.8\text{mJ}/\text{m}^2$) sample was comparable to Z-oriented sample $24(\text{mJ}/\text{m}^2)$ but surface energy of Z-orientation with roughness effect is around $50\text{mJ}/\text{m}^2$ while X-oriented sample is $30\text{mJ}/\text{m}^2$.
- The roughness of X-oriented samples is 5-13 times the roughness of Z-oriented sample due to fused unmolten powder.

- X-oriented topology consists of spherical fused powder particles and Z-oriented samples comprise of meltpool structures and layers aligned with scanning direction.
- Microstructure is similar in both orientation with Widmanstatten structure of α - β Ti-6Al-4V
- The primary phase is HCP (α) Anatase Titanium.
- Vickers hardness of printed samples is higher than wrought samples but scratch hardness is similar to wrought samples.

5.2 SS316L characterization

Sessile drop experiment revealed that both X and Z oriented SLM SS316L had hydrophilic behavior with Z oriented samples having higher contact angle of 69° and X oriented sample having lower contact angle around 42.2° . Surface energy was analyzed after grinding and polishing the sample. Polished sample had water contact angle of 98.3° and glycol contact angle was found to be 70.95° which resulted in surface energy value of 26.7mJ/m^2 using Owen Wendt model. Z oriented samples had $1.153\text{ }\mu\text{m}$ horizontal and $0.631\text{ }\mu\text{m}$ vertical average roughness and X oriented sample had $1.811\text{ }\mu\text{m}$ and $2.12\text{ }\mu\text{m}$ average horizontal and vertical roughness respectively. Z oriented samples have similar roughness and wetting state to Ti-6Al-4V but X oriented sample has half the average roughness when compared to X oriented Ti-6Al-4V thus resulting in hydrophilic behavior. As unmelted powder is the primary source of roughness in X orientation having smaller size for starting SS316L

powder has resulted in lesser roughness. Smaller size of micro/nano pillars of molten powder result in high percentage of solid in contact with liquid. In Cassie-Baxter state higher roughness ratio of solid to liquid contact results in lower contact angle. Microstructure of SLMed SS316L is cellular dendritic structure with columnar grains while wrought SS316L has an equiaxed grain structure. Cellular structure consists of both equiaxed cells and elongated cells in cooling direction towards meltpool boundaries. Meltpool boundaries are visible in the etched sample which was not the case for Ti-6Al-4V. SEM of cross section reveals the microstructure of the molten powder layer with large dendrites. Meltpool layers and unmolten structure in the heat affected zone are visible in SS316L. This can be attributed to higher absorption depth of laser when compared to electron beam and SS316L having higher thermal conductivity than the Ti-6Al-4V. XRD analysis revealed presence of austenitic FCC structure. Hardness was found to be 226 HV which is higher compared to 200HV of cast SS316L. Increase in hardness is due to high cooling rates resulting in fine subgrain cellular structure. Finer structure has higher dislocation density which hinders dislocation movement resulting in higher hardness value, but higher hardness can result in lower toughness of the material. Progressive load scratch resulted in critical load of 22.5N resulting in crack formation. Micro indentation was performed to find effective modulus, stiffness and HV which was recorded to be 178.98GPa, 5.01N/um and 261.15 respectively. Fracture toughness was analyzed using indentation method and was found to be 71.527 MPa m^{1/2}. This is lower than reported range of 112 – 278 MPa m^{1/2} for Grade 316 (UNS S31600). The decrease in toughness is the result of higher hardness and finer subcellular microstructure which doesn't hinder crack growth like wrought SS316L.

