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Advanced Coating: Laser-Metal Deposition of Titanium Aluminide Composites

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(217037413)

A thesis submitted to the Faculty of Engineering and the Built Environment, at the University of Johannesburg, in fulfillment of the requirements for the degree of Doctor of Philosophy in Mechanical Engineering Science

Supervisor: Prof. E. T. Akinlabi
Co-supervisor: Dr R. M. Mahamood

January, 2019
DECLARATION

I declare that this thesis is my own work. It is submitted for the Doctor of Philosophy degree (DPhil) in Mechanical Engineering, at the University of Johannesburg. It has not been submitted to any other University for a degree, or for an examination.

26/01/2019

(Candidate signature)  (Date)
DEDICATION

This work is first of all dedicated to Almighty God, who has brought me so far. I also owe my dedication to my family that has remained patient and has been supportive all the way through – until the end of my program.
ACKNOWLEDGEMENTS

My acknowledgement goes to my supervisors, Prof. E. T. Akinlabi and Dr R. M. Mahamood and the entire staff in the Mechanical Engineering Department for their input in the successful completion of my program.

I would like to single out the efforts of my supervisors for the great role they played in sharing their wealth of experience in the field of advanced coating (laser-metal deposition).

I would also like to acknowledge the staff of the CSIR, most importantly Prof. Sisa Pityana, Dr Monnamme Tlotleng, Nana Arthur and Emjay, for their immense contribution to the successful completion of this work.

In conclusion, I would like to thank the members of my family, in particular, my parents, wife and children for their prayers, understanding, moral and financial supports that enabled me to fully concentrate and complete my programme in due course.
ABSTRACT

Over the last few years, research projects on gamma titanium aluminides (γ-TiAl) have been intensified. These research projects are mostly aimed at obtaining the specific microstructural and mechanical properties of those materials that would make them highly suitable for structural applications. Research projects are indicating that this group of intermetallic compounds possesses a high strength-to-weight ratio, with strength that can be compared to that of steel and with far less weight; and that this group of materials displays high-corrosion resistance and good wear-resistance properties. These properties make them suitable for high-structural thermal applications in aeronautics, in the automobile industry, and in the generation of nuclear energy. Currently, the future of gamma titanium aluminides depends on how well the alloy can be processed, in order to enhance its micro-structural combinations, thereby improving its properties and making it highly suitable for specific structural applications.

The production interest of γ-TiAl alloy is mainly centred on producing an alloy with a duplex structure (with both γ-TiAl grains and lamellar α2+γ structure) in the right proportions, thereby enhancing the properties of the γ-TiAl alloy. The method of raising its service temperature and the way of improving its strength, and its high temperature strength-retention ability also remain areas of interest. Titanium, despite being one of the most abundant metals in the earth’s crust, remains expensive. As such, a fabrication technique that would cut down wastages in the production of quality components, using titanium and its alloys as raw materials has become a matter of paramount importance.

The Laser-additive manufacturing (AM) technique is an advanced manufacturing technique that has been developed in recent times; and it remains a manufacturing
route with the capacity of producing components directly from laser and metallic powder - on the instructions of computer-aided design (CAD) data, thereby eliminating tooling, as employed in the traditional method of production. This technique has shown numerous advantages; since the components are produced via a layer build-up method, thereby eliminating subtractive types of manufacturing, like machining, and eventually reducing material wastages.

This technique is also sustainable; as it has shown the ability to reduce the fly-to-buy ratio, increasing the production of complex parts that seem un-reproducible, the repair and the introduction of extra functional features on existing parts that are environmentally friendly; since no significant pollution is caused to the environment. Laser-metal deposition (LMD) is a type of AM that uses metallic powder guided by a shielding gas; and it is deposited into a melt pool produced by a concentrated laser beam in the fabrication of the components.

LMD remains one of the most sought-after AM techniques used in the feature addition, repair and fabrication of new components, because of its production accuracy and the quality of the parts produced. However, despite the merits of the technique, it is sometimes associated with thermally induced stresses that are responsible for crack initiations in the deposited components. The aim of this research is to fabricate titanium aluminide by using the laser-metal deposition technique; and by studying the effect of process parameters and the preheating of the substrate on the properties of the deposited samples. Three major scenarios were considered in the deposition of TiAl powder onto commercially pure titanium (CP-Ti) substrates. These three scenarios were to deposit the metal powder (Ti-4822-4 or Ti-Al-Nb-Cr in a prealloyed proportion) on
unpreheated, laser preheated and heating-bed preheated substrates. To do this, careful study of the previous work from literature in the selection of deposition parameters was used to deposit the TiAl alloys, as in this study.

Design expert 6.0.8 was used to analyze the influence of the deposition parameters on the height and the microhardness of the deposited samples. The deposited samples were characterized through naked-eye observation, microstructure, microhardness, X-ray diffraction, corrosion, dry-sliding wear, and nano-indentation to test for hardness, modulus of elasticity, stiffness and creep. The resulting outcome revealed that an increase in the energy intensity (increase of laser power and reduction in scanning speed) can totally eliminate cracks in the deposited samples.

The microstructures of the deposited samples were made up of different densities of duplex structures of γ-TiAl grains and lamellar structures. The structures of the deposited samples at high laser power also showed the formation of Widmanstatten colonies in the lamellar structures. The Vicker’s microhardness analysis also revealed different trends for the scenarios, based on the various deposited parameters. The x-ray diffraction analysis also revealed the presence of TiAl₂, Ti₃Al and Ti₃Al₂ phases in the sample of UA4 (deposited at 450 W, 3.174 mm/s and 4.09 g/min).

Sample H2 (deposited at 450 W, 3.174 mm/s and 2.7 g/min) of heating bed preheated substrate showed the presence of TiAl₃ in addition to the TiAl and Ti₃Al phases seen in the sample LA1 (deposited at 200 W, 10.58 mm/s and 4.09 g/min), LA2 (deposited at 300 W, 10.58 mm/s and 4.09 g/min), LA3 (deposited at 400 W, 10.58 mm/s and 4.09
g/min) and LA4 (deposited at 500 W, 10.58 mm/s and 4.09 g/min) of the laser-
preheated substrate.

The XRD results of sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min), LB2
(deposited at 300 W, 9.522 mm/s and 4.09 g/min), LB3 (deposited at 300 W, 8.464
mm/s and 4.09 g/min), LC3 (deposited at 300 W, 10.58 mm/s and 4.85 g/min) and LC5
(deposited at 300 W, 10.58 mm/s and 6.38 g/min) gave a single intermetallic TiAl
phases. Based on the other results obtained (wear, corrosion, hardness, modulus of
elasticity, stiffness and creep), the findings revealed that the gamma titanium aluminide
alloy is hugely affected by the manufacturing method and the cooling rates.

Therefore, the ability to produce a quality product lies in the proper selection and control
of the manufacturing method and the cooling rate. This study also modelled and
simulated an exhaust valve in a SOLIDWORKS 2017 environment, in order to provide
an idea as to how well the titanium-alloy material would do under thermal and buckling
conditions. The outcome indicated that the material, as compared with Ti-6Al-2Sn-2Zr-
2Mo-2Cr-0.25Si titanium alloy would comfortably do well under such conditions.

The study has produced gamma-titanium aluminide alloy with improved properties,
based on the manufacturing method, and on the selection and the control of the
deposition parameters.
# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>AM</td>
<td>Additive manufacturing</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-centred cubic</td>
</tr>
<tr>
<td>CAD</td>
<td>Computer-aided design</td>
</tr>
<tr>
<td>Ca</td>
<td>Calcium</td>
</tr>
<tr>
<td>CIT</td>
<td>Indentation creep</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>CP-Ti</td>
<td>Commercially pure titanium</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
</tr>
<tr>
<td>CMB</td>
<td>Controlled metal build-up</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer-numerically controlled</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>DOE</td>
<td>Design of experiment</td>
</tr>
<tr>
<td>DMD</td>
<td>Direct-metal deposition</td>
</tr>
<tr>
<td>DMLS</td>
<td>Direct laser-metal melting</td>
</tr>
<tr>
<td>DPSS</td>
<td>Diode-pumped solid state</td>
</tr>
</tbody>
</table>
EBM  Electron-beam melting
EDS  Electron-dispersive spectroscopy
EIT  Indentation modulus
Fe   Iron
fcc  Face-centred cubic
FDM  Fused-deposition modelling
H    Hydrogen
HAZ  Heat-affected zone
hc   Contact depth
hcp  Hexagonally closed packed
HIP  Hot-isostatic press
HIT  Indentation hardness
HR   Rockwell hardness
LBAM Laser-based additive manufacturing
LCI  Life-cycle inventory
LENS Laser-engineered net shaping
LMD  Laser-metal deposition
LOM  Laminated-object manufacturing

LSV  Linear-sweep voltammetry

m     Power-law exponent

MMCs Meta-matrix composites

Mo    Molybdenum

Ni    Nickel

OCP   Open-circuit potential

OM    Optical microscope

POM   Precision-optical manufacturing

RPD   Rapid-plasma deposition

S     Contact material stiffness

SEM   Scanning-electron microscope

Si    Silicon

SDM   Shape-deposition manufacturing

SiC   Silicon carbide

SLS   Selective-laser sintering

Sn    Tin
SLA  Stereo-lithography apparatus

SLM  Selective-laser melting

STL  Surface-tessellation language

Ti   Titanium

TiAl  Titanium aluminide

3DMW  Three-dimensional micro-welding

UTS  Ultimate tensile strength

V   Vanadium

$W_{plast}$  Plastic-deformation work of indentation

$W_{elast}$  Elastic-reverse deformation work of indentation

$W_{total}$  Total mechanical work of indentation

XRD  X-ray diffraction

YS  Yield strength

Zr   Zirconium
NOMENCLATURE

A  Dimensionless material constant, Indentation area

a  Indentation radius, Contact radius

$A_o$  Original cross-sectional area

$A_f$  Final cross-sectional area

$A_p$  Projected contact area

$A_W$  Atomic weight

$A_{W_{Total}}$  Total atomic weight

d  diagonal length of impression, Impression diameter

$D$  Laser-beam diameter, Ball diameter, Density of element

$D_{Total}$  Total density

$E$  Elastic modulus of specimen, Incident energy

$E^*$  Reference-sample modulus

$E_i$  Elastic modulus of diamond

$E_r$  Reduced elastic modulus

F  Gas-flow rate

$F_N$  Applied load

H  Hardness
$h_c$ Contact depth

$K$ Wear rate

$K_Q$ Fracture toughness

$L$ Test load

$L_K$ Stroke length

$L_o$ Original-gauge length

$L_f$ Final-gauge length

$L_0$ Original gauge length

$n$ Stress exponent

$P$ Laser power, applied load

$PC$ Percentage composition

$P_m$ Indentation stress

$Q$ Volume flow

$R$ Indenter radius

$R_P$ Pitch radius

$R$ Universal gas constant

$S$ Sliding distance
T  Time

V  Scanning speed, Poisson’s ratio of specimen, Wear volume

V_i  Poisson’s ratio of diamond

VHN  Vicker’s hardness number

W  Wear-scar width

W_i  Wear-volume

W_d  Wear depth

α  Alpha

β  Beta

%  Percentage

<  Less than

>  Greater than

(°)  Degree

Qc, ∆H  Activation energy

ε  Strain

δ  Stress

δ_a  Applied stress
δ_{min}  Minimum stress  

δ_{max}  Maximum stress  

δ_{y}  Yield stress  

Θ  Theta  

μ  Coefficient of friction
**UNITS**

- $\text{cm}^3$ cubic centimeter
- $0^\circ\text{C}$ degree centigrade
- eV electron volt
- g gram
- GPa Gigapascal
- Hv Vicker’s hardness
- J Joules
- K Kelvin
- Kg Kilogram
- kV Kilovolt
- kW Kilowatts
- l liter
- l/min litre per minute
- mA milliampere
- ml milliliter
- µm micrometer
- mm millimeter
mm²  square millimeter

mm³  cubic millimeter

MPa  Megapascal

N    newton

ppm  Parts per million

rpm  revolution per minute

s    seconds

TBtu Trillion British thermal units

V    volt

W    watts
GLOSARY OF TERMS

- **Abrasion**: The process of grinding, rubbing or wearing away due to friction.
- **Adhesion**: The force of attraction between atoms or molecules of two different phases.
- **Adjusted R-squared**: This is a modified type of R-squared that has been adjusted for a number of predictors in a model which increases only when the recent term enhances the model more than what is anticipated by probability and the adjusted r-squared reduces if a predictor enhances the model less than anticipated by probability.
- **Alloy**: A substance with metallic properties and which comprises of two or more chemical elements and of which not less than is an elemental metal.
- **Alloying element**: Element included or added to a metal to cause change in properties.
- **Analysis of variance (ANOVA)**: This refers to a set of items of statistical models and their related estimation procedures that can be employed to estimate the differences among the group means.
- **Brittleness**: Quality or property of a material that leads to the propagation of crack without considerable plastic deformation.
- **Creep**: A time-dependent strain happening under stress.
- **Dendrite**: A crystal with tree-like or fish-bone structure normally witnessed when cast metals are gradually cooled through solidification range.
- **Design model**: This refers to a model design of an experiment mainly designed to analyze the created design.
- **Ductility**: The capability of a material to plastically deform and not fractured. Measured by area reduction or elongation in a tensile test.

- **Effect**: This means the change in mean response when a factor changes from low-pitch to a high-pitch.

- **Experimental model**: Is an empirical statistical model that is attached to a data.

- **Factor**: This refers to an independent variable.

- **F-Value**: F distribution refers to a probabilistic distribution employed to assess similarities and differences between ratio variances. In ANOVA table, the ration of model mean square to error mean square is referred to as the F-value.

- **Grain**: Individual crystal in a polycrystalline alloy or metal.

- **Grain growth or coarsening**: Increase in grain size in polycrystalline metal as a result of elevated temperature heating.

- **Inclusion**: Nonmetallic material present in a metallic matrix.

- **Parameter**: A parameter is a factor that forms one of a set that determines an operation or set of conditions of its operation.

- **Phase**: A physically distinct and homogenous area of a material system.

- **Predicted R-squared**: This quantify the value of differences in new data that can be interpreted by the model.

- **Predicted value**: This refers to the value of predicted response by a statistical model.

- **Preheating**: Prior heating before additional thermal or mechanical treatment are made.
- **Residual error**: This is the difference between the predicted value and observed response by a model from a certain design point.
- **Mean square**: This is equal to sum of squares to the number of degrees of freedom.
- **Root mean square**: Refers to mean profile height’s deviation from a mean line.
- **Stiffness**: Capacity of a metal to resist or withstand elastic deflection.
- **Studentized residual**: Studentized residual is obtained by dividing residual by estimated standard deviation of the residual.
- **Substrate**: An underlying layer of a metal on which coating are built on.
- **Laser scanning speed**: This is a parameter used to quantify the speed at which laser traversed a path.
- **Powder flow rate**: This is the rate at which powder flow or moves per unit time.
- **Laser power**: This is a deposition parameter of power responsible for creating melt pool in a deposition process.
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CHAPTER ONE

1.0 INTRODUCTION

Since processing complexities during manufacturing are partly responsible for the high cost of products and machined parts, the users of high performance metal parts, such as the casting industry, the aerospace industry and the heavy machinery consumers can now prolong the service of damaged parts through remanufacturing and repair technology. Additive manufacturing (AM) technologies employ 3D model data to produce layer upon layer of nearly net-shaped components.

The fast development of 3D technology over the past three decades has made a tremendous impact on the engineering area, medicine, dentistry and other health-care sectors (Ganesan et al. 2016). AM technologies have the ability to change many manufacturing sectors through the reduction in material waste, costs, carbon footprints, energy usage, and component leading time. AM technologies also provide the ability to manufacture and repair great innovative product designs that could not be manufactured by using conventional processes (Herderick 2011).

The technology could be employed in the aerospace industry to reduce the raw quantity of materials used in the fabrication of in-service components. The technologies could also lead to the development of light-weight structures. AM could also be applied in creating parts from the CAD file of legacy parts that are still required in service in those areas where manufacturers are no longer in business.

Laser-metal deposition, an additive-metal technique, is employed in the manufacturing and the repair of parts through the use of computer-aided design data.
The technique now gives us the ability to deposit from a nozzle, powdery or wire materials that are shielded by an inert gas onto a melt pool produced by a laser beam on the substrate. Different metals, alloys, ceramic and intermetallic compounds such as TiAl and Ti6Al4V have been deposited by using this technique. Despite the paucity of papers that have been published on the micro-structural characterization and the mechanical properties of TiAl alloys deposited through this technique, very little significant research has been carried out on the deposition of TiAl on pure titanium substrate, using the laser-metal deposition technique.

This work carried out a thorough research on the manufacture of TiAl-Ti composites through the laser-metal deposition technique, using TiAl powder shielded by a gas and deposited on a melt pool of pure titanium substrate. This provided the ability to examine the micro-structure and the mechanical properties, such as hardness (Nano- and microhardness) and the wear of the composite produced.

Furthermore, the incorporation of preheating the substrate in the deposition process is considered important, as a way of reducing the residual stresses that build up, due to the rapid solidification in the laser-metal deposition process. This causes cracks in some depositions. This is another interesting area that has been studied in this research.

1.1 BACKGROUND

The concept of additive manufacturing was first discovered in 1987 through a technique from 3D systems called stereolithography (SL), which is a process that solidifies thin layers of ultraviolet light-sensitive liquid polymer by making use of a laser (Gornet & Wohlers 2014). The partnership between 3D systems and Ciba-Geigy in
1988 led to the development of SL materials and the commercialization of the first generation of acrylate resins. In the same year, Dupont's Somos stereo-lithographic materials and the machine used for this process, were developed. Three AM technologies were commercialized by 1991; these include fused-deposition modelling (FDM), solid-ground curing (SGC) and laminated object manufacturing (LOM). By 1992, selective laser sintering (SLS) and solid-form stereo-lithography were rendered available. The development of different additive manufacturing methods continues; and by 1998, the laser-engineered net-shaping (LENS) metal powder system was commercialized by Optomec. By 1999, the controlled metal build-up (CMB) machine was sold by Röders (Gornet & Wohlers 2014).

By April 2000, the development of a 3D printer that deposited and hardened the photopolymer by employing nozzles and a UV light source was witnessed. In the same month, the direct-metal deposition (DMD) that employs a laser-cladding process of repairing and the production of parts by using metal powder, was introduced by precision-optical manufacturing (POM). The formation of the Rep-Rap project in 2005 by Dr Gordon, with the sole aim of making 3D printing technologies accessible to all, led to the starting of a 3D printing company by three participants (Bre Pettis, Adam Mayer and Zach “Hoeken” Smith) in the project (Matias & Rao 2015).

Research projects are continuously being conducted on titanium and its alloys. These projects have provided researchers and engineers with the best method of improving the production of titanium alloys and enhancing their properties. Titanium is one of the readily available lightest metals (Balla et al. 2016) with unique characteristics. These unique characteristics possessed by titanium and its alloys include the low
density-to-strength ratio, high resistance to fracture, and good resistance to corrosion. Perhaps, these unique properties explain the reason why they are most desired for numerous applications, such as that of energy generation, in the aerospace and automobile manufacture.

Alloys of titanium also find applications in medicine and biomedicine, because of their excellent biocompatibility (Lutjering & Williams 2007).

Research has shown that titanium alloys are very reactive with other gases (hydrogen, oxygen and nitrogen) at highly elevated temperatures (Nurul Amin & Shah Alam 2012). Titanium alloys also give desirable properties at elevated temperatures, where the creep resistance of titanium alloys can be chosen for temperatures that are as high as 600 °C (Erinosho 2015). This has made them applicable as gas turbine hot components and engine parts (Lapin 2009).

Improvements in the properties of titanium alloys are generally achieved by the addition of other alloying elements (Lutjering & Williams 2003; Peters et al. 2003b). Currently, progress is being made in the gamma-titanium aluminide alloy developments that show considerable improvement in creep and corrosion resistance and which has displayed strength, similar to that of other titanium alloys.

However, neither ductility nor toughness have been substantially improved (Appel & Oehring 2003). The conventional gamma alloys comparable with Ti-48Al-2Cr-2Nb are neither superior, nor are not they comparable with most titanium alloys; since most of the already discovered titanium-aluminide alloys are superior in temperatures that can reach to 750 °C (Dimiduk 1999).
Alloys developed currently, display permissible ductility of about 2.5% at room temperatures, show specific creep strength surpassing that of most superalloys; and they display superior specific stiffness (Dimiduk 1999). However, wrought high-strength gamma alloys are preferred in situations where materials need to withstand extreme loading conditions. The recent manufacturing potential of gamma alloys in application in automobiles, gas turbines and jet engines, show that they can be made to compete with superalloys and other titanium alloys (Appel & Oehring 2003). This indicates the reason for further development in the manufacture and application of gamma titanium aluminide.

Laser powder injection is a method that uses powder injection as a means of providing the material required to be deposited. Powder injected through a nozzle is melted to the deposited material. The powder is injected by gravity feed, or through an inert gas. The molten weld pool is protected from oxidation through a separate supply of shielding gas, or through the powder injection method. The high price of titanium alloy is partly responsible for the creation of a manufacturing rout that should reduce material wastage, thereby making additive manufacturing (AM) technique a viable option (Yvonni-Effrosyni 2014).

Laser-metal deposition (LMD) is a technique in AM that can be employed in the production of solid components, or parts from a model of computer-aided design (CAD) (Akinlabi & Akinlabi 2016a). In this process, powder supported by a shielding gas is fed into a melt pool produced by a collimated laser beam on the substrate. Laser-cladding through powder injection is a trending area in the technique of laser-material processing which permits the deposition of thick protective coverings or coatings on substrates,
through the use of a high powered laser beam that serves as the heat source (Cárcel et al. 2014). The deposition process is illustrated in Figure: 1.1

![Figure: 1.1: Schematic laser metal deposition process (Yvonni-Effrosyni 2014)](image)

The ability of varying the injected powder material needed to fabricate graded parts and in repairing an existing highly valued part by adding material to the part has rendered the laser-powder injection method highly valuable. The technique is very useful for repairing and cladding purposes; but it has limitations, as a result of its inability of depositing the same volume of material, as the powder-bed technique (Herderick 2011).

Optomec laser engineered net shaping (Optomec LENS) is a technique that was first developed at the Sandia National Laboratory. The technique involves the injection of metal powder into a molten pool of metal via an energy source from a laser. MR-7, LENS 750 and LENS 850-R are some of the LENS systems available in the market.
The MR-7 is mainly developed for research purposes in the areas of fundamental solidification research, rapid solidification research and rapid-alloy screening. The LENS 750 and 850R machines are developed to be used in areas, such as advanced product development, rapid manufacturing and repair and the fabrication of parts in defense and aerospace applications.

The laser-engineered net shaping (LENS) is a technique of AM that manufactures parts through a layer-by-layer build-up by concentrating a laser beam on a base metal to produce a melt pool, onto which metal powder is deposited (Mahamood et al. 2013; Malshe et al. 2015; Lundback & Lindgren 2016). The technique is capable of fully dense, near-net shaped components (X. D. Zhang et al. 2001). The technique is taken as an acceptable route that can be employed in the manufacture and repair of components (Hedges & Calder 2006).

The effect of process parameters on the properties of laser-deposited components has been studied in the literature (Akinlabi et al. 2012; Pityana et al. 2013; Shukla et al. 2012). Thermal cracking is one of the most prominent problems that have been outlined by researchers in the deposition of titanium aluminide (Brueckner et al. 2015; Liu & Dupont 2004; Srivastava et al. 2000). It was, however, suggested that crack-free building can be produced with the provision of an additional heating system in the form of an induction coil or a heating bed, which would help to control the rate of cooling (Sharman et al. 2018).

In this research, titanium-aluminide powder (Ti-48Al-2Cr-2Nb) was deposited on a CP-Ti substrate by employing the laser-metal deposition (LMD) technique, and by
using different deposition procedures (deposition parameter and mode of preheating of the substrate). The deposition of Ti-48Al-2Cr-2Nb metal powder, using the LMD process, is currently limited in the literature. The characterization of the deposits, in order to determine the effect and trend of the deposition parameters, as well as the effect of preheating, as highlighted in the research objectives, was carried out.

1.2 STATEMENT OF THE PROBLEM

Research in the area of parts repair and manufacturing through additive manufacturing has been an interesting area of research. Not only does it give the opportunity of reproducing or the repair of near-net-shaped components, but also as a way of adding to and improving the properties of components’ materials. Laser-metal deposition as an aspect of additive manufacturing provides the opportunity of adding metals and alloys in powdery form onto a substrate, thereby giving a unique composite material. The process is sometime associated with rapid solidification, which causes high residual stress build-up resulting in cracks. The incorporation of preheating into the Optomec LENS, as a way of reducing the residual stresses that can lead to cracks and the effect of deposition parameters on the parts produced are interesting areas, which are worth exploring. The study also seek to explore methods of fabricating titanium aluminide alloys with improved properties as lamellar microstructure alloys are poor in ductility at low temperatures and duplex microstructures are of lesser quality when high fracture toughness, high temperature strength and high creep-resistance are required. These make the processing, handling and machining of TiAl alloys difficult to handle.
1.3 AIM OF THE RESEARCH

This study aimed at investigating the effect of preheating temperatures and residual stress behaviour on the properties of the deposited composite using laser-metal deposition technique.

1.4 OBJECTIVES OF THE RESEARCH

The research objectives are to:

- Produce TiAl-Ti composites by using the laser-metal deposition technique to deposit titanium aluminide powder on a pure titanium substrate.
- Carry out micro-structural and chemical compositional analysis on the composites by using the scanning-electron microscope (SEM) and the X-ray diffractive machine.
- Determine the mechanical properties (such as microhardness, wear, corrosion, tensile strength, toughness, hardness, etc.) of the composites that would be produced in the process.
- Study the relationship between the laser-metal deposition processing parameters and the effect on the microstructure and the mechanical properties of the composites.
- Study the effect of preheating temperature on reducing the residual stress build-up due to the rapid solidification in the metal-deposition process, which usually results in cracking in some depositions.

1.5 HYPOTHESIS STATEMENT

It is expected that the research study will lead to the development of TiAl-Ti composites, with unique and competing properties, produced through an effective and
sustainable technique. It is also expected that the findings that will emanate from this study will serve as a guideline to manufacturers and the end-users of composite materials produced through the additive manufacturing technology.

1.6 SIGNIFICANCE OF THE RESEARCH

There has been an increasing interest in the fabrication of titanium and its alloys via powder metallurgy, which is now seen as a viable cost-effective option. Titanium alloys produced through this technique can present crack issues that are largely developed through the build-up of high stress. This research study is of great value to material researchers, manufacturers, and all end-users of composite materials, in the sense that the TiAl-Ti composite will be produced by using the laser-metal deposition technique by employing the preheating of the substrate, as a way of reducing the high stress build-up that normally lead to cracks.

Furthermore, the properties of the composite will be studied as a way of finding areas of application for the composite. It is expected that the composite will be of huge importance for high temperature applications especially in gas turbine and automobile engine components.

1.7 THESIS ORGANIZATION

The structural arrangement of this work comprises five chapters, with each chapter connected to the one preceding it, as a way of giving an insight and a comprehensive report on the subject.

The first chapter starts with the introduction of the subject matter, and consequently, a look at the background of the study and its aim, objectives, hypothesis formulation and the significance of the research.
Chapter two, which is the literature review discusses the existing works that have been done by different researchers and organizations in additive manufacturing (AM), the laser-metal deposition (LMD) of titanium aluminide, and AM sustainability, as well as the environmental impact.

Chapter Three discusses the methodology of the research, including the equipment used, the experimental set-up and the procedure for the deposition. Also discussed in this chapter is the experimental study that comprises the metallurgical preparation and the characterization of the deposited composites. This study includes optical microscopy (OM), scanning electron microscopy (SEM), microhardness, corrosion test, wear test and X-ray diffraction (XRD).

The following chapter (Chapter 4) focuses on the experimental results and the discussion of the characterizations carried out on the deposited composites. Under this chapter, comparison and analysis of results and variance, desirability and the validation of the experiment were discussed. Characterization of the best optimized deposited titanium aluminide composite was also discussed.

The last chapter (Chapter five) concludes the study, summarizing the research work by presenting the main points in the research and proffering some recommendations for future works.
CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

This chapter critically reviews the previous work of researchers and organizations on the laser-metal deposition of titanium aluminides history, development, microstructure, phase transformation, their material characterization and properties. The literature review has presented topics in the following areas:

- Additive manufacturing (AM)
- Powder metallurgy
- Laser Metal Deposition (LMD)
- Processing parameters and effects on the LMD process
- Effect of preheating of the substrate
- Titanium and its alloys (noting the microstructural and the mechanical properties thereof)
- Importance, and the uses of titanium and its alloys in different industries
- Fabrication/manufacturing of titanium and its alloys
- Titanium alloys’ material characterization
- Gamma titanium aluminides
- Sustainability and environmental impact of AM

2.2 TITANIUM AND ITS ALLOYS

Titanium as an impure oxide was first discovered in 1791 by William Gregor after treating ilmenite (black sand) with hydrochloric acid; and he called the new element
produced mechanite. Martin Heinrich Klaproth in 1791 successfully collected titanium oxide from rutile mineral. In 1910, Mathew Albert Hunter obtained titanium metal after heating titanium tetrachloride and sodium. Wilhelm Kroll in 1932 was able to produce a great amount of titanium after processing titanium tetrachloride with calcium; and by 1948, the DuPont Company became the first to produce titanium in commercial quantities (Peters et al. 2003a).

Titanium is a very light metal with a silvery colour; and it is noted as the fourth most plentiful structural metal after aluminium, iron and magnesium in the earth’s crust (Buijs & Stainless 2008; Lutjering & Williams 2003; Nurul Amin & Shah Alam 2012). Titanium has a relatively low density (between Aluminium and iron, as shown in Figure: 1.1) with good strength. It possesses high resistance to corrosion and good resistance to fracture at low temperatures.

Titanium alloys are very reactive with atmospheric gases, like oxygen, hydrogen and nitrogen (Nurul Amin & Shah Alam 2012). The TiAl-based alloys are intermetallic compounds in the class of high-temperature structural materials with unique physical and mechanical properties that could be applied in industrial gas turbines, aircraft engines and the automotive industry (Lapin 2009). Some of the unique characteristics of the intermetallic compound include: good corrosion resistance, high strength and low weight ratio, which explains why they are mostly used in the chemical, aerospace and medical industries.

The alloying of titanium rapidly progressed from 1950 in the USA, with the addition of aluminium to strengthen the alloy. Tin was further added to the alloy to form Ti-5Al-2.5Sn specifically for high-temperature applications. Molybdenum (β stabilizing
element) addition produced Ti-7Al-4Mo (α + β) alloy used in high-strength applications. In the mid-1950s, Ti-13V-11Cr-3Al (α β titanium alloy) was first produced as a sheet alloy in the USA. The alloy of titanium, Ti-6Al-4V (α + β) with relative ease of production, exceptional properties, and despite being expensive, remains the most widely sought-after titanium alloy. As such, the need to reduce the probable waste of the material become a matter of paramount importance, which made the rapid-prototyping technique the best option in utilizing the material (Yvonni-Effrosyni 2014).

By 1956, the UK had become more interested in the production of titanium alloy mainly for high-temperature applications, such as in aero-engines, produced Ti-4Al-4Mo-2Sn-0.5Si. This became the first time silicon (Si) was introduced as an alloying element, and as a creep-resistance enhancer (Lutjering & Williams 2003).

The commercial production of pure titanium (CP titanium) is mainly for non-aerospace applications, where a corrosion-resistant material is desired. The biomedical

| 14 |
field is a well-known area of application of titanium, where pure titanium and Ti-6Al-4V have been used as materials for biomedical implants in the past. The toxicity of vanadium to the human body gave rise to the development of other titanium alloys, such as Ti-6Al-7Nb and Ti-5Al-2.5Fe. More efforts are currently being made in the production of β titanium alloys through the addition of non-toxic alloying elements, like Mo, Zr, Ta and Nb. The major benefits of the β alloys over Ti-6Al-4V alloy are the lower modulus of elasticity, higher fatigue strength and enhanced biocompatibility (Lutjering & Williams 2003).

The higher specific strength of titanium alloys is achievable at higher temperatures; but the oxidation behaviour of the alloys makes it difficult to handle at maximum application temperature. Titanium aluminides are slightly affected by this problem, which makes the development of alloys in this area highly important (Peters et al. 2003a).

Titanium and its alloys have become very valuable materials; and they are mostly used in defense, aerospace, automobile and energy industries. Titanium and its alloys provide the highest strength-to-weight ratio, when compared with other metals. This provides the advantage of picking this class of material over steel - mainly because they are as strong as steel; and they have approximately half the weight of steel (Norsk Titanium 2016).

The melting point of titanium (up to about 1650 °C) also makes it desirable for armor-plating, missiles, spacecraft and naval vessels.

Component production using titanium material raises issues of waste, complexity and lead-time. As such, the rationale between components’ performance and the cost of
production is questioned. Additive manufacturing becomes a viable alternative route in solving the issues; as it provides the ability of reducing the processing time, the cost of production; and it also preserves the strength and the weight of titanium. The highly desirable applications being experienced by titanium aluminide composites - mostly in the areas of automotive, aerospace and energy sector - are because of the competitive advantages they offer with respect to fuel economy and enhanced properties, largely evidenced in oxidation resistance and high temperature performance.

The fuel economic advantage is achieved through the mass reduction of the alloys.

In summary, the strong desire for the fabrication of complicated designs required for new machine components, reduction in material wastage, reduction in lead time, stiffer regulations aimed at reducing the environmental impact - due to the traditional manufacturing technique and the cost of production, have made additive manufacturing the preferred option.

2.2.1 Metallographic preparation of Titanium alloy

Metallographic preparation and micro-structural investigations are of great importance, due to the fact that the microstructure and the chemical composition largely determine the mechanical properties of titanium alloys. Titanium (with comparatively low thermal conductivity, when compared with other metals) during preparation, needs to be cut with water-cooling with cutting-blade velocity and feed rate reduced to prevent local overheating (Peters et al. 2003a). The production of deformed surface layers, sometimes showing pseudo-microstructures are seen in titanium; and electrolytic polishing is recommended for pure titanium as a way of solving the problem. The
electrolyte with perchloric acid concentration is handled with care and repeatable results are obtainable by following the accurate specifications of voltage, current, time and etching area.

Titanium alloy micro-sections are normally prepared by using mechanical polishing. This involves water-cool grinding of the specimen by using SiC-paper with about grit 1200, then polishing with a strong synthetic cloth containing diamonds of grit 6µm or 3µm that usually take more polishing time; and finally polishing with fine grit 0.04µm colloidal silicon dioxide lased on synthetic cloth. The suspension use in grinding is a weak etchant that is basic with about a pH 9.8.

For the final polishing, fine-grained aluminium trioxide suspension containing hydrous oxalic acid can be used. However, the final polishing is repeated in shot steps for different periods of time, after which the micro-section is etched; and the microstructure investigation under an optical microscope is then conducted. A transmission-electron microscope can be used to view very fine precipitate images of the titanium alloys.

2.2.2 Microstructure of Titanium alloys

The microstructure of titanium alloys has a great effect on the properties of the alloys. Largely, the microstructure of titanium alloys is defined by the size and arrangement of the α and β phases (Peters et al. 2003a). The lamellar microstructure and the equiaxed microstructure respectively produced during the β phase field cooling, due to the process of recrystallization are the highest situations in phase arrangements. Fine and coarse arrangements can be found on the micro-structural phases. Table: 2.1 reveals how the size of the phases (comparison between fine and coarse
microstructure) on the left-hand side and the arrangement of the phases (comparison between lamellar and equiaxed microstructure) on the right-hand side, affect some of the mechanical properties.