5.3 TiN PVD coating characterization

Wetting state of TiN PVD coated substrates was hydrophilic with Ti-6Al-4V and SS316L substrate showing water contact angle of 72.1° and 69° . Smaller water contact angle of steel substrate suggests higher surface energy value due to better coating adhesion. Surface energies of the Ti-6Al-4V and SS316L coated substrates were 31.11mJ/m^2 and 33.65mJ/m^2 . Surface of coated polished substrates is covered with several defects in the form of craters and protrusions. These defects are typical for cathodic arc evaporation and result from ejected melt pool particles in the ionized cathode regions. Defects are in the form of protrusions, craters and sinkholes. Main sources of defects are ejected molten particles, pores in the substrate and foreign particles. Surface energy affects the adhesive and cohesive forces between the liquid metal and the substrate creating a force governing the resultant coating behavior. XRD diffraction was performed to analyze the phase of the coating. TiN peaks were identified as FCC structure with preferential orientation in (111) direction. Small peaks from substrates were also identified as X-rays penetrated thin film coatings. SEM was performed at the cross section and average thickness of the coating was found to be $2.05\text{ }\mu\text{m}$ for Ti-6Al-4V substrate and $3.73\text{ }\mu\text{m}$ for SS316L substrate. SS316L showed better coating adhesion due to slightly higher surface energy. Critical load and friction coefficient for Ti-6Al-4V substrate was 4.998 N and 0.32 respectively and for SS316L substrate was 11.08 N and 0.34 respectively. TiN coating showed better adhesion and performance for SS316L when compared to Ti-6Al-4V substrate.

5.4 Future Recommendations

This thesis has presented characterization based on non-destructive techniques. Following suggestions are given for extending current work.

- Study and analyze the wetting behavior and topology of the SLMed sample based on its printing direction.
- Coat the sample using PVD to study the viability of 3D printed samples as substrates for different materials.
- Numerical study of the microstructure evolution in EBM using phase field modeling.
- Analyze the fractal dimension of the microstructure and compare it with wrought microstructure and use image based threshold to examine α/α' content.
- Use continuum damage mechanics to obtain fracture toughness from loading/unloading curves.

APPENDIX A

SUPPLEMENTARY MATERIAL

Matlab code for Owen Wendt Model

```
x1=0;

x2=0;

c= 1:2:180;

d =1:1:70;

z=size(c);

result1=zeros(31,1);

for i=1:6:180

result=0;

for j=0:6:179

y1=-8.763*(1+cosd(i))+9.4661*(1+cosd(j));

y2=24/sqrt(19) + 24/sqrt(19)*cosd(j) -(sqrt(29)/sqrt(19))*y1;

x1= y1.^2;

x2=y2.^2;
```

```

z=real(x1+x2);

if z == 0;

z= 10;

end

result=[result;z];

end

result1=[result1,result];

end


a=1:6:180;

[X,Y]=meshgrid(a,a);

mesh(X,Y,result1(2:end,2:end))

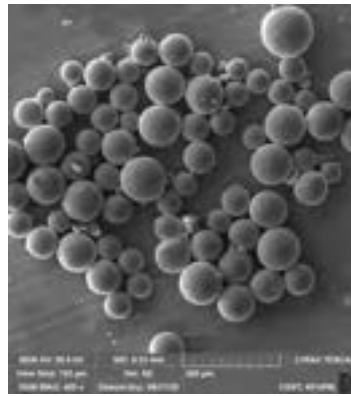
colorbar

xlabel('Surface Energy mJ/m2')

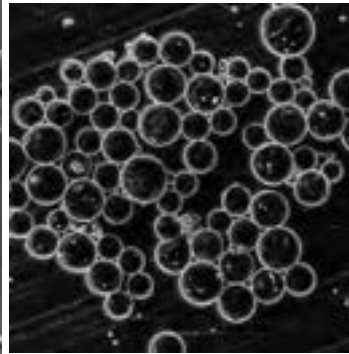
ylabel('\theta_{glycol}')

xlabel('\theta_{water}')
```