Table: 2.1: Influence of microstructure on some properties of titanium alloys  (Peters et al. 2003b)

<table>
<thead>
<tr>
<th>Fine</th>
<th>Coarse</th>
<th>Property</th>
<th>Lamellar</th>
<th>Equiaxed</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>-</td>
<td>Strength</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>o</td>
<td>o</td>
<td>Elastic modulus</td>
<td>o</td>
<td>+/-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(texture)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Ductility</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Fatigue crack initiation</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>Fatigue crack propagation</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>Fracture toughness</td>
<td>+</td>
<td>-</td>
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<tr>
<td>-</td>
<td>+</td>
<td>Creep strength</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Oxidation behavior</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>Superplasticity</td>
<td>+</td>
<td>-</td>
</tr>
</tbody>
</table>

Various microstructures are produced by thermo-mechanical treatments, which are a complicated series of solution, comprising heat treatment, recrystallization, deformation, ageing and annealing to relieve the stresses. Simple cooling from temperatures above $\beta$-transus temperature produces lamellar microstructures. Immediately the temperature slides below the $\beta$-transus temperature, $\alpha$ is created at the grain boundaries, which then grow as lamellar into $\beta$ grain. Figure: 1.1 gives an example of such a microstructure.
Lamellar microstructures can either be fine or coarse, depending on the cooling rate. Pure lamellar microstructures, as shown in Figure: 1.1(a) result from the slow cooling of the β phase field. Martensitic transformation of the β phase results from fast quenching, which then gives a very fine needle-like microstructure, such as the one shown in Figure: 1.1(b).

Both lamellar and equiaxed microstructure play a great role in the mechanical properties of titanium alloys. Fine microstructures increase the strength and ductility and
tend to hold-up or slow crack nucleation. On the other hand, coarse microstructures are better resistant to fatigue crack growth and creep. Mostly preferred for plastic deformation are the equiaxed microstructures known for their high ductility and fatigue strength. Whereas, lamellar microstructures have better fracture toughness; and they display higher resistance to creep and fatigue-crack growth. A bimodal microstructure, which comprises lamellar and equiaxed microstructures, combines the advantages of the two microstructures to give well-balanced properties. Fine equiaxed, coarse equiaxed and bimodal microstructures of Ti-6Al-4 are shown in Figure: 1.1.

![Microstructures of Ti-6Al-4V](image)

**Figure: 2.4:** Microstructures of Ti-6Al-4V via recrystallization for: a) fine equiaxed, b) coarse equiaxed and (c, d) bimodal in OM and TEM respectively (Peters et al. 2003b)

Titanium crystalizes in different crystal structure like other metals, such as Ca, Fe, Sn, Co, and Zr. However, the crystalized structures are only stable within a specific range of temperatures; and the total transformation from one crystal structure into another is referred to as allotropic transformation; and the corresponding temperature at
which the transformation occurs is referred to as transient temperature. Pure titanium and most titanium alloys crystalized at low temperatures in a hexagonal closed packed structure (hcp), normally referred to as α-titanium. However, at high temperatures, the body-centred cubic (bcc) structure is stable; and it is called β-titanium. Atomic unit cells of hcp α-titanium and bcc β-titanium are shown in Figure: 1.1 (a) and (b).

![Atomic unit cells of hcp α-titanium and bcc β-titanium](image)

It is essential to note from the figure above that the state of plastic deformation easily increases from hcp lattice to bcc lattice and to a face-centred cubic (fcc) lattice. This process unfolds the plastic deformability limitation of hcp α-titanium, as compared to bcc β-titanium. Basically, hcp structure has three number of dislocation glide opportunities (also describe as slip system) in crystal lattice; while bcc lattice has twelve. With respect to von-Mises criterion, not less than five independent slip systems are needed to achieve uniform plastic deformation of metals. This reason makes it very difficult for polycrystalline hcp α-titanium to deform.

On cooling form the β phase field, the majority of the densely packed planes of the bcc β phase transform to the basal planes of the hcp α phase. The distance between the basal planes in α is marginally larger than that in the β planes; and as such, the β/ α transformation leads to minor atomic distortion. The diffusion of hcp α-
titanium is slightly lower than that of the bcc β, because of the way the atoms in hcp α-
titanium have been densely packed. The α and β titanium diffusion coefficients are
influenced by the micro-structure, which, therefore influences the mechanical behaviour
of the two phases (Peters et al. 2003b).

It is good to note that an increase in the aluminium content in titanium alloys
increases the resistance to creep and oxidation; while concurrently deteriorate its
ductility and deformation capability. As such, care must be taken in developing new
alloys; so that the aluminium equivalent does not exceed 9 wt. % (Peters et al. 2003b).
Mo, V, and Nb are β strengtheners, as Nb is also known to improve the oxidation
behaviour of titanium alloys.

2.2.3 **Classification of titanium alloys by their alloying elements**

Alloying elements of titanium are basically classified as neutral, α –stabilizers and β-
stabilizers based on their influence on β-transus temperature.

- **Neutral elements:** these are elements that have little influence on the β-transition
temperature, or play any insignificant role or influence on the α/β phase
boundary. Examples of such elements are: Tin (Sn) and Zirconium (Zr). The
elements strengthen the α phase; and as such, they are regarded as non-
neutral, when considering strength.

- **α –stabilizers:** these are stabilizing elements that extend the α phase to elevated
temperatures. Examples of these elements include oxygen, carbon, nitrogen and
aluminium. Apart from extending α phase field to elevated temperatures, α –
stabilizers also change to α+β two phase field. The α –stabilizers are split into β-
isoamorphic and β-eutectic elements. β-isomorphic, such as Molybdenum
(Mo), Tantalum (Ta) and Vanadium (V) are more relevant because of their high solubility rate in titanium. For β-eutectic, even very small amounts of the β-eutectic elements, such as Manganese (Mn), Cobalt (Co), Chromium (Cr), Copper (Cu), Silicon (Si), Nickel (Ni) and hydrogen (H) can produce intermetallic compounds

- β-stabilizers: the β elements move the β phase field to lower temperatures. If a small amount of β-stabilizers is introduced to α phase, it creates a near α alloy.

Titanium alloys are generally grouped into α, α+β and β alloys, which is further subdivided into near α and metastable β alloys. The α alloys are made up of commercially pure titanium and alloys that have not been alloyed with α-stabilizers or neutral elements. The most commonly employed alloy group are the α+β alloys. The α+β alloys at room temperature have a β volume fraction between 5 to 40%. Supposing the β-stabilizers is increased further to a point, where β cannot further change to martensite on fast quenching, the alloys will still be in the two-phase field and a metastable β alloy class would be said to have been attained.
The most relevant and perhaps the most studied titanium phase diagram is the Ti-Al system in Figure: 1.1. Aside from the conventional titanium alloys (α and β phases), different intermetallic phases are found. These phases include TiAl₂, TiAl₃, α₂-Ti₃Al and γ-TiAl. TiAl₂, TiAl₃ are very brittle, making only α₂-Ti₃Al and γ-TiAl of technical relevance. Technically, the important titanium aluminide alloys are found in the two-phase fields of α+α₂ and γ-TiAl.

Supposing the aluminides are combined with niobium (Nb), an intermetallic phase Ti₂AlNb, which is the foundation of orthorhombic titanium aluminides, is thereby created.

2.2.4 Common titanium alloys and their applications

- α alloys: these alloys are generally employed in chemical and process engineering industries. They are used where excellent corrosion resistance and deformability are of paramount importance, before considering high
strength. The grade 1-4 commercially pure (CP) titanium comes into this category, where they only differs in the level of oxygen content that is responsible for increased strength and simultaneously reduced ductility. Elements, such as iron and carbon are considered as impurities introduced during the manufacturing process. Applications of these alloys are found in deep drawing, pressure-vessels, fittings and mountings.

- Near α alloys: these are high-temperature alloys, which possess the excellent creep properties of α alloys and of α+β alloys high strength properties. High Al content above 6% has been shown to results in stress-corrosion problems. Research has also shown that a small percentage of silicon (Si), less than 0.1wt %, would significantly improve the creep properties of Ti-6-2-4-2; and the alloy was referred to as Ti-6-2-4-2-S (Peters et al. 2003b). Among the most enhanced available high-temperature titanium alloys is TIMETAL 834.

- α+β alloys: among this category is Ti-6Al-4V, which is the most common and the most-used titanium aluminide nowadays. This is because Ti-6Al-4V has obtained good balance in its properties; and it is the most extensively researched, developed and tested alloy, which gives it a significant edge over others. The aerospace industry is believed to be the biggest user of the alloy.

- Metastable β alloys: these alloys are gaining relevance, due to their ability to be hardened to high-strength levels beyond 1400 MPa. These alloys find applications in the automotive industry and moderate temperature gas turbine engines. However, the application of these alloys is limited by their modest
weldability, complex microstructure, poor oxidation behaviour and high specific weight.

2.3 PROPERTIES OF TITANIUM AND ITS ALLOYS

Improving the properties of titanium alloys is anchored in alloying, processing and the production of composites. Alloying paves the way for improved strength, creating the way for the creation of an ordered structure; controls the material's chemical resistance (corrosion and oxidation); and it determines the physical properties (like elastic modulus, density and the coefficient of thermal expansion).

Processing permits careful balancing of the material properties. Based on any required property, various microstructures can be created for titanium alloys through thermo-mechanical treatment by optimizing for strength (grain boundary strengthening, solution strengthening, texture strengthening, dispersion strengthening), toughness, ductility, creep resistance, superplasticity, and stress corrosion etc.

The production of composites involves the combination of different materials to produce a composite with superior properties (Babalola et al. 2014). Titanium alloys and aluminides can be strengthened through the use of fibres or particles - to form metal-matrix composites (MMCs). The nature, orientation and volume fraction of the strengthening component, the matrix and the matrix-reinforcements boundaries all play a role in influencing the mechanical properties of the composite (Peters et al. 2003b). Titanium and its alloys are known to have good strength, low density, excellent corrosion- and fracture-resistance (Nurul Amin & Shah Alam 2012).
2.3.1 **Strength of titanium and its alloys**

Apart from the highest strength steel among metallic materials, titanium alloys have an excellent specific strength, with yield strength between 800-1200 MPa for conventional titanium alloys. In order to increase the strength of a titanium alloy, all the three methods, comprising alloying, processing and the production of composites can be employed (Peters et al. 2003b). An SiC fibre-reinforced Ti-6Al-4V, with SiC fibre volume fraction of 35% can produce tensile strengths above 2000 MPa along the fibre direction. However, increasing the strength - either by the alloying, processing or through composite production – can lead to a decrease in the ductility (Peters et al. 2003b).

2.3.2 **Stiffness**

The stiffness of a material is shown by a measure from its Young's modulus. This value is directly associated with the crystal lattice atomic bonding, which increases with the level of ordering. Alloying with aluminium increases the elastic modulus, due to resultant changes in microstructure. Processing can also increase the stiffness of a titanium alloy. The main objective of the fabrication of particle-reinforced titanium composites is to increase the stiffness. Particles are normally introduced into the material, in order to be strengthened by a powder-metallurgical process, with the exception of the exothermic dispersion process, where the strengthening components are introduced into the titanium matrix by precipitation from a liquid melt.

2.3.3 **Strength at Elevated temperatures**

Titanium and its alloys are often employed for limited engineering applications, due to their inadequate tribological properties (like poor fretting behaviour, poor
abrasive-wear resistance and high coefficient of friction). The poor properties exhibited by titanium alloys, such as fretting behaviour, can be improved through the application of various surface treatments and coating (Boyer et al. 1994). The tribological behaviour of titanium alloys can be improved through the increase in hardness, decrease in the coefficient of friction, increase in surface roughness and the introduction of compressive residual stress (Fu et al. 1998). Friction is a factor that is associated with titanium reactivity and its crystal structure. This problem of friction can therefore be solved by using surface-engineering technologies, to change the nature of the surface (Fu et al. 1998).

Increase in the elevated temperature capability is an area in which titanium alloys are being studied. Lamellar microstructure originated from cooling from the β phase field and equiaxed microstructure emerging from recrystallization, can both have either fine- or coarse- grain distribution, or be present in the bimodal microstructures. Lamellar microstructures, as a result of their coarser structure, have better creep properties than equiaxed microstructures. However, equiaxed and bimodal microstructures exhibit far better fatigue properties, as a result of their fine microstructures. For this reason, lamellar microstructured creep-limited titanium alloys are employed in the compressors of gas-turbine engines; whereas for some fatigue-limited parts, bimodal microstructures are selected (Peters et al. 2003b).

The remarkable creep behaviour is due to the ordered structure of titanium alloys, which is also the root cause of brittleness; and this makes them difficult to deform. Improving the ductility of titanium alloys (Ti₃Al-base alloys) can be achieved by
alloying with β stabilizing elements, such as Nb, V or Mo. Less ductile γ aluminides are alloyed with Nb, Cr, V or Mo for the same reason (Peters et al. 2003b).

2.4 GAMMA (γ) TITANIUM ALUMINIDE

Sagel et al. (1956) earlier reported that the solubility limit of Al in Ti is below 10 wt.% and that this would produce new phases of α₂ and ε. By 1961, it was discovered that 7-15 wt.% Al alloy produces two intermetallic phases of δ-Ti₂Al and γ-Ti₃Al (Ence & Margolin 1961) as illustrated in Figure: 2.7(a). With further investigation on TiAl with 8, 10, 12 wt.% Al, the earlier claims were rejected; and the intermediate phase of Ti₂Al earlier reported, was a transformation from the peritectoid β+α₂ → α, which may have been as a result of the presence of oxygen or nitrogen; as they tend to increase the β-transus temperature and increase the α+β phase region (Tsujimoto & Adachi 1966).

In general, the phase diagram of titanium aluminide is made up of various intermetallic compounds, like TiAl, Ti₃Al, TiAl₃ and TiAl₂ (Cumpsty 2003). Titanium aluminide alloys with intermetallic phases α₂(Ti₃Al) and γ(TiAl) are largely known for possessing the capability to meet design requirements, like lighter weight, higher service temperatures and higher operational speeds (Westbrook & Fleischer 1995; Sauthoff 1995).

The directional bonding and ordered nature of the compounds are mainly responsible for the distinct thermo-physical properties of the materials (Appel & Oehring 2003). The outstanding properties include low density (3.9-4.2 g/cm³), low diffusion coefficient, high melting point (1460°C), high elastic moduli, good structural stability, good corrosion- and oxidation-resistance. The large aluminium content in the alloys increases the corrosion-resistance compared to that of other titanium alloys. These
properties make the titanium-aluminide alloys highly suitable for gas-turbine engines, power-plant turbine engines and in the automotive industry. Over the past few years, structural materials have been developed from these alloys, largely on hexagonal D0_{19} $\alpha_2$(Ti$_3$Al) phase or tetragonal L1$_0$ $\gamma$(TiAl) phase structure. For engineering applications, more interest is placed on $\gamma$-TiAl alloys that largely have small amounts of the $\alpha_2$(Ti$_3$Al) phase.

For engineering alloys mainly centred on the $\gamma$(TiAl) phase, Al concentrations are normally at 45-48t%; and they solidify peritectically in consistence with the phase diagram (Figure: 2.7b). After solidification, the single-phase of $\alpha$ solid solution emerges from binary $\gamma$(TiAl) alloys. This further breaks down on cooling to reactions $\alpha \rightarrow \alpha+\gamma \rightarrow \alpha_2+\gamma$ or $\alpha \rightarrow \alpha_2 \rightarrow \alpha_2+\gamma$ (Kim 1992; Denquin et al. 1992). And $\alpha \rightarrow \alpha_2+\gamma$ is an eutectoid transformation that also occurs on cooling in all $\gamma$(TiAl) alloys (Appel & Oehring 2003). Cupid (2009) proposed a binary phase diagram for titanium aluminide as shown in Figure: 2.7c.
2.4.1 Microstructure and phase transformation

As earlier discussed in section 2.4, after solidification, γ(TiAl) alloys go through α solid-solution single-phase region. Different phase transformations are attainable after the temperature drops below the α-transus temperature. Because of the inability of α phase to break down at the highest cooling rate, it transforms into the α₂ phase. The cooling rate decrease lead to α to γ transformation. The formation of γ grains is witnessed at very low cooling rates (Cheng & Loretto 1998). Two different variables of lamellar reactions (formation of Widmanstatten colonies and feathery structures) results at the highest cooling rate (Zhang et al. 2001). Lamellar microstructures with small
colony sizes and fine lamellar spacing gives very good mechanical properties (Appel & Oehring 2003).

The $\alpha_2$ phase is usually found at 22-39 % Al (Lundstrom 2001); and it remains ordered until a temperature of $1180^0\text{C}$; and at 32 % Al is reached before it is transformed into a disordered hexagonal closely packed structure (Recina 2000). The $\alpha_2$ alloys are found in two phases ($\alpha_2$ and $\beta$). However, the $\beta$ phase is a disordered Ti bcc phase (Lundstrom 2001). The two-phase alloys, however, display a strength roughly twice that of the $\alpha_2$ single phase. Stabilizing elements, such as Cr, Mo, and Nb are mostly the cause of the two-phase formation (Franzén & Karlsson 2010).

The strong bond that exists between the Ti and Al in $\gamma$(TiAl) makes deformation difficult; and it also makes such materials brittle. At high temperatures, the bond assists one to maintain creep-resistance and strength. The energy barrier also provides the $\gamma$(TiAl) phase material with good stiffness over a large temperature range (Franzén & Karlsson 2010). The $\gamma$(TiAl) phase occurs at a 48-69.5 % Al (Lundstrom 2001). Two main structural $\gamma$ alloys exist (single phase $\gamma$ and $\gamma+\alpha_2$ phase). However, the two-phase materials are mostly utilized for engineering applications (Murr et al. 2010).

The alloys also contain elements, such as Cr, Nb, Mo, Mn and Vn. There has been much attention on research and development on rather $\gamma$ than $\alpha_2$ titanium alloys for engineering applications (Franzén & Karlsson 2010); and the most assuring composition for high temperature and longer-time operation applications remains Ti-(34-39)Al-(5-10)Nb-(2-5)Cr (Murr et al. 2010).

Generally, the phases that emerge from $\gamma$(TiAl) with 46-52 % Al are either single phase $\gamma$ or two-phase (combination of $\gamma$ and $\alpha_2$) (Stoloff & Sikka 1996). Depending on
the heat treatments applied to the $\gamma$(TiAl) and the cooling rate, the various microstructures that can emerge from $\gamma$(TiAl) include equiaxed, lamellar, near lamellar, duplex and pseudo-duplex structures (Leyens & Peters 2003; Lundstrom 2001).

The **equiaxed microstructure** only has the single phase $\gamma$(TiAl) of Ti and Al in the same amounts. A large quantity of Al would result in the formation of equiaxed plain $\gamma$ structure, being the stable phase in the phase diagram; while small Al concentrations may result in plain $\alpha$, $\alpha_2$ and $\beta$ (Leyens & Peters 2003). This is the microstructure build-up of equiaxed grains of smaller sizes (Westbrook & Fleischer 1995).

The $\gamma$(TiAl) microstructure of this size is characterized by having high temperature properties and high elastic modulus (Franzén & Karlsson 2010). However, the demerit of the structure is its poor room temperature properties such as ductility and toughness (Stoloff & Sikka 1996). Furthermore, the microstructure is known to be too brittle, which makes it not very desirable for structural applications (Franzén & Karlsson 2010).

The **Lamellar microstructure** is made up of alternating $\gamma$ and $\alpha_2$ plates arranged in zebra-like grains to form lamellas. The spacing between the lamella plates makes the lamellar microstructure more ductile than the equiaxed microstructure. There is a build-up of twinning and dislocations in the interfaces between lamellas (Leyens & Peters 2003). These improve the properties, such as fracture toughness, high temperature strength and creep resistance of the structure (Franzén & Karlsson 2010). However, the lamellar microstructure at low and ambient temperatures exhibits poor ductility. Notwithstanding this, its low-temperature properties are better than that of the equiaxed TiAl (Leyens & Peters 2003).
For sufficient ductility to be attained, the lamellar microstructure must be of small grain sizes within the range of 10-30 µm (Wang et al. 2002).

The **duplex microstructure** is made up of both the equiaxed and the lamellar microstructures. This type of microstructure is more desirable for structural applications because it combines the properties of the initial two microstructures that are in their pure state, and which are too brittle at minimal temperatures (Franzén & Karlsson 2010). The duplex microstructure, therefore, combines the properties of the equiaxed γ grains and the lamellar colonies to give a more ductile TiAl and to improve the mechanical properties (Srivastava 2002).

The structure, therefore, is made up of γ and γ+α₂ phases. These two phases are only together when there is 45-51 % of Al; and when the TiAl material is well heat-treated. With the improvement of ductility, other properties, such as creep resistance, fracture toughness and high-temperature strength can be improved with lamellar microstructural addition in between the fine γ grains (Leyens & Peters 2003). The **pseudo-duplex structure** is similar to the duplex structure, with both γ grains and γ+α₂ lamellar plates, but with more of the γ phase. The structure is characterized by diffuse interfaces existing between the γ grains and the lamellas (Lundstrom 2001). These have emerged from the lamellas γ grains and γ phase, with similar crystallographic orientation or direction (Lapin & Namzy 2004).

Above all, the cooling rate and the manufacturing method determine the resulting different microstructure that emerges from the TiAl (Porter et al. 2009). To change the microstructure of the TiAl material, it can be made to undergo different types of
treatment, such as hot-working, heat-treatment and hot isostatic pressurizing (Westbrook & Fleischer 1995; Stoloff & Sikka 1996; Yamaguchi & Inui 1993).

Under heat treatment, the rate of diffusion and the time at elevated temperatures is minimal compared to the one required in the formation of a fully lamellar microstructure; and the emerging microstructure would contain small quantities of lamellas with Widmanstatten colonies (Li & Loretto 1994; Takeyama et al. 1993). This type of microstructure contains fine-grain lamellas with Widmanstatten needles that are randomly distributed. The amount of the Widmanstatten colonies created changes based on the quantity of Al in the TiAl material (Ramanujan 2000).

It is presumed that the Widmanstatten colonies are created by twinning and recrystallization; and they emerge from α grain with distinct orientation from the surrounding material. Supercooling at the applied rate of cooling is believed to be the force responsible for the formation of the Widmanstatten colonies. It is also agreed that the emergence of Widmanstatten colonies is to ease the thermal stresses or minimized stresses from restraining α phase, when cooling continues below the solution line. This is because the α phase is not stable below the solvus line and changes with the γ+α₂ lamellas (Takeyama et al. 1993).

### 2.4.2 Mechanical properties

The strength, toughness, creep, fatigue and ductility of titanium aluminide used for engineering applications can be predicted when considering the metallurgical factors, such as grain refinement, alloy-composition effects, the solid-solution effect caused by the addition of Nb and precipitation hardening. High temperature strength, creep resistance and fracture toughness are useful properties that can be obtained from
fully lamellar micro-structured alloys (Appel & Oehring 2003). However, these types of alloys have poor ductility at low temperatures. Most preferred for tensile ductility would have been duplex structures; but they are of low quality; when high creep-resistance, high temperature strength and fracture toughness are required. Therefore, lamellar alloys are considered to be the material with balanced mechanical properties for high-temperature applications. Fine-grained lamellar microstructures have been produced from two-phase alloys by using different techniques (Wang et al. 2000; Balla et al. 2016).

Detailed research has shown that alloy composition greatly affects the mechanical properties of materials (Appel & Oehring 2003). In attaining the desired properties, empirical rules are established to serve as guidelines (Huang 1993). These rules are that:

- Reduction in the content of aluminum would improve the strength; but ductility and oxidation-resistance would be reduced.
- Adding of up to about 2 % of each of the following elements: Cr, V, and Mn element has been found to improve the ductility.
- To attain sufficient oxidation-resistance, 1-2 % of Nb addition is required.
- Addition of 0.2-2 % of each of the following elements: W, Si, C and Mo enhances the creep-resistance.
- For grain-refining coagulation and the stabilization of the micro-structure during high-temperature service, 0.2-2 % of boron addition is needed.

For TiAl alloys, the major issue has always been to strengthen the alloys, while not compromising on other properties, such as toughness and low-temperature ductility.
Studies have also shown that 5-10 % Nb addition to TiAl alloys has improved the strength of the alloys (Huang 1993). The 5-10 % Nb addition in TiAl alloys has improved the yield stresses of the alloys beyond 800 MPa. Studies have revealed that Nb strengthens the alloys by occupying the Ti sub-lattice (Mohandas & Beaven 1991). With respect to creep and high temperature deformation-resistance, alloys containing Nb have been shown to have activation energy ($\Delta H = 4-4.5$ eV) that is considerably higher than that of convectional alloys (Paul et al. 1998; Appel et al. 2000). Size and particle dispersion are essential in the precipitation strengthening of TiAl alloys (Appel & Oehring 2003).

In most high-temperature applications, restrictions are made on the operating temperatures, based on the creep properties of the material. The creep properties of $\gamma$(TiAl) alloys are found to depend on the composition of alloy and the microstructure and minimum creep-rate are determined by using the Dorn equation, shown in equation 2.1 (Appel & Oehring 2003).

$$\varepsilon = A \sigma^n \exp\left(-\frac{Q_c}{RT}\right) \quad \text{eqn. 2.1}$$

Where $A$ is a dimensionless material constant, $\sigma$ is the applied stress, $n$ is the stress exponent, $Q_c$ is the activation energy, $R$ is the universal gas constant, and $T$ is the temperature. Tests for creep have been carried out at testing temperatures from 625 to 750°C, with applied stresses from 150 to 550 MPa (Abdallah et al. 2012; Harrison et al. 2014; Lancaster et al. 2014); and the creep curves of the alloys have been determined. The creep characteristics proves that the creep strength of $\gamma$(TiAl) alloys can be affected by nature and the level of the microstructure; and fully lamellar microstructures give the optimum creep-resistance. The creep rate of a component for the duration of its life can
be estimated by using equation 2. This method gives a connection between creep strain \( (\varepsilon) \) and time \( (t) \); and it considers the shape of the creep curve from primary, through tertiary to rupture (Harrison et al. 2014).

\[
\varepsilon = \Theta_1 (1 - e^{-\Theta_2 t}) + \Theta_3 (e^{\Theta_4 t} - 1) \quad \text{eqn. 2.2}
\]

Where \( \Theta_k (k=1-4) \) are 4-\( \Theta \) coefficients obtainable from experimental behaviour. The first part of the equation \( \Theta_1 (1-e^{-\Theta_2 t}) \) represents the primary creep. In this case, the magnitude of the primary strain is \( \Theta_1 \); and \( \Theta_2 \) determines the decay rate. The second part of the equation \( \Theta_3 (e^{\Theta_4 t} - 1) \) represents the accelerating creep-rate caused by the tertiary effects. \( \Theta_3 \) is the measure of the tertiary creep-strain; and \( \Theta_4 \) is to determine the \( \Theta_3 \) rate increase. Figure: 2.8 illustrate the creep strain/time curve for Ti-45Al-2Mn-2Nb.

Normal deformation occurred, due to the initial strain loading, which was followed by the primary creep-deformation; where the creep rate decreases with the minimum value of the creep-strain. Further creep deformation occurred from tertiary creep (an increase in creep rate) until the final failure.
TiAl alloys, like other intermetallics, are associated with the problem of brittleness at low ambient temperatures. This makes the processing, handling and machining of the alloys hard to manage; as the fractural behaviour is highly responsive to the microstructure (Chan & Kim 1992). Cleavage and intergranular fracture are the most common causes of fracture in the duplex microstructure; while the most common failure occurrences that can be observed in lamellar alloys are interfacial delamination, decohesion of lamellar colonies and trans-lamellar fracture. However, γ(TiAl) is liable to cleavage fracture (Appel & Oehring 2003).

Two-phase alloys intrinsic brittleness can exist up to about 700°C and transition from brittleness to the ductile characteristic is dependent on the strain rate. The
brittleness may also be connected to the plastic anisotropy of the $\gamma$(TiAl) and $\alpha$(Ti$_3$Al) phases.

Alloys with duplex microstructures exhibit fracture toughness ($K_Q$) of 12 to 15 MPa m$^{0.5}$, while the fracture toughness ($K_Q$) exhibited by the fully lamellar microstructure and the colony orientation without definite direction fall within 25 to 30 MPa m$^{0.5}$ (Appel & Oehring 2003). The high fracture-toughness exhibited by lamellar alloys is connected to the formation of micro-crack shielding and shear ligaments (Chan 1993). Crack propagation along the lamellae can be attributed to different in interactions between crack-tip and the lamellar boundaries, which involve crack tip immobilization and crack deflection. This interaction causes more crack path to be traversed.

Fatigue failure may result when the components are subjected to cyclic or fluctuating loading conditions; and as such, caution should be taken with TiAl alloys; as they are liable to cleavage fracture. Cleavage cracks can grow very fast under the action of rapidly applied repeated loads once nucleated. Information regarding fatigue has been figured out at 25 Hz and the stress ratio (R) of 0.1. The stress ratio (R= $\sigma_{\text{min}}$/ $\sigma_{\text{max}}$) is the ratio of the minimum stress ($\sigma_{\text{min}}$) to the maximum stress ($\sigma_{\text{max}}$) that the component has been subjected to over the fatigue cycle (Appel & Oehring 2003).

In the case of lamellar and duplex TiAl alloys, 70-80% of the tensile strength resulted from fatigue in the strength cycle of $10^7$. It is observed that fatigue crack in duplex and equiaxed gamma microstructures grow faster than that in lamellar alloys. The reason for this may be linked to the differences in the failure modes; as duplex and equiaxed microstructures mainly fail by transgranular cleavage of the gamma grains;
while under fatigue condition, crack resistance is witnessed when cracks try to propagate across the lamellae structure.

Gamma titanium aluminide provides desirable properties to design and structural engineers due to their high stiffness and high strength at elevated temperatures (Abdallah et al. 2012). The greatest applications of this alloys are in reusable launch vehicles (RLVs) and hypersonic airplanes (Ranjana Kumari 2015). Gamma titanium aluminide alloys remain a credible replacement for Ni-based super alloys in gas turbine engine components, because of their specific properties, such as low densities (Harrison et al. 2014).

In the work of Padilla et al. (2015), nano-indentation measurement was carried out with the Agilent Nano-indenter G200 with a maximum load of 5 mN, to determine the mechanical properties (hardness, stiffness and modulus of elasticity) of γ-TiAl alloys. The alloys (Ti-54 at% Al and Ti-56 at% Al) were produced on a water-cooled crucible, in an argon-atmospheric condition. The resulting outcome revealed that the elastic modulus of alloys vary with the Al content, with the Ti54 modulus given as 218.5±3.1 GPa and Ti56 given as 230.6±9.1 GPa. The hardness, stiffness and yield stress obtained for Ti54 were 8.6±0.6 GPa, 147910 N/m and 5.5 GPa, respectively; while that obtained for Ti56 alloy as given as 11.0±0.5 GPa, 174675 N/m and 6.0 GPa, respectively.

The alloys also showed different hardness values, stiffness and yield stress. The difference in these properties was linked to the presence of dislocations and super-dislocations (anti-sites atoms).
2.5 ADDITIVE MANUFACTURING

Additive manufacturing (AM) is sometimes called three-dimensional (3D) printing or rapid prototyping. It is a process of fabricating components by adding material in a layer-by-layer manner through data instruction from a 3D CAD model. This technique differs from the traditional manufacturing technique. It is machining that requires material removal in the production of the components (Herderick 2011; Aliakbari 2012). Additive manufacturing was introduced in 1987 by 3-D systems that produced the first stereo-lithography apparatus (SLA). AM primarily uses plastic and metals, as raw materials in the production of engineering components (Abdulrahman et al. 2018). Techniques, such as Stereo-lithography apparatus (SLA), the selective laser-sintering (SLS), and fused deposition-modelling (FDM) are commonly used in additive manufacturing, where plastics are employed as raw materials.

However, techniques like selective-laser melting (SLM), direct metal-laser sintering (DMLS), and electron-beam melting are commonly used, in which metals are employed as the raw materials.

The main aim of AM technology is to maintain and enhance the performance of produced components through reduction in their material usage, reduction in the cost of production and in the production lead time (Kobryn et al. 2006). The production of AM equipment is hampered by the slow processing rate of patent-commercialized metal 3-D printers, the high capital cost and the unavailability of open-source metal alternative (Anzalone et al. 2013). As such, the applications of the commercialized AM printer are currently limited to costly finished products.
The high cost of AM equipment makes it practically out of reach by small and medium-scale laboratories and industries. Herderick (2011) pointed out that the amount of AM technology available for commercial applications is currently in small quantities only; and furthermore, tangible work is required to fully develop the processes for commercial-scale applications.

Lasers are known for their rapid-heating ability, which makes them provide a vital role in control operation. The convection forces in a melt pool produced by lasers increase the diffusion rate, thereby creating a base for the fed metal powder to mix (Tlotleng et al. 2016). Laser-metal deposition (LMD) is a type of AM technique that is sometimes used in the fabrication of solid components from the information received from a CAD data.

In the LMD technique, feeding metal powder coming from a delivery nozzle and supported by a shielding gas is spread on a melt pool produced by a well-focused laser beam (Akinlabi & Akinlabi 2016b). Lorenz et al. (2015) explained that in hybrid manufacturing, the union of laser-based AM and computer-numerically controlled (CNC) machining is becoming common.

In the hybrid manufacturing technique, where the directed energy-deposition process is used, the feedstock (metal powder) is fed into the melt pool created by a laser. Although there is little that has been achieved on the commercialization of the technique; however, the technique has the power to deliver a high deposition rate and to build products with a good surface finish and high accuracy (Lorenz et al. 2015).
2.5.1 **The additive manufacturing process**

Additive manufacturing (AM) uses the data from a three-dimensional CAD model to create layer-by-layer near-net-shaped components. AM technology is redefining the manufacturing sector through its ability to reduce material wastage, energy usage and component lead-time. AM technology also has the capacity of creating complex components that ordinarily cannot be fabricated by using the traditional manufacturing technique (Herderick 2011). AM techniques (Figure: 1.1), like three-dimensional (3-D) welding, shape-deposition manufacturing (SDM), electron-beam melting (EBM), three-dimensional (3-D) micro-welding (3DMW) and laser-based additive manufacturing (LBAM) have been developed. The direct process of additive manufacturing involves the production of layer-by-layer metallic parts; while in the indirect process, a casting process is used with the pattern produced in a layer-by-layer manner (Karunakaran et al. 2010).

![Layer manufacturing techniques for metals](Figure: 2.9: Layer manufacturing techniques for metals (Karunakaran et al. 2010))
The direct AM processes are sub-divided into laminated tooling, in which the tooling shape is obtained through cutting and stacking of metal sheets, powder-bed, in which the metal-powder layer is first spread before the desired area is then sintered); and direct deposition occur, where the metal powder is deposited onto the desired area.

2.5.2 Laser-beam melting or selective-laser melting

Laser-beam melting (LBM) or selective-laser melting (SLM) is an AM process in which complicated components can be produced directly from metal powder via information supplied by the CAD file. The SLM principle (Figure: 1.1) involves slicing the 3D CAD model into several pieces and sending the information to a selective laser-melting machine for production. Metal powder of grain fraction 10-45µm is then spread as light layer on the substrate. The geometric information of the layer is transmitted by the laser beam into the powder bed. A solid-piece layer is created, after the area that should contain the solid material, is scanned.

The process is continuously repeated; as the substrate is simultaneously lowered, until the process is completed.

The component produced through this process has a density that is approximately 100%, because of the standard metallic powders that are normally employed in the fabrication process. The mechanical properties of the components fabricated via this manufacturing route are similar or superior to the ones obtained via the conventional manufacturing route (Bremen et al. 2012).

The SLM process is currently not applicable for series production. However, development is ongoing, in order to remove the limitation (Bremen et al. 2012).
2.5.3 **Electron beam melting (EBM)**

In electron-beam melting, the energy needed for high melting and productivity capacity is produced by a high powered electron beam. This process takes place in a vacuum under a high temperature. For each layer to be laid, the electron beam heats up the powder bed to the needed temperature. The components that emerge via this process are basically free of martensitic structures in their microstructure; and they are often free of residual stresses.