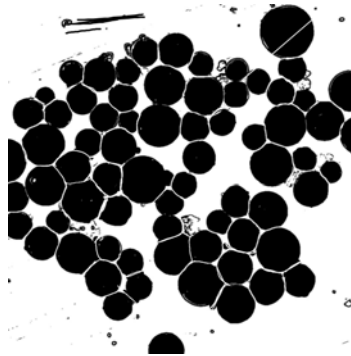
Calculation of Particle Size Distribution



(a) Powder



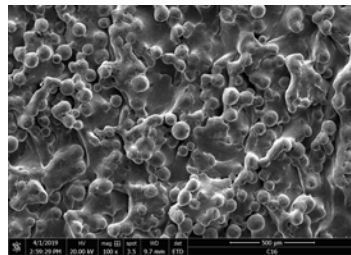
(b) Edge Detection



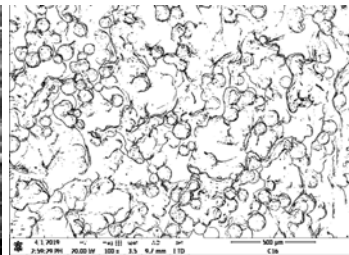
(c) Thresholding



(d) Detected Grains



(e) Printed structure



(f) Edge Detection



(g) Thresholding



(h) Calculated grains

Figure A.1: Calculating powder size using image Analysis(ImageJ)

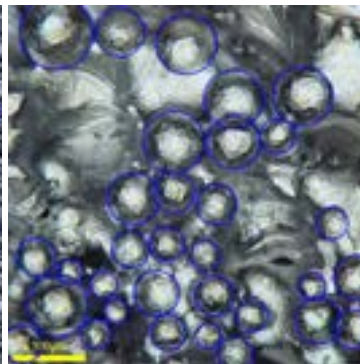
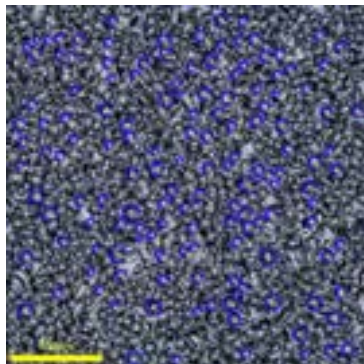
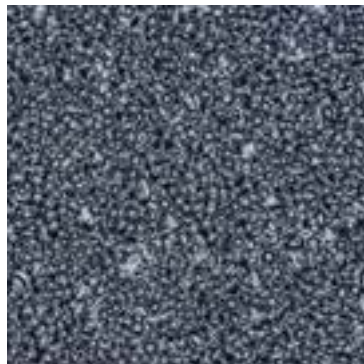
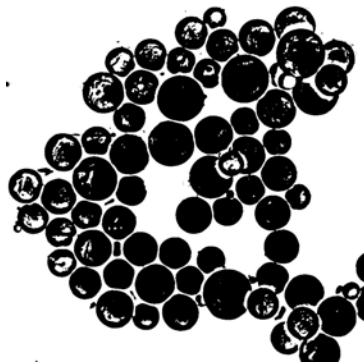
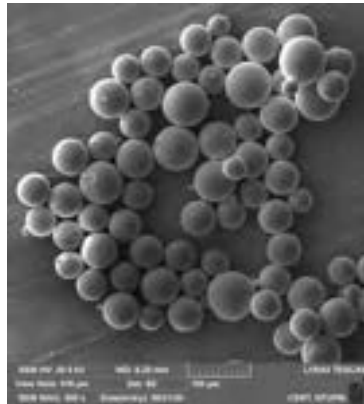


Figure A.2: Calculating powder size using image Analysis(ImageJ(a,b,c) and Olympus DSX (d,e,f))