2.5.4 **Three-dimensional (3D) printing**

3D printing is another form of AM process often regarded as a two-step indirect process. The powder layer laid on a built platform is agglomerated by a binder introduced by the printer nozzle. The process continues until the production of the
component complete. After the production has been completed, the component is carefully removed; as it still in a green stage.

2.5.5 Direct-energy deposition (DED) or Laser-metal deposition (LMD)

A laser-metal deposition process uses a nozzle that directly delivers the melted material onto the needed surface, where the final solidification takes place. This technique is deemed to be better than selective-laser melting in terms of productivity. The comparisons between the two are highlighted in Table: 2.1. A schematic representation of the process is shown in Figure: 1.1.

Table: 2.2: Comparison between LMD and SLM (Weisheit & Rolink 2016)

<table>
<thead>
<tr>
<th>CHARACTERISTICS</th>
<th>LMD</th>
<th>SLM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>• Monolithic</td>
<td>• Monolithic</td>
</tr>
<tr>
<td></td>
<td>• Gradient, hybrid</td>
<td></td>
</tr>
<tr>
<td>Part dimensions</td>
<td>Limited by handling system</td>
<td>Limited by the process chamber (Ø:400mm, height: 500mm)</td>
</tr>
<tr>
<td>Part complexity</td>
<td>Limited</td>
<td>Nearly unlimited</td>
</tr>
<tr>
<td>Build-up rate</td>
<td>3-140mm³/s</td>
<td>1-20mm³/s</td>
</tr>
<tr>
<td>Build-up on</td>
<td>• 3D-surface</td>
<td>• Flat surface</td>
</tr>
<tr>
<td></td>
<td>• On existing parts</td>
<td>• Flat preforms</td>
</tr>
</tbody>
</table>
The LMD process is often applied in the production of new components, the repair of components that seem irreparable and the adding of new functional features to the existing components. The process also provides the ability to control the material deposition, thereby reducing the material loss; and the output from the process is of excellent metallographic quality. It is limited to the dimensions or the size of the components that can be produced by using the process; and these are mostly subject to the machine’s size.

Research breakthroughs have already been noted in the development of composites. They have superior properties and various merits linked to the laser-metal deposition (LMD) technique. However, this does not really infer that there are no limitations in the LMD or the AM in general. The limited number of the additive manufacturing laboratories and commercially available technology, scarcity and the hike in the cost of some metal powders are some of the challenges limiting research in
additive manufacturing. Uneven deposition of the powder, optimization of the processing parameters, and the microstructural defects (micro-cracks) sometimes associated with this route; indicate that some areas of the AM techniques needed to be explored further in the development of composites and the areas of their applications.

2.6 ADDITIVE MANUFACTURING PROCESSES FOR TITANIUM ALUMINIDE COMPOSITE

Titanium aluminide composites are gaining wide acceptability in numerous areas, largely because of their special properties. The special properties of titanium and its alloys include: low density, good corrosion resistance and high strength, comparable to that of steels. These remarkable properties have made these materials highly useful in various places of applications that require high class performance reliability, like the aerospace industry, automobile, chemical plant, defense, power generation, oil and gas, medicine and surgery. The special properties exhibited by this special class of materials make researchers, engineers and designers to continue to work in determining suitable and cost-effective ways in developing high-class grades of titanium alloys that would be suitable for other applications.

Norsk Titanium (2016) developed an AM process called the rapid-plasma deposition (RPD) process. The RPD process (Figure: 1.1) was used in the fabrication of aerospace structures. Near-net-shaped structures that needed little machining were rapidly built in an inert gas atmosphere by melting titanium wire.
Svensson et al. (2010) worked on the fabrication of gamma titanium-aluminide components by using an electron-beam melting technique (Figure: 1.1). A 3 KW electron-beam power was utilized to melt metal powder the size of 45-105µm (-140/+325 mesh). It was highlighted that the EBM technique can be utilized for numerous applications, such as aerospace, automotive and medical implants.

From the findings, it was noted that gamma-titanium aluminides are standard structural materials that can be used for aerospace applications. The merits of the EBM technique include low material wastage, the ability to produce components with homogeneous microstructures with fine-grain size, the production of components with minimal internal defects, and the low or the non-existence of residual stresses, because of the high processing temperature involves in the process.
Honeywell aerospace created a non-powder based process referred to as ion-fusion formation (IFF) (Herderick 2011). This method uses wire held on arc-based welding torch; and this was used as a feedstock in the deposition process; and an inert gas was used as a plasma-forming gas. An electronic interface controllable positioning platform was utilized in the component fabrication in the deposition process. The process has been used in the deposition of metals and alloys, including 374 stainless steel and Ti6Al4V. The merits of this process include fast build-up speed and fabrication of fully dense components that do not require the hot isostatic press (HIP) post treatment. The machining of the fabricated components' surfaces and the inaccurate production precision when a lower-deposition rate is needed are some of the limitations of the process.
Dey (2014) developed another approach that can be employed in the aerospace industry for the repair of Ti-6Al-4V components, using the laser-metal deposition (LMD) technique. The approach employed a multi-axis hybrid production system. In this system, laser deposition and machining processes were integrated together for the repair process. The research process looked at the preparation of defects on components, the laser deposition, the machining of repaired components and samples preparation for the mechanical tests.

The mechanical tests were conducted to determine and compare the mechanical properties (ultimate tensile strength, yield strength and percentage elongation) of the repaired samples to those of ideal conditions. The outcome of the study showed that the properties of the materials were enhanced by the compressive stress introduced during the deformation process. Average value results of mechanical properties were almost those of the ideal values. The work revealed that the approach could be employed by the aerospace industry for their repair processes.

Akinlabi and Akinlabi (2016a) carried out a research on the laser-metal deposition of aluminium powder on a titanium substrate. The process carried out involves the deposition of aluminium powder at different laser-scanning speeds; as the laser power and the gas-flow rate remain constant. The micro-structures of the samples revealed the presence of alpha-phase grains at lower scanning speeds; while the beta-phase grains where observed at a higher scanning speed. It was also noted that laser-material interaction causes geometrical properties (width, height, and heat affected zone (HAZ)) of the deposits of all the samples to decrease; as the scan speed
increases; while the microhardness and corrosion rates of the samples increase; as the laser-scanning speed increases.

Yvonni-Effrosyni (2014) studied the connection between some direct laser-metal deposition (DLMD) parameters and their effect on the microstructure and the mechanical properties of the final sample produced. The research on Ti6Al4V was done at a laser power of 500 W; and some of the samples re-melted at 600 W laser power at a speed of 200 mm/min and 400 mm/min. Analysis on the microstructure was conducted on the samples by using the optical microscope, the scanning-electron microscope (SEM) and the electron-backscatter diffraction technique (EBSD); while the analysis on the mechanical properties was based on the microhardness measurements and the tensile tests. It was observed under the effect of the remelting factor that there was a homogeneous distribution of the dendrites and the introduction of a remelting parameter led to an improvement in the homogeneity of the dendrites distribution and the proportion of unmelted particles.

It was also noted that the hardness was not really affected by the remelting factor. Samples fabricated with a velocity of 200 mm/min showed better results as regards their hardness and surface roughness.

Cárcel et al. (2014) investigated the deposition of a TiAl intermetallic coating on the Ti6Al4V substrate, using the laser-cladding technique. The main process parameters, like the laser power, scanning speed, powder-feeding rate and preheating temperature were optimised. The optical microscope and the scanning-electron microscope (SEM) were used to characterize the microstructure and the geometrical
quantities (dilution and clad) of the coating. Furthermore, the clad-cooling rate was measured with a dual-colour pyrometer. It was noted that the main defectology issue needed to be reckoned in the cladding processing of TiAl. It was concluded that previous heating and reheating during the process improve the cracking results. Noting that cooling rate affects hardness and the cracking of coatings and tracks; and it increases in the cooling rate led to an increase in hardness and an increase in cracking.

Guessasma et al. (2015) highlighted some of the challenges of additive manufacturing technologies from an optimization point of view. CAD objects are directly imported, as machine instructions through the transformation of the surface-tessellation language (STL) file of the geometry of the virtual part into a set of toolpaths. Challenges and limitations for additive manufacturing include the generation of the tool paths; and depending on the local curvature, discontinuities may be seen, internal structural features may not be properly represented; and there may be limitations in the surface finishing state due to rough profiles.

These challenges do not really limit the purpose of additive manufacturing, as the research continuity in the field is justified by some of the relevant results in the areas of dimensional accuracy, acceptable roughness and processing time for repair, or for the production of the components.

Tang et al. (2015) investigated the microstructural defects normally caused by aluminum vaporization. In the study, the selective-electron beam melting technique was used to deposit high niobium-containing Ti-45Al-7Nb-0.3W titanium aluminide alloy. High preheating temperatures and the reheating of every solidified layer, as an
intermediate reheating process, were carried out to prevent micro- and macro-cracks. The process completely removes the thermal stresses produced in the selective electron-beam melting process, and consequently thereby eliminating crack-formation. The alloy fabricated via this process displayed good mechanical properties. The work concluded that with the right deposition-parameters and approach, high-performance titanium aluminide alloys can be produce using the EBM process. However, it was mentioned that the fabrication of a pore-free microstructure of the titanium alloy with the EBM process remains a challenge.

Ma et al. (2015) uses a method of in situ alloying, where different commercially available pure titanium and aluminium wires are fed into a weld pool. With a heat source created by the gas-tungsten arc welding, gamma-titanium aluminide alloy components were fabricated. The influence of location, microstructure and the mechanical properties of the deposited titanium aluminide deposits were studied. The results of microhardness and tensile test carried out revealed approximate homogeneous mechanical characteristics across the fabricated material. However, the result of the region close to the substrate did not follow the homogeneity trend, which may have been because the alloying process was not well controlled at the region.

In another research, carried out by Gasper et al. (2017), a direct-metal deposition technique was used to study the in situ synthesis of titanium aluminide, using three different approaches. One of the approaches used was satelliting, which is a process of powder preparation in AM, in which a smaller powder fraction is employed in the coating of the larger parent powder. Gasper et al. (2017) used fine TiO₂ to satellite aluminium parent particles to produce a particulate intermetallic matrix composite of Al₂O₃.
In the second approach, titanium wire and aluminium powder were used to produce Ti-50Al. The final approach used mixed powders and wire to create the Ti-48Al-2Cr-2Nb alloy. The simultaneous delivery of wire and powder in the process was done to deal with the problems mostly encountered when only wire or powder feedstocks are used. The optical microscope, the scanning-electron microscope and electron-diffraction X-rays were utilized to characterize the effect of processing the parameters of the produced parts. The resulting outcome revealed that the three feedstock approaches produced titanium-aluminide alloys that differ in composition, microstructures and the track quality of the deposits.

2.6.1 Laser deposition parameters

Deposition parameters play a very crucial role in the quality and the properties of manufactured components. Therefore, a proper understanding of the relationship between the deposition parameters would guide the research in the proper selection of the deposition parameters required in a deposition process (Bayode et al. 2018). Choosing the right deposition parameters, together with careful control of the deposition process is very important in the manufacture of high grade components. The most frequently employed process parameters are discussed below.

- Laser power: Laser power is one of the most important factors that affect the quality of the manufactured components. This is because it is directly responsible for creating the melt pool needed to ensure the production of quality components. This has been demonstrated in the literature (Yvonni-Effrosyni 2014; Sharman et al. 2018). Research has shown that laser power can affect the quality of the build, either by the height of the build, crack reduction, or
elimination, microstructural and the mechanical properties of the deposited samples (Corbin et al. 2016; Gasper et al. 2017; Erinosho et al. 2015). The effect of laser power on the quality of the build can be linked to the role it plays in laser-material interaction. During the laser-deposition process, the rate of cooling of any material largely depends on the heat input (Kou 1987).

- Laser-scanning speed: This is a parameter for defining the speed that the laser beam travels along a desired route. Like the laser power, the laser-scanning speed also has a relationship with the laser/material interaction and the cooling rate in the solidification process. Akinlabi et al. (2012) explained that any change in the scanning speed is related to the dwell time; and it is an increment in the scanning speed, which leads to a decrease in the powder efficiency in the deposition of Ti6Al4V. The work of Sobiyi et al. (2017) also explained the effect of scanning speed on change in the height of the heat-affected zone (HAZ) during the deposition process of titanium carbide powder on a titanium substrate. Other work that has been carried out on the role played by the scanning speed in the deposition process is documented in the literature (Kumar et al. 2014; Sateesh et al. 2014; Akinlabi et al. 2012).

- Laser-beam diameter: This is one of the major factors to consider in the laser-deposition process; as it defines the laser-spot size; and it affects the laser concentration. The beam diameter and the laser power are responsible for the laser beam intensity. Equation 3.1 under section 3.2.1 expresses the relationship between the spot size, laser power and the scanning speed and
energy density used in the deposition process. The energy density refers to the overall input of energy per unit area (Mazumder et al. 1999).

- **Powder flow rate:** This is basically the rate at which the powder flows; or it can be described as the quantity of powder flowing into the deposition area per unit time; and it is normally expressed in g/min or rpm. Powder flowability greatly depends on the particle size and the morphology. The high ability of spherically shaped powder to react with the laser beam renders it highly preferable for laser-metal deposition processes (Schade et al. 2014). Literature has established the effect of the powder flow rate on surface roughness (Shah et al. 2010), wear-resistance (Shukla et al. 2012; Saboori et al. 2017), dimensional accuracy and the material efficiency of builds (Schade et al. 2014; Kumar et al. 2014). A high powder flow rate has the tendency to increase the nucleation density of the melt pool (Ahsan et al. 2011).

- **Gas flow rate:** This is the rate of flow of gas during the laser-deposition process; or it could also mean the amount of gas flowing through a medium per unit time. The gas-flow rate is usually in l/min; and it is mathematically expressed, as in equation 2.3.

\[
F = \frac{Q}{T} \quad \text{Eqn. 2.3 (Erinosho 2015)}
\]

Where \( F \) is the gas flow rate, \( Q \) is the flow volume and \( T \) is time.

- **Overlap percentage:** This is referred to as the overlap area of spread between successive layers in a deposition process. The overlap percentage, just like other deposition parameters, also affects the porosity, the density and the mechanical properties of the deposited material (Ludovico et al. 2010).
2.6.2 The laser-metal deposition of titanium aluminide

Lapin (2009) described titanium aluminide alloys as intermetallic compounds that fall into the group of high-temperature structural materials. This class of materials has exemplary properties, which makes them very valuable in different manufacturing fields. Ti-6Al-4V alloy is expensive; but it remains the most useful titanium alloy. Because of its cost, the need for reducing the waste generation in the manufacturing process became a serious concern; and this made AM a suitable manufacturing option (Yvonni-Effrosyni 2014). The numerous benefits associated with this class of materials make users and researchers in the field of engineering materials to continue developing possible ways of fabricating components via different additive manufacturing routes.

In the work studied by Tlotleng et al. (2016), the effect of laser power on hardness, the microstructure and the composition of the fabricated TiAl coatings was examined. The manufacturing of TiAl coatings was carried out by using the laser-metal deposition technique. The laser-scanning speed was kept constant; as the laser power was varied. Titanium and aluminium metal powders in different hoppers were delivered simultaneously. The deposits fabricated at 2.0 KW revealed a refined dendritic structure; while the deposits at laser powers of 1.0, 1.3 and 1.5 KW displayed the lamellar structure. The research outcome also revealed that the coatings are made up of TiAl$_3$ and TiAl$_5$ stable phases at high processing temperatures. The hardness test indicated that the coatings manufactured are TiAl/TiAl$_3$ based.

Cárcel et al. (2014) studied the deposition of TiAl intermetallic coating on Ti6Al4V substrate, using the technique of laser cladding. Deposition parameters, like feeding rate, laser power, scanning speed and preheating temperature were optimized. The
optical microscope and the scanning-electron microscope were used to characterize the microstructure of the coating produced from the process. It was observed that the cooling rate affected the hardness of the produced coatings and the cracking witnessed in the coatings. The work also acknowledged that the increase in cooling rate led to an increase in the hardness and the cracking witnessed in the coatings. It was noted that preheating, and process reheating, are likely to reduce cracking, which remain the chief defect in the TiAl cladding processes.

In another study carried out by Zhang et al. (2001), a microstructural study of titanium aluminide manufactured using the laser-engineered net-shaping (LENS) technique was presented. The study carried out was not only to enhance the knowledge of the microstructural and mechanical properties of fabricated composite obtained from the LENS process; but it was also aimed to compare the microstructures obtained from the LENS process to the ones obtained from the conventional processing method.

In the findings, it was observed that the processing parameters largely determine the microstructural outcome of the produced parts. Gamma or equiaxed metastable $\alpha_2$-$\text{Ti}_3\text{Al}$ microstructure was obtained in the deposition of the titanium aluminide alloys. The post-heat treatment done at 900°C for 15 min. on the metastable $\alpha_2$ microstructure led to the formation of a high percentage volume of $\alpha_2$-$\text{Ti}_3\text{Al}$ and gamma-titanium aluminide. It is anticipated that the microstructure thereby created would greatly increase the tensile strength of the alloy.

Srivastava et al. (2000) used Ti-48Al-2Mn-2Nb gas-atomized powder, as the feedstock to produce TiAl alloy. The effects of processing parameters: powder size,
laser power, scan rate, feed rate, and Z-increment on the micro and macrostructure, build height and width were examined. Srivastava et al. (2000) employed a feedback mechanism to monitor and control the processing parameters during the fabrication process, which enabled the fabricated component produced at constant build rate to be studied. In another work, carried out by Srivastava et al. (2001), the same powder was used to study the microstructures of the produced samples by using the same direct laser-fabrication (DLF) process. To control the microstructural morphology, both laser power and laser-scanning speed were used. The optical microscope, the scanning-electron microscope and the transmission-electron microscope were used to carry out the material characterization of the deposits obtained from the laser-deposition process, as well as those after the heat treatments.

The research findings revealed a fine non-homogeneous microstructure; when compared to the products obtained via the conventional method.

Laser-treated samples at 973 K displayed a stable microstructure, with coarse grains that begin to be visible at 1273 K. A uniform recrystallized microstructure was reached after annealing for 24 hours at a temperature of 1073 K.

Mahamood et al. (2013) conducted research on the effect of laser power on microhardness and the microstructure of the fabricated material produced from Ti6Al4V powder deposited on Ti6Al4V substrate when using the laser-metal deposition technique. The powder flow rate was kept at 1.44 g/min, the gas flow rare at 4 l/min, and the scanning speed was kept at 0.005 m/s. Laser power 0.8 – 3.0 KW was then used to deposit the tracks of Ti6Al4V powder on the Ti6Al4V substrate. The Vickers
hardness tester and the optical microscope were used to study the microhardness and the microstructure of the produced samples. From the microstructural study, layer bands were formed, as a result of the re-melting of old layers by new layers. This was seen in all the samples. The shrinkage process that took place in the fusion zone, as a result of the interaction of deposited melt pool created on the substrate, was regarded as another factor that might also be responsible for the formation of the layer band. The research findings led one to conclude that an increase in laser power leads to a corresponding increase in the microhardness; while a decrease in the density of columnar β-grain structure was found.

Liu and Dupont (2004) fabricated a matrix composite by reinforcing the carbide-particles in titanium aluminide by using the LENS (Optomec LENS 750 machine) process. TiC and Ti-48Al-2Cr-2Nb powders were used as feedstocks; and Ti-6Al-4V as an (α+β) titanium alloy was used as substrate. 20 vol pct TiC was mixed with 48Al-2Cr-2Nb powder and deposited by using laser power between 170 to 340 W, traverse speed between 4.2 to 16.9 mm/s, and a powder-feed rate between 2.4 to 3.5 g/min. Monolithic 48Al-2Cr-2Nb powder was also deposited as a basis of comparison. Examinations were conducted under the optical microscopy, scanning-electron microscopy, x-ray energy-dispersive spectroscopy, x-ray diffraction, electron probe microanalysis and microhardness measurement under 300g load, using Vickers indenter. The monolithic and titanium aluminide matrix composite fabricated were associated with solid-state cracking, as a result of the high thermal stresses produced during the LENS process. It was noted that the microstructure of the deposits contained unmelted TiC particles; and re-solidified TiC and Ti$_2$AlC carbides were spread in the $\alpha_2$ and $\gamma$ matrix phases.
The monolithic 48Al-2Cr-2Nb deposited microstructure consisted of small amounts of the \( \alpha_2 \) phase and the well-transformed \( \gamma \) phase. The deposited composites displayed hardness (average hardness of 700 VHN) that quite doubled that of Ti-6Al-V alloy (320 VHN) and monolithic 48Al-2Cr-2Nb deposits, having an average hardness of 380 VHN. It was, however, noted that, preheating of the substrate between 450 to 500\(^\circ\)C during the LENS processing can help to achieve the deposition of crack-free deposits.

In the work carried out by Balla et al. (2016), the influence of laser power and scanning speed on the processing, micro-structure, electrochemical and tribological properties of TiAl alloy were studied by using the LENS technique. Defect-free parts were obtained from energy input range between 40-50Jmm\(^{-2}\). It was discovered that high cooling rates brought about the formation of heavy \( \gamma \) matrix, together with small amounts of the \( \alpha_2-\gamma \) lamellar. It was also highlighted that tribological and electrochemical properties of the processes \( \gamma\)-TiAl in 3.5% sodium chloride (NaCl) solution where largely determined by the process parameters, and also by the abrasive wear type were noted with no sign of corrosion on the wear tracks.

It was therefore concluded that near-net-shaped defect-free \( \gamma\)-TiAl components can be produced via the LENS process.

Hu et al. (2016) studied the effect of fabricating variables in the deposition of CP-Ti powder, using the LENS (OPTOMEC LENS 450 machine) process. The variables used were the powder-feed rate (between 0.33 to 2.29 g/min at constant laser power of 150 W and scanning speed of 11 mm/s), the laser power (between 125 to 200 W at
constant powder feed rate of 2.29 g/min and scanning speed of 11 mm/s) and scanning speed (between 11 to 23 mm/s at a powder feed rate of 2.29 g/min and a laser power of 150 W.

Sixteen layers of each deposition variable were deposited on the titanium-alloy substrate; while taking the first deposited layers as the substrate, on which other layers are deposited. Evaluating the quality of the deposits, the effect of deposition variables on the height and the hardness of the deposited parts were analyzed. The outcome revealed that the average height of the deposits increases with an increase in the powder-feed rate, a decrease in the scanning speed, and a subsequent increase in the laser power. The Rockwell hardness test performed showed that an increase in the laser power and a decrease in the scanning speed led to a corresponding increase in the hardness. An increase in the powder-feed rate from 0.5 to 1 rpm led to a sharp decrease in the hardness; and not much change was noted in the hardness; as the powder-feed rate was increased to 3rpm.

The fabrication of functionally graded Ti/TiAl was carried out by Yan et al. (2017). The laser-metal deposition technique was used to fabricate the functionally graded Ti/TiAl, in which a high-energy input was utilized at the beginning to create a molten pool; and then later, this was decreased to prevent overheating. The laser power that was used to manipulate the energy input was varied; while keeping the scanning speed at 600 mm/min. A transition path with six different zones (each zone is 50 layers of 0.1 mm thick) with weight the percentage of titanium and Ti4822 was deposited on the CP-Ti plate. The analysis carried out with energy dispersive x-ray spectroscopy and x-ray diffraction revealed that the composition and the phases (α, α₂ and γ) obtained match
closely with what was expected. The results also indicated that the Vickers hardness gradually increases, as the percentage by weight of Ti4822 increases, which led to brittleness.

In the study conducted by Maliutina et al. (2015), titanium aluminide alloy (Ti48AL2Cr2Nb also referred as Ti48Al-2-2) was deposited on a preheated titanium (Ti6242) alloy substrate by using a Trumpf LASMA Nd:YAG laser with a 4 KW maximum power. The substrates were preheated to 300°C for an hour to minimize the temperature gradient between the substrate and the cladding layer, which would assist in eliminating any crack development usually caused by residual stress. Deposition parameters, such as laser power, were varied between 0.5 to 2 KW, powder flow between 3 to 27 g/min, and scanning speed between 100 to 500 mm/min.

The results obtained from the optical microscopy, the scanning-electron microscopy, the energy-dispersive spectroscopy and the x-ray diffraction examinations revealed that the duplex structure phases of γ-TiAl and α2-Ti3Al were seen in the coatings. The coatings also displayed higher micro-hardness values of 477 ± 9Hv under a 300 gf (2.94 N) load. The wear resistance result obtained indicates that the volume of 5mm³ worn materials was obtained under 0.31 average friction coefficients after 400 m.

In a similar work carried out by Sharman et al. (2018), an optomec LENS MR7 machine was utilized for the depositions. Using a fixed powder-flow rate of 2.3 g/min, laser power and traverse speed were varied between 150 to 400 W and 10.2 to 19 mm/s, respectively. The deposition process was operated in an argon-sealed chamber, which the oxygen level was below 10 ppm, to prevent contamination in the deposition
process. The threaded lens in the optics tube was used to control the laser focus. With a distance of 3.81 mm, under- and over-focused tests were conducted to check the effect of defocusing the laser. Examinations on the optical and the scanning electron microscopy and via energy-dispersive spectroscopy were conducted on the deposits. The result of the experiments revealed that it is possible to produce a crack-free titanium aluminide, without using an extra heat source to moderate the cooling rate. It is noted that this can be achieved when the laser is defocused above the deposition plane, which helps to preheat the powder before it gets deposited in the melt pool thereby reducing the temperature gradient, which induces cracking.

2.6.3 AM sustainability and environmental impact

The material’s availability, its cost, the development and the commercialization of the additive manufacturing technology is still growing, thereby limiting the use of the technology in the research laboratories, as well as in small- and medium-scale sectors. Even with some of the challenges facing AM technology, industry, it is becoming a means of censuring the operations of the tooling industry that have led to environmental pollution - mostly observed during the tool fabrication and the repair of other parts. The AM technology has proven to be an effective technology in the areas of fabrication, cladding and repair of the components. The technology also provides near-net shaped finished products with good mechanical properties. In addition, laser AM technology has proven that components can be produced from metal powders via the instructions supplied by a computer-aided design (CAD) model.

Sustainable manufacturing can be described as the fabrication of economic products through processes that are geared to managing the natural resources,
reducing the required energy, which is safe for workers, consumers, communities and reduces undesirable environmental impacts (DOC 2014). The AM process sustainability is an area of concern for researchers and manufacturers (Aliakbari 2012; Kobryn et al. 2006; Anzalone et al. 2013).

In areas, where large amounts of materials and energy are used, clean and more sustainable production are matters of high interest in the manufacturing processes; and traditional manufacturing tooling techniques can be seen as time-consuming (Bourhis et al. 2013). This is because the traditional manufacturing techniques made use of skilled and unskilled workers, specialized materials, and other means of manufacturing. Production lead time is one of the problems sometimes associated with tooling production, especially when it comes to large complex tools. This sometimes made the method to be seen as time-consuming, expensive and difficult in the design and production of tooling.

The use of limited material and energy resources by traditional manufacturing techniques, like casting, forging and machining, are now regarded as unsustainable because of the aquatic, terrestrial and atmospheric pollution caused by these processes (Morrow et al. 2007).

Manufacturing sectors are being tracked to ensure that their activities in the production and the delivery of quality products are geared at reducing negative environmental impacts (Environmental Protection Agency 2003). The increasing campaign and consciousness on the environmental impact of the tooling industries in the developed countries are posing more economic challenges to some tooling
industries. These are forcing the industries to relocate to regions, where, low production costs, low labour costs and low environmental standards are attainable.

The issues confronting industries in developing an environmental benign manufacture (EBM) were investigated by the panel set up by the International Assessment of Environmentally Benign Manufacture Technology. In the panel's findings, after visiting Japan, Europe and US, it was noted that the regions have diverse methods used in creating the strategy with different drivers. In Japan, for instance, export economy, high population density, and ISO 1400 are major drivers. In Europe, the major drivers are also the high population density, the recycling mindset, and take-back provisions. However, in the US, the major drivers are cost-savings and environmental benefits. The panel submitted that the main success recorded in EBM are attainable with the use of technology and collaborative effort contributed by academia in science and engineering, industry and government policy (Allen et al. 2002).

A sustainable characterization guide or outline (Figure: 1.1) that can assist in providing a measurement framework, aimed at improving the sustainability of the manufacturing processes, and which could also help to compare the diverse manufacturing methods for sustainability, was proposed by Mani et al. (2014). The first step out of the four steps proposed in the guide, involves an understanding of physics and the collection of adequate data involving the process. This step is then followed by the actual performance of the sustainability characterization. The manufacturing-process data are then applied in the third step, as evidence to back the information model and the metrics computed. The process needs to be undertaken to provide life-
cycle inventory (LCI) data. The outcome in step three is then used in the development of an action plan.

The availability of the required life-cycle inventory (LCI) data remains a difficult task; and it tends to limit the analytical accuracy of the manufacturing process (Kellens et al. 2017). The traditional manufacturing technique using heavy presses, milling machines and melting machines uses up more energy than the AM systems (Farinia Group 2017); since AM only needs a single machine for similar production ability. With respect to waste generation, AM is proven to have a comparative environmental edge; because only the required materials are used up. In areas where powder waste is produced, the processes are highly efficient to reuse the material. However, the subtractive manufacturing technique generates chippings that cause environmental waste; or they require recycling before they can be reusable.

Morrow et al. (2007) studied the rate at which the Direct Metal-Deposition production of molds and dies can be utilized, to achieve reduced energy consumption and reduced environmental pollution, when compared with the conventional manufacturing techniques, like injection-moulding, forging and stamping. The result of the investigation revealed that success can be made in minimizing the environmental impact of the tool-and-die production through the remanufacturing ability of the Direct laser-deposition technique. The merit associated with the laser-based remanufacturing of tooling, as the size and the tool production increase includes a reduction in the cost of production and that of the environmental impact.
The ability of AM to fabricate sophisticated components would ensure that the components are designed and produced with minimal materials that can compete with the components produced by traditional manufacturing, in terms of the functional specifications. AM provides an opportunity to the business leaders in the industries to improve their current processes and designs (McGrath et al. 2015). With the use of AM, more than 40% mass reduction in aircraft production has been achieved in the aeronautic industry. The use of AM technology can guarantee energy savings of 115.7 TBtu/year, with about 4000 tons/year of aluminium alloys, 8100 tons/year of nickel alloys, and 7600 tons/year of titanium alloys weight reduction in the U.S. fleet by 2050 (U.S. Department of Energy 2015).
The technique of LMD, among other AM technologies, is improving and gaining positive recognition for different industrial applications. LMD is very useful in the production of complex geometrical parts. The Wohlers Associates report of 2014 revealed that the market of services and products of AM continues to rise. In the report, a survey was carried out on 29 manufacturers and 82 service-providers of industrial AM systems. The companies gave information on the industries, to which they render services, and the revenues obtained for their services. The outcome of the survey (summarized in Figure: 1.1) shows that AM services cut across architectural, academic institutions, mechanical/dental, industrial/business machines, motor vehicles, government/military, consumer products/electronics and aerospace.

Figure: 2.15: Serviced rendered by AM manufacturers and service providers (Wohlers et al. 2014)

From the survey, industrial/business machines, consumer products/electronics, mechanical/dental, motor vehicles and aerospace remain the major areas where AM
technology services are of immense importance. AM services and service providers in
government/military, architectural and academic institutions are still growing.

2.7 SUMMARY

Titanium and its alloys have been shown to be superior engineering materials,
having a high strength-to-weight ratio, and with excellent physical, mechanical, and
corrosion resistance. The materials have also shown that with the right composition and
manufacturing process, they could be applied at elevated temperatures, as high as
750°C, especially for automotive and gas-turbine components. These unique properties
have made them choice materials in automotive, aerospace, marine, chemical,
biomedical, nuclear and energy sectors.

Titanium alloys’ properties have always been improved by the addition of other
alloying elements, such as V, Mo, Mg, Si, Cr and Nb. The stabilizing elements are
responsible for the formation of the two phases (α2 and β) in structural α2-alloys with α2-
Ti3Al DO19 structure. The alloying elements are added mainly to improve the strength,
ductility, oxidation and creep-resistance. The γ-TiAl with fcc L10 structure has a strong
bond existing between Ti and Al and this makes deformation difficult, thereby making
the material brittle. This bond helps to maintain the strength and creep-resistance at
elevated temperatures.

Two structural γ alloys that have been developed (single phase γ and two-phase
γ+ α2); however, the γ+ α2 phase has always been preferred for most engineering
applications. Considerable research and developmental interest have been placed on γ-
based alloys for engineering applications (Franzén & Karlsson 2010) and the most
promising alloy for high temperature and long-time application is Ti-(34-39)Al-(5-10)Nb-(2-5)Cr (Murr et al. 2010). The known microstructures exhibited by γ-TiAl include equiaxed, lamellar, near lamellar, duplex and pseudo-duplex. The emergence of these microstructures largely depends on the kind of heat treatment applied; and the process of the cooling rate (Leyens & Peters 2003; Lundstrom 2001). The duplex microstructure is a mixture of equiaxed γ grains and lamellar colonies. The microstructure combines both the properties of equiaxed and lamellar microstructures, thereby making it more ductile. This type of microstructure is therefore preferred for structural applications; as it is made up of γ and γ+ α₂ phases. These phases are only achieved when the material is properly heat treated.

To achieve improved material properties, developments are continuously being made to alter the microstructure of the material; since the manufacturing method and the cooling rate are largely responsible for the actualization thereof (Porter et al. 2009). The cooling rate has been associated with fine lamellar structure with Widmanstatten needles found inside the lamellar grains. It is believed that the Widmanstatten colonies have been formed, due to the super-cooling that took place at the cooling rate. It is also believed that the Widmanstatten colonies are formed to ease thermal stresses.

Titanium and its alloys are expensive raw materials and the production of components with such raw materials needs to be achieved with minimal wastage. LMD, an AM technology used in the repair and the fabrication of components have been proven to be a sustainable method that can be used in the manufacturing of titanium-alloy components. This technology has been proven to deliver near-net-shaped, finished quality components. However, the quality of the components that can be
delivered by the technique largely depends on the manufacturing method and the deposition or process parameters employed. Different deposition parameters have been used to understand the optimum parameters that give the best laser material interaction. However, research and development are still on-going, to improve the properties of gamma-titanium aluminide; and to make these alloys highly suitable for certain applications. The limited research work on Ti-4822-4 alloy has led to this research study.
CHAPTER THREE

3.0 RESEARCH METHODOLOGY AND EXPERIMENTAL PROCEDURE

3.1 INTRODUCTION

This chapter presents a detailed research methodology, the methodology flow chart, the experimental set-up, as well as the procedures utilized in the deposition and characterization of deposited TiAl alloy. The materials and equipment utilized in the study have also been described in this chapter. The test carried out on the material characterization includes the use of the optical and scanning-electron microscopes, the Vicker’s microhardness, the electrochemical (corrosion) test, the dry sliding-wear test, the X-ray diffraction and the nano-indentation test for material hardness, stiffness, Young’s modulus and the creep.

3.2 RESEARCH METHODOLOGY AND EXPERIMENTAL SET-UP

A detail research study was carried out on the existing literature, to throw more light on what has been done so far on additive manufacturing, while using laser-metal deposition in the deposition of titanium aluminide. More attention was placed on the processing parameters employed to arrive at the findings, the shortcomings and the recommendations proffered.

The wide discussions surrounding the necessity of preheating the substrate before deposition, as a way of reducing the thermal stresses that can lead to cracks in the deposits, thereby leading to the development of three different scenarios. These three scenarios are: to deposit different samples on the un-preheated substrate; on the laser-preheated substrate; and lastly, on heating bed preheated substrate. The samples
of the un-preheated substrate were the samples produced without any preheating process being carried out. The literature study led to the development of an experimental matrix (processing parameters variation) needed for the deposition process and the manufacturing of TiAl-Ti composites using the laser-metal deposition process. The deposition process was carried out by using the Optomec LENS system at the National Laser Centre, Council for Scientific and Industrial Research (NLC-CSIR) South Africa.