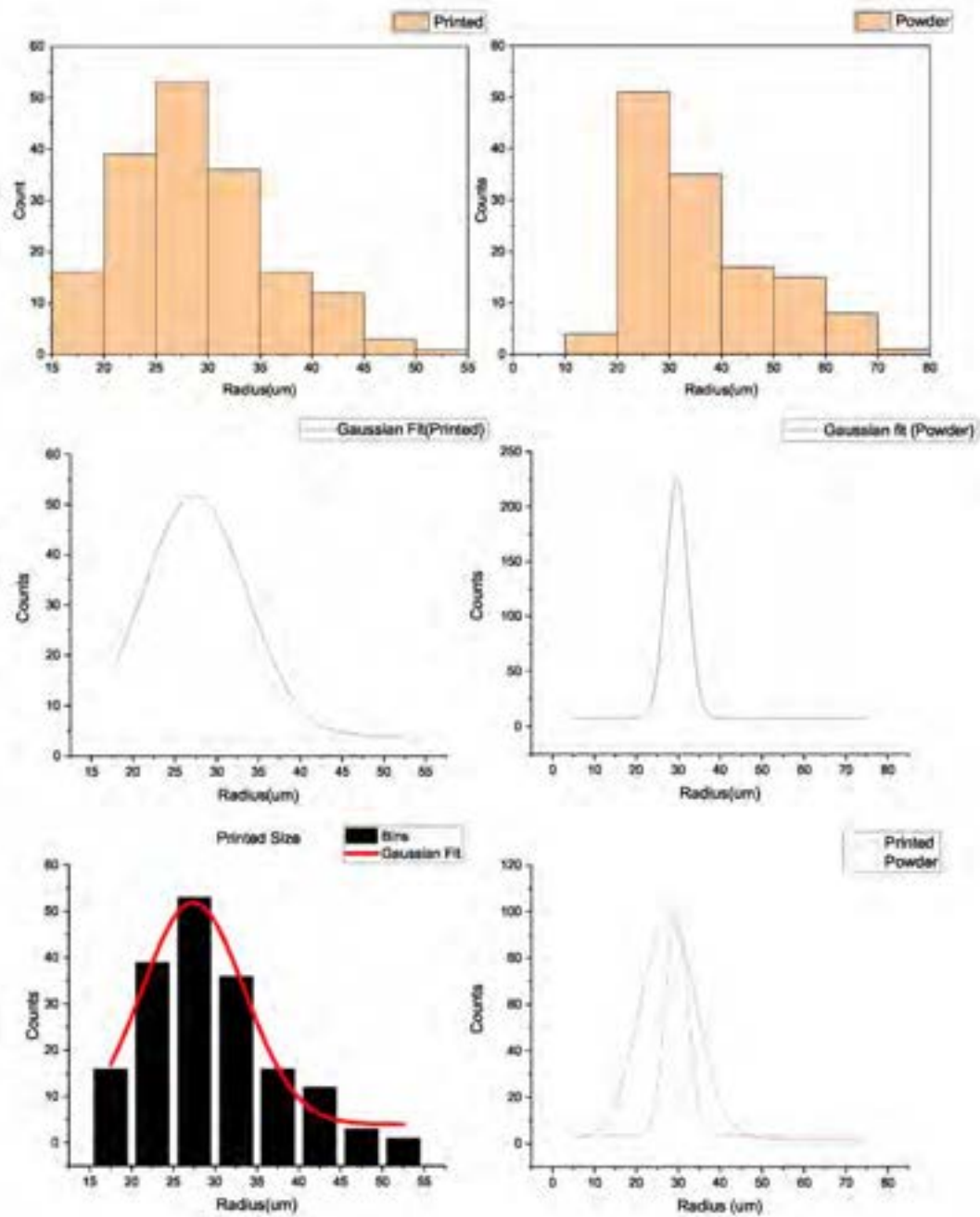


Figure A.3: Gaussian Distribution of Particle Size with Fitted curves

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Publications

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- Mahmut Şamil Kaya, Remzi Ecmel Ece, Omer Keles, Abdul Qadeer & Bekir Sami Yilbas (2021) Effect of Post Process Treatments On Mechanical and Metallurgical Properties of 3D Printed Ti6Al4V Alloy Parts, *Journal of Materials Engineering and Performance*