Wear, corrosion, hardness, stiffness, modulus of elasticity and a creep test were conducted on the deposited samples to determine the mechanical properties of the composite produced. Further tests including, the microstructural and chemical compositional analysis test, using the scanning-electron microscope (SEM), X-ray diffraction (XRD) and the Electron-Dispersive Spectroscopy (EDS) were conducted. The tests were conducted to provide an opportunity for determining the microstructural properties through grain size and distribution, size and shape of phases, and inclusions, which contribute tremendously to the mechanical properties of the material.

The characteristics of the composite, based on the research result that will be determined, will then be compared to those of established similar materials from the literature, based on the properties obtained and the areas of application.
3.3 METHODOLOGY FLOW CHART

The flow chart for the research methodology is shown in Figure: 1.1.

Figure: 3.1: Methodology flow chart
3.4 METHODOLOGY DESCRIPTION

The Literature Review: In order to achieve the stated aim of the research, studying the effect of preheating and determining the optimum parameters suitable for the deposition of titanium aluminide, the literature review on previous works relating to the stated aim was carried out. The reviews where sourced from different mediums, such as published and unpublished theses, journal papers, printed or soft-copy textbooks etc. The reviews provided the necessary background information that drives this current study.

Material Sourcing: Having been equipped with some background knowledge needed for the study, the sourcing of the materials needed for the study was next in line. The materials (titanium aluminide powder and CP-titanium substrate) were sourced from reputable metal stores, Praxair surface technologies, USA and Titanium a2z, South Africa.

Experimental Matrix Development: Before the deposition process can take place, the processing parameter-design needs to be developed. The development of the experimental matrix emerged from the previous work carried out and the type of laser equipment available for the deposition process. The laser equipment needed for the deposition process is an important factor in the development of an experimental matrix; as laser equipment has limits in terms of maximum laser power and speed. Design-Expert version 6.0.8 was later utilized to analyze the influence of the processing parameters on the height and the micro-hardness of the deposited samples. The Design-Expert software is a very sophisticated tool that aids in
the analysis and the interpretation of experiments involving multiple factors or parameters (Buxton 2007).

**Sample Deposition at CSIR:** Having designed the processing parameters needed for the deposition process, the next stage will be to carry out the deposition. The laser-metal deposition has been carried out at the National Laser Centre, the Council for Scientific and Industrial Research (NLC-CSIR) South Africa, using the OPTOMEC LENS laser-equipment with a maximum laser power of 1 KW.

**Sample Preparation:** The deposited samples were properly cleaned (removing un-melted metal powder on the substrate, while holding the deposited samples) after their removal from the glove box of the LENS system. This is important; as knowledge has clearly shown that the outcome of a microscopic study largely depends on the attention taken in the specimen preparation (Avner 2005).

Physical eye examinations on the deposited samples were performed; as this provides an early stage in the distinction between the parameters that have been used for the deposition processes. The issues that can easily be examined are the expected height and the shape of the depositions, the presence of cracks, colour (burns on depositions), and the quality of the surface finish of the deposits. After the physical examinations, the deposits were then prepared for chemical, microstructural and mechanical analysis. For most of the analyses performed, the deposited samples were cut to the required sizes, mounted on resin in some cases, grounded, polished and
etched. The samples had been prepared by using standard experimental procedures.

**Sample Characterization:** The characterizations of the samples involve different stages. The first stage is physical examination, partly discussed under sample preparation, in which the deposited samples were physically examined. Another stage is the chemical-characterization stage, such as the corrosion test, where the samples were tested for how they react to corrosive medium and Energy-dispersive X-ray spectroscopy (EDS), in order to determine the chemical elements present in the deposited samples and their comparative amounts. Microstructural analysis presents a stage, where the microstructures (grain size, shape, composition, cracks, pores, inclusions, etc.) of the deposited samples were carefully analyzed. Some of the tests performed at this stage include optical microscopy, scanning-electron microscopy (SEM), Electron Dispersive Spectroscopy (EDS), and X-ray diffraction (XRD). The last characterization was the mechanical analysis (wear, micro- and nano-hardness, stiffness, modulus of elasticity and creep test). These tests also help in determining the deposited sample with the superior properties. Some of the results (mechanical properties) obtained were utilized to form a custom material (Ti-4822-4) for the simple engineering part (exhaust valve) modelled and simulated in this study. The exhaust valve was modelled and simulated by using SOLIDWORKS 2017 software.
Results and discussion: The detailed discussion and report were then written, presenting a careful analysis of the research work. Short-comings and challenges involved in the research work that were liable to have contributed to the results obtained, were also discussed.

Conclusion and Recommendation: From the work carried out, a conclusion was drawn out; and some recommendations that would help shape future work were made.

3.4.1 Materials and equipment

Commercially pure CP-TI (pure titanium) substrate of size 100 X 100 X 6 mm supplied by Titanium A2Z (Pty) Ltd, a company based in South Africa and titanium power (Ti-4822) with product name Ti-4822-4 obtained from Praxair Surface Technologies, USA were used in this research. The particles of the Ti-4822-4 powder are spherical in shape, with particle sizes between 45 to 150 microns. The material certificate of both the substrate and the titanium powder are shown in Appendix 1 and Appendix 2, respectively. The percentage chemical compositions of CP-Ti and Ti-4822-4 are shown in Table: 2.1 and Table: 2.1, respectively.

Table: 3.1: Chemical composition of CP-Ti

<table>
<thead>
<tr>
<th>C</th>
<th>Fe</th>
<th>N</th>
<th>O</th>
<th>H</th>
<th>Others</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max.</td>
<td>Max. 0.30</td>
<td>Max.</td>
<td>Max.</td>
<td>Max.</td>
<td>Each</td>
<td>Total</td>
</tr>
<tr>
<td>0.08</td>
<td>0.03</td>
<td>0.25</td>
<td>0.015</td>
<td>0.03</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>0.03</td>
<td>0.15</td>
<td>0.014</td>
<td>0.18</td>
<td>0.002</td>
<td>0.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Balance (approx. 99.224)
Table: 3.2: Chemical composition of Ti-4822-4

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Test Lab</th>
<th>Min</th>
<th>Max</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium (Al)</td>
<td>Praxair</td>
<td>34</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>Carbon (C)</td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.009</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td></td>
<td>2.45</td>
<td>2.75</td>
<td>2.60</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td></td>
<td></td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>Hydrogen</td>
<td></td>
<td></td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>Nitrogen (N)</td>
<td>Praxair</td>
<td>0.015</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Niobium (Nb)</td>
<td></td>
<td>4.5</td>
<td>5.1</td>
<td>4.6</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td></td>
<td></td>
<td>0.09</td>
<td>0.06</td>
</tr>
<tr>
<td>Other elements,</td>
<td></td>
<td></td>
<td>0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Each</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Other elements,</td>
<td></td>
<td>0.20</td>
<td>&lt;0.10</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance (approx. 58.588)</td>
<td></td>
</tr>
</tbody>
</table>

The LENS 850-R (shown in Figure: 3.2) used for this research, employs a high power IPG fibre laser in the building up of fully dense parts from the metal powder (Optomec Inc. 2016). The LENS systems utilizes a 3-dimensional CAD model, which
automatically slices a model into a tool path that gives commands to the LENS machine on how the part is to be built. The LENS system is normally enclosed in a chamber purged with argon gas to keep the oxygen level below 10 parts per million, as a way of preventing oxidation or the inclusion of impurities during the deposition process. The metal powder gets into the process through the powder-feed system. Other operations (like machining, heat treatment, hot isostatic press, etc.), if so desired, can then be performed after the completion of the deposition process.

![Optomec LENS 850-R (Optomec Inc. 2016)](image)

**Figure: 3.2: Optomec LENS 850-R (Optomec Inc. 2016)**

### 3.5 LASER AND SAMPLE DEPOSITION

Laser is an acronym for Light Amplification by Stimulated Emission of Radiation. The main concept was discovered by Charles Hard Townes (an American scientist), Alexander Mikhailovich Prokhorov and Nikolai Gennadiyevich Basov (Soviet scientists). However, it was only in 1960 that Theodore Maiman of Hughes research laboratory demonstrated the flashing of light through a ruby crystal to produce lasers (Singh et al. 2012). A laser can be regarded as a device produced; and it amplifies a narrow intense
beam of coherent light (Lucent Technologies 1998). A laser consists of three major components (see Figure: 1.1), which include, active/laser medium (amplifier), excitation (energy input) and the optical resonator (partial and total reflective mirror).

![Figure: 3.3: Components of a laser](image)

Energy is supplied into an amplifying medium and laser beam, and millions of photons come out as output through the partial reflector. The laser medium can be in the form of gas (carbon dioxide (CO$_2$), argon and krypton), Liquid (pulsed dye, rhodamine dye), diode, semiconductors, solid-state crystals (Nd: YAG, Erbium: YAG, Holmium: YAG, etc.). The energy input, or the excitation mechanism might be in the form of electricity, diode-pumped solid state (DPSS) laser stimulated, gas and semiconductor etc. Lasers have been known to show distinctive properties, which include:

- **Monochromatic**: Meaning they have a single wavelength or colour.

- **Directional**: Meaning that laser beams are not known to expand as swiftly as other light beams.

- **Coherent**: Meaning that all the waves are created in phase with each other.

- **High intensity**: which is as a result of directionality

- **Short-pulse duration**
Lasers are now part of our daily lives as they are used in several applications of human endeavour. HeNe and diode lasers now find applications in laser pointers and printers, scanners, video-compact disc players, construction and surveying equipment. Nd: YAG, Carbon dioxide and fibre lasers are now used in the industries for welding, marking, drilling, cutting and surface-treatment operations. Carbon dioxide, argon, Nd: YAG, visible, dye and MIR lasers are used in medical applications in areas of general surgery, skin treatment, urology, cardiology and ophthalmology (vision correction). The military also employs the use of lasers in tracking, targeting, range-finding, and finally, as a direct energy weapon.

3.5.1 The deposition process

The laser deposition process used the Optomec LENS 850R shown in Figure: 3.2. The LENS machine comprises of the laser, powder feed system, controlled environment (glove box) and the motion control system. The deposition process is operated in a controlled environment, purged to keep oxygen level below 10 ppm and filled with argon, an inert gas to prevent contamination of the deposits. Before the deposition processes, the 10 x 10 x 6 mm substrates were sand blasted and cleaned with acetone to remove any impurities. The nozzles of the powder feed system were checked for blockage; and the powder flow was confirmed. Then, the initial deposition runs (trials) where carried out, to ensure that the experimental set-up was right, after which the deposits described in the three scenarios were deposited.

3.5.2 Experimental matrix

The experimental matrices were developed, based on the literature references consulted, and the limitations in the LENS 850-R machine (having a maximum power
rating of 1 KW) used for the depositions. These experimental matrices for the three different scenarios are represented in Table: 2.1, Table: 2.1 and Table: 2.1, respectively. The incident energy (E) input for each of the parameter used was calculated by using equation 3.1.

\[ E = \frac{P}{v.D} \]  

\textit{eqn. 3.1} (Sharman et al. 2018)

Where, \( P \) is the laser power, \( v \) is the laser-scan speed and \( D \) is the laser-beam diameter.

For the un-preheated scenario, using a spot size of 1.4 mm, 8 layers of build were done, in order to produce a deposit for each deposition parameter. For the first set of deposits, the laser power was varied between 0.3 to 0.5 KW while the scanning speed and the powder-flow rate were kept constant at 3.174 mms\(^{-1}\) and 4.09 gmin\(^{-1}\) respectively. For the second set of deposits, the laser power and the powder-flow rate were kept constant at 0.4 KW and 4.09 gmin\(^{-1}\) respectively; while the scanning speed was varied between 3.174 to 7.406 mms\(^{-1}\).

For the last set of deposits, in which the powder flow-rate was varied between 4.09 to 7.12 gmin\(^{-1}\); and the laser power and the scanning speed were kept constant at 0.4 KW and 4.232 mms\(^{-1}\) respectively.
Table: 3.3: Experimental matrix for the unpreheated scenario

<table>
<thead>
<tr>
<th>Parameter variation</th>
<th>Sample designate</th>
<th>Laser power (KW)</th>
<th>Scanning speed (% / mms(^{-1}))</th>
<th>Powder flow rate (rpm / gmin(^{-1}))</th>
<th>Energy input (Jmm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser power variation</td>
<td>UA1 0.3</td>
<td>30 / 3.174</td>
<td>2.0 / 4.09</td>
<td>67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UA2 0.35</td>
<td>30 / 3.174</td>
<td>2.0 / 4.09</td>
<td>78.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UA3 0.4</td>
<td>30 / 3.174</td>
<td>2.0 / 4.09</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UA4 0.45</td>
<td>30 / 3.174</td>
<td>2.0 / 4.09</td>
<td>101.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UA5 0.5</td>
<td>30 / 3.174</td>
<td>2.0 / 4.09</td>
<td>112.5</td>
<td></td>
</tr>
<tr>
<td>Scanning speed variation</td>
<td>UB1 0.4</td>
<td>30 / 3.174</td>
<td>2.0 / 4.09</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UB2 0.4</td>
<td>40 / 4.232</td>
<td>2.0 / 4.09</td>
<td>67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UB3 0.4</td>
<td>50 / 5.290</td>
<td>2.0 / 4.09</td>
<td>54.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UB4 0.4</td>
<td>60 / 6.348</td>
<td>2.0 / 4.09</td>
<td>45.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UB5 0.4</td>
<td>70 / 7.406</td>
<td>2.0 / 4.09</td>
<td>38.6</td>
<td></td>
</tr>
<tr>
<td>Powder flow rate variation</td>
<td>UC1 0.4</td>
<td>40 / 4.232</td>
<td>2.0 / 4.09</td>
<td>67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UC2 0.4</td>
<td>40 / 4.232</td>
<td>2.5 / 4.85</td>
<td>67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UC3 0.4</td>
<td>40 / 4.232</td>
<td>3.0 / 5.67</td>
<td>67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UC4 0.4</td>
<td>40 / 4.232</td>
<td>3.5 / 6.38</td>
<td>67.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UC5 0.4</td>
<td>40 / 4.232</td>
<td>4.0 / 7.12</td>
<td>67.5</td>
<td></td>
</tr>
</tbody>
</table>

For the laser-preheated scenario, using a spot size of 1.4 mm, 10 layers of build was done to produce the deposit for each deposition parameter. For the first set of deposits, the laser power was varied between 0.2 to 0.6 KW; while the scanning speed and the powder-flow rate were kept constant at 10.58 mms\(^{-1}\) and 4.09 gmin\(^{-1}\) respectively. For the second set of deposits, the laser power and the powder-flow rate were kept constant at 0.3 KW and 4.09 gmin\(^{-1}\) respectively; while the scanning speed was varied between 10.58 to 6.348 mms\(^{-1}\). For the last set of deposits, in which the powder-flow rate was varied between 3.49 and 6.38 gmin\(^{-1}\), the laser power and the scanning speed were kept constant at 0.3 KW and 10.58 mms\(^{-1}\) respectively.

Before the deposition process was carried out, the laser power was set at 0.2 KW; and this was actually used to scan each of the surfaces of the substrate on which the deposit is to sit. The laser scanning was done thrice; and it was measured with a laser-thermometric instrument. The average measured temperature of the surface was
81°C before the deposition commences. The preheating was done, as a way of enabling the proper fusion of deposits on the substrate. This also helps to reduce the residual stress that normally leads to cracks in the deposition process, due to the high temperature gradient between the substrate and the deposit.

Table: 3.4: The experimental matrix for the laser-preheated scenario

<table>
<thead>
<tr>
<th>Parameter variation</th>
<th>Sample designate</th>
<th>Laser power (KW)</th>
<th>Scanning speed (% / mms⁻¹)</th>
<th>Powder flow rate (rpm / gmin⁻¹)</th>
<th>Energy input (Jmm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser power variation</td>
<td>LA1</td>
<td>0.2</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>13.5</td>
</tr>
<tr>
<td></td>
<td>LA2</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>LA3</td>
<td>0.4</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>27.0</td>
</tr>
<tr>
<td></td>
<td>LA4</td>
<td>0.5</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td>LA5</td>
<td>0.6</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>40.5</td>
</tr>
<tr>
<td>Scanning speed variation</td>
<td>LB1</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>LB2</td>
<td>0.3</td>
<td>90 / 9.522</td>
<td>2.0 / 4.09</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>LB3</td>
<td>0.3</td>
<td>80 / 8.464</td>
<td>2.0 / 4.09</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>LB4</td>
<td>0.3</td>
<td>70 / 7.406</td>
<td>2.0 / 4.09</td>
<td>28.9</td>
</tr>
<tr>
<td></td>
<td>LB5</td>
<td>0.3</td>
<td>60 / 6.348</td>
<td>2.0 / 4.09</td>
<td>33.8</td>
</tr>
<tr>
<td>Powder flow rate variation</td>
<td>LC1</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>1.5 / 3.49</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>LC2</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>2.0 / 4.09</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>LC3</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>2.5 / 4.85</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>LC4</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>3.0 / 5.67</td>
<td>20.3</td>
</tr>
<tr>
<td></td>
<td>LC5</td>
<td>0.3</td>
<td>100 / 10.58</td>
<td>3.5 / 6.38</td>
<td>20.3</td>
</tr>
</tbody>
</table>

For the third scenario (the heating-bed scenario), using a spot size of 1.4 mm, 5 layers of build were done to produce a deposit for each deposition parameter. Before the deposition started, the substrate was preheated to 450°C with a heating bed. For this scenario; while the laser power and the scanning speed were varied, respectively, between 0.4 to 0.5 KW and 3.174 to 2.645 mms⁻¹, the power-flow rate was kept constant at 2.7 gmin⁻¹.
Table: 3.5: Experimental matrix for the heating bed preheated scenario

<table>
<thead>
<tr>
<th>Sample designate</th>
<th>Laser power (KW)</th>
<th>Scanning speed (% / mms$^{-1}$)</th>
<th>Powder flow rate (rpm / gmin$^{-1}$)</th>
<th>Energy input (Jmm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.40</td>
<td>30 / 3.174</td>
<td>1.0 / 2.7</td>
<td>90.0</td>
</tr>
<tr>
<td>H2</td>
<td>0.45</td>
<td>30 / 3.174</td>
<td>1.0 / 2.7</td>
<td>101.3</td>
</tr>
<tr>
<td>H3</td>
<td>0.40</td>
<td>25 / 2.645</td>
<td>1.0 / 2.7</td>
<td>108.0</td>
</tr>
<tr>
<td>H4</td>
<td>0.45</td>
<td>25 / 2.645</td>
<td>1.0 / 2.7</td>
<td>121.5</td>
</tr>
</tbody>
</table>

3.6 MICROSCOPY

Microscopy or metallography is referred to as microscopic study of the structural characteristics of metals and alloys (Avner 2005). The microscope has proven to be a very relevant tool to the metallurgist. The microscope has provided the opportunity of viewing and magnifying miniature images, thereby providing the ability to analyze the microstructure of the materials. This ability helps in determining the mechanical properties of such materials, which made it possible to predict the probable behaviour of the material under certain conditions. Electron microscopy is mainly used in most research applications; because it possesses the capability of producing higher quality images at higher magnifications.

Because the main aim of microscopic image analysis is microstructure quantification, several ASTM standards that give specific microscopic procedures are now available. These standards can be found in the ASTM annual book of standards. Some of the ASTM standards available on scanning-electron microscopy are E562, E766, E986, E1245, E1508 and E2142 (Friel 2003).
In this research, an optical microscope with maximum magnification X100 (OLYMPUS BX51M) and a TESCAN scanning-electron microscope (SEM), fitted with Electron Dispersive Spectroscopy (EDS) equipment, as shown in Figure: 3.4 was used for the microstructural analysis.

Figure: 3.4: SEM/EDX equipment

3.6.1 Metallography preparation

Physical inspection is the first examination procedure that needs to be made on a specimen, before embarking on other metallographic procedures. Visual inspection is clearly done on a microscope. This inspection is fast, easier than figures or a verbal
description; and it holds a lot of information about a specimen. The inspection gives the approximate chemical composition, as well as the physical and structural properties of a specimen.

A specimen, on which microscopic examinations need to be performed, is first of all prepared, using the standard metallographic procedure. Care must be taken to ensure that damages (from thermal, in the form of overheating, mechanical in the form of deformation, and foreign matter or embedded particles) are introduced into the specimen. The steps in this procedure may include cutting, mounting, grinding, polishing, microscopy, etching, and finally the microscopic procedure.

- **Cutting:** This is usually the first step taken in the sample preparation. Cutting involves the slicing of a sample into smaller piece that can easily be further prepared (through mounting, grinding and polishing) for mechanical, microscopic or any other examination required. This operation is normally conducted on a wet abrasive cut-off machine. A quality cut is achievable with special cutting blades and water cooling. Achieving a quality cut that is free of thermal damage and burrs is also dependent on the selection of the feed speed and the contact area when cutting. Specimens from deposited titanium aluminide were cut, using the cut-off machine. The water jet cut-off machine runs at a speed of 3800 rev; and the water steam from the system ensures that the blade and the specimen are kept cool; so as to prevent the heating up of the specimen; since this might alter the properties of the specimen being cut.

- **Mounting:** Mounting is an operation that involves the embedment of cut specimen piece into resin. Mounting operations are normally employed in
situations where the specimens that need to be examined are small, has a complicated shape, has sample cracks, or is porous and edge retention, or where support is necessary, in order to make further preparations, like grinding, polishing and other examinations easier. The two mounting techniques usually used are cold mounting and hot-compression mounting.

Cold mounting is used to mount any type of desired shape; and it is mostly employed in mounting fragile and brittle specimens. However, some of the cold mounting materials (such as epoxy and acrylics) are not really hard; and they have high shrinkage, which makes them fail to respect tolerances. Cold-mounting operations do not need any special equipment; as the resin is thoroughly mixed in a bowl and poured into a mounting cup (mould), in which the sample to be mounted has been properly positioned. Cold mounting requires a relatively long curing time at low temperatures. Hot compression mounting uses heat and pressure to melt the resin; and it employs a cooling system to cool the mounted sample. The most commonly used resin is the polyfast. Hot compression mounting produces superior quality and hardness compared to that of cold mounting. However, heat-sensitive, fragile and brittle materials cannot be hot mounted. A hot compression-mounting press and sample obtained from hot compression mounting are shown in Figure: 3.5 (a) and (b).

In this research, both mounting techniques have been used. Specimens that needed to be analysed under hardness machine, optical microscope and SEM/EDX have been mounted by using a hot compression mounting technique. While specimens
examined under electrochemical (corrosion) testing have been mounted by using the cold-mounting technique.

The hot mounting of specimens has been carried out by using the Struers hot-mounting press machine, with the heating stage set for three and half minutes, using a heating temperature of 180\(^{0}\)C and a pressure of 250 bar. The cooling stage took one and half minutes at a high cooling rate.

For cold mounting, the mixing ratio to form the acrylic resin was done by volume. 5 parts of ClaroCit powder were mixed in 2 parts of ClaroCit liquid and stirred thoroughly for about one and half minutes. The resin was then poured into the mounting cups containing well-positioned samples that have been fitted with electrical wires. The mounts are then allowed to cure at room temperature for about twenty-four hours; before the mounts are removed from the mounting cups. The cold-mounting materials, the cold-mounted samples, and a mounted sample after curing, are shown in Figure: 3.6.
Grinding and polishing: Grinding and polishing operations are mechanical preparations that are usually conducted on specimens, so that the specimen can be clearly viewed under the microscope. Mechanical preparations are conducted by using standard metallographic procedures. The options of consumables selected for any grinding and polishing operations and the operational time will determine the final outcome of the polished specimen. Grinding and polishing operations of titanium are normally done in a three-step operation as, described in Table: 3.6. The first step, plane-grinding is done with resin combined with diamonds on a solid disc that mainly removes any damage introduced by cutting.
Abrasives in the grinding process comprise chip-off materials from the specimen. This is followed by a fine-grinding step, which reduces the surface roughness of the specimen to a level that is suitable for polishing. Silicon carbide (SiC) papers of different grain sizes are normally employed in the grinding operations of titanium. The papers are normally selected from one of large grain size, to the smallest grain size, such that grinding is gradual. The final step is a chemical-mechanical polishing process, which uses a mixture of colloidal silica (OP-S) and about 30% hydrogen peroxide (H₂O₂). The polishing operation is done to remove any scratches that are left behind during the grinding operations. The choice of consumables selected and the preparation time for mechanical preparations will influence the final quality of the samples obtained. The mechanical preparation of the Titanium alloys is obtained from a Struers application note (Taylor 2015).
Table 3.6: Titanium alloys preparation method (Taylor 2015)

<table>
<thead>
<tr>
<th>Grinding</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step</strong></td>
<td><strong>Plain Grinding (PG)</strong></td>
<td><strong>Fine Grinding (FG)</strong></td>
</tr>
<tr>
<td>Surface</td>
<td>MD-Mezzo</td>
<td>MD-Largo</td>
</tr>
<tr>
<td>Abrasive</td>
<td>Type</td>
<td>Diamond</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>#220</td>
</tr>
<tr>
<td>Suspension/Lubricant</td>
<td>Water</td>
<td>DiaPro Allegro/Largo 9</td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td>300</td>
<td>150</td>
</tr>
<tr>
<td>Force (N)/specimen</td>
<td>40***</td>
<td>30</td>
</tr>
<tr>
<td>Time (min)</td>
<td>Until plane</td>
<td>5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polishing</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Step</strong></td>
<td>Oxide Polishing (OP)</td>
<td></td>
</tr>
<tr>
<td>Surface</td>
<td>MD-Chem</td>
<td></td>
</tr>
<tr>
<td>Abrasive</td>
<td>Type</td>
<td>Colloidal Silica</td>
</tr>
<tr>
<td></td>
<td>Size</td>
<td>0.04 µm</td>
</tr>
<tr>
<td>Suspension/Lubricant</td>
<td>OP-S*</td>
<td></td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Force (N)/specimen</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Time (min)</td>
<td>5**</td>
<td></td>
</tr>
</tbody>
</table>

Note, * 90% of OP-S is mix with 10-30% H₂O₂ (30%). ** polishing time depends on area of sample as large samples will require more time. *** Reduce force to 25N to prevent pencil shape in the preparation of a single mounted sample.

- Etching: After polishing, before etching a specimen, it is desirable to view the specimen under the optical microscope. This provides the surface quality
assessment regarding deformation, scratches and smearing. Pores, inclusions and layers can also be observed without etching. Etching of the specimen will provide more information about the material. Etching refers to a surface-controlled corrosion process, in which corrosion tends to remove, attacks; or it can cause certain changes in the consistency of a material, with the sole aim being to create an optically identifiable contrast. Polarized light can be used to observe the surface of a well-polished unetched titanium sample. It is used to check whether a sufficient polish has been attained.

The most commonly used titanium etchant is the Kroll’s reagent, which is a mixture of 100 ml water, 6 ml nitric acid and 3 ml hydrofluoric acid. This etchant give a dark brown colour to the titanium β phase. Titanium can also be colour-etched by using Weck’s reagent. Weck’s reagent is a mixture of 100 ml of water and 5g ammonium bifluoride. In this research, the Kroll’s reagent has been used for the etching of the samples. Each sample was etched for about 15 seconds. The micro-structure of the samples can be seen under the optical microscope; but it could not been seen by using the SEM, which might have been due to the different principles of operation of the equipment, or the weakness in the concentration of the chemicals used. As such, the samples were re-polished and re-etched for 20 seconds, using a mixture of 100 ml water, 6 ml nitric acid, 4 ml hydrofluoric acid, together with the addition of 1 ml hydrogen peroxide. With this etchant, the microstructure becomes visible under the SEM.
3.7 MECHANICAL AND TRIBOLOGICAL TESTING

One of the major objectives of this research is to determine the mechanical properties (hardness, wear, stiffness, modulus of elasticity and creep, etc.) of deposited samples; and as such, mechanical tests are essential in determining these properties.

3.7.1 Hardness

The hardness of a material can be referred to as the resistance of the material to indentation from another material that is usually harder. As such, hardness is mainly associated with the elastic and plastic properties; and it is not a fundamental property. Hardness is normally defined in respect of the specific test employed in obtaining its value. Sample preparation and the test procedure in hardness are normally easy. Resistance to indentation is a test mainly executed through impressing an indenter under an identified load into a specimen that is positioned on a fixed stage. Popular techniques of hardness-test indentation are briefly discussed below.

1. Brinell hardness test: The tester mainly consists of vertical press that has been designed to drive a ball indenter into a test sample. According to the standard procedure, it is necessary that the test be carried out by using a 10mm diameter ball with a load under 3000kg for ferrous metals and 500kg for non-ferrous metals. It is also important to note that for ferrous metals, the ball under the load is only pressed into the test sample for not less than 10s; and that of non-ferrous metals is 30s (Avner 2005). The Brinell hardness test is popularly employed on large specimens or work-pieces (like cast or forged pieces) having coarse structures that are not homogeneous. The test description can be found in ASTM E10 standards (ASTM International 2015). The Brinell hardness number (HB) is
given as the ratio of the applied load to the impressed area. This is expressed mathematically in Equation 3.2.

\[ HB = \frac{L}{\pi \left( \frac{D}{2} \right)^2 \left( D - \sqrt{D^2 - d^2} \right)} \]  

\text{eqn. 3.2 (Avner 2005)}

Where, \( L \) = the test load (kg)

\( D \) = the diameter of the ball (mm)

\( d \) = the diameter of the impression (mm)

2. The Rockwell hardness test: This employs a straightforward reading instrument, which is founded on the differential depth-measurement principle. The sample in the test is normally carried out by gently lifting the test sample against the indenter until the time a small stationary load is applied, which is shown on a dial gauge. The lever system is then made use of to apply the main load. The main load is withdrawn after the dial pointer has come to rest. The value of the Rockwell hardness (HR) is then read on the dial gauge. A slight impression on a hard sample will result in a high Rockwell number; while a heavy impression on a soft sample would result in a low Rockwell number; because of the way the numbers on the dial gauge have been arranged in a reverse fashion. The standards for the Rockwell hardness test are available in ASTM E18 and ISO 6508 (ASTM International 2017b).

3. The Vickers hardness test: A diamond-pyramid indenter is used in the Vickers hardness test. The Vickers hardness tester uses the same principle as that which the Brinell hardness tester is based, where-by the number is determined by the load and the area of impression. Because of the shape of the indenter, the impression created on the surface of the test specimen is normally square or
rhombic-like. The ocular microscope with moveable knife edges that have been fitted to a microscope is used to measure the length of the diagonal of the indentation. A counter that has been calibrated in millimetres displays the distance between the knife edges. The conversion of the measured diagonal to the Vickers hardness number is done by using standard tables. However, the recent Vickers hardness tester now provides the ability of displaying directly the Vickers hardness number (HV) of the test specimen. Standards on the Vickers hardness are available in ASTM E384 (ASTM International 2017a). The standard formula used in the determination of the Vickers hardness tester (HV) is given, as represented in equation 3.3.

\[ HV = \frac{1.854L}{d^2} \] ........................ eqn. 3.3 (Avner 2005)

Where, \( L \) = the applied load (kg)

\( d \) = the diagonal length of the impression (mm)

4. Microhardness test: Sometimes the microhardness terms used might be misleading; as they could be taken to mean the test to determine the hardness of small values; while it actually refers to the use of small indentations. The square-based diamond pyramid Vickers tester and elongated Knoop diamond indenter are the main types of indenters used for the microhardness testing. The Knoop hardness method has been created as an alternative to the Vickers hardness test, in order to be able to determine the hardness in coatings and thin layers; and to prevent cracks in brittle materials. The load divided by the area of the indentation is used to determine the Knoop number. Standards in describing this hardness test are available in ASTM E384, ISO 4545 and JIS Z 2251 (ASTM
International 2017a). Standard tables are also available to convert the measured diagonal to the Knoop hardness number. Sometimes, the Knoop hardness number (HK) can also be determined from the Equation 3.4.

\[ HK = \frac{14.229L}{d^2} \]  

[eqn. 3.4 (Avner 2005)]

Where:
- \( L \) = the applied load (kg)
- \( d \) = the length of the long diagonal (mm)

### 3.7.2 Indentation hardness test accuracy

The accuracy of indentation-hardness tests is dependent on some factors. These factors, such as the condition of the indenter, the accuracy of the load applied, the condition/surface of the specimen, the specimen thickness, the shape of the specimen, the impression location and the material uniformity all have a significant influence on the accuracy of the hardness values.

The degree of accuracy needed and the ease of performance are used in the selection of the hardness test. Big impressions normally created by the Brinell test, limit its usage to heavy sections. The surface of the specimen does not necessarily need to be smooth; as this is normally required for small impressions. Nevertheless, the measurement of the impression diameters is not easy with the microscope; since this requires using the dial gauge. The deformation of steel ball also affects the accuracy of the Brinell hardness tester. The Rockwell hardness tester may be employed on smaller sections; since the load and the indenter are smaller than those in the Brinell test. This makes it possible to test hard and soft materials. The most sensitive is the Vickers hardness tester; as it almost independent of the load; and it uses a single continuous scale for different types of materials. It has the ability to test thinner sections than with
other hardness testers; and the square indentations created by the Vickers tester are much easier to measure accurately. The microhardness test uses very small loads, which make it possible to test thinner sections and very small parts.

In this research, the microhardness of the samples was conducted by using the TIME digital microhardness tester. The microhardness profiling was conducted with a Test force of 4.9N (500 gf) and a dwelling time of 15 seconds, from which the microhardness results were obtained. The space between the indentations was observed at a distance of 0.15 mm. Microhardness indentations were conducted right from the top of the deposits via the fusion zone (FZ) into the substrate region; and indentation tests close to the surface of the deposits were also conducted.

The Vicker’s hardness (VHN) can be calculated from the diagonal length of the diamond indentations. These are represented as D1 and D2, by using the expression in equation 3.5. The average hardness of each samples was calculated from ten hardness indentation results obtained.

\[
VHN = 1854.4 \left( \frac{P}{D^2} \right) \quad \text{Eqn. 3.5}
\]

Where, \( P \) is the applied load (N); and \( D \) is the average of the indentation diagonals (D1 and D2) (µm).

The hardness of some samples was also determined with the aid of an Anton Paar indentation (7.3.15) equipment. The indentation stress-strain curve relationship can be obtained from Tabor’s theory (Tabor 2000).

The indentation area is related to the indentation radius, with the expression in equation 3.6.
\[ A = \pi a^2 = \pi \left(2Rh_c - h_c^2\right) \] Eqn. 3.6

Where, \( A \) is the indentation area; \( a \) is the indentation radius, \( R \) is the indenter radius and \( h_c \) is the contact depth.

Hertz (1896) came up with an expression for an elastic contact of an elastically isotropic material to be:

\[ a = \left(\frac{3PR}{4E_r^2}\right)^{1/3} \] Eqn. 3.7

Where \( a \) is the contact radius, \( P \) is applied load, \( R \) is indenter radius and \( E_r \) is reduced elastic modulus. To obtain the elastic modulus \( (E) \), equation 3.8 is used.

\[ E = 1 - v^2 / \left(\frac{1}{E_r} - \frac{1-v_i^2}{E_i}\right) \] Eqn. 3.8

Where \( E, E_i \) and \( v, v_i \) are the elastic modulus and Poisson’s ratio of specimen and diamond indenter respectively.

The indentation stress is presented as mean contact pressure (Tabor 2000) and expressed as:

\[ P_m = \frac{P}{A} \] Eqn. 3.9

Where \( P_m \) is indentation stress, \( P \) is applied load and \( A \) is indentation area.

Merging Tabor, Meyer and Hertz theory, gives the expression in equation 3.10.

\[ P_m = \left(\frac{4E_r}{3\pi}\right) \times \frac{a}{R} \] Eqn. 3.10

This expression represents elastic and elastoplastic regimes where stress at which yielding \( (\sigma_y) \) takes place can be experimentally predicted (Padilla et al. 2015).

Indentation strain \( (\varepsilon) \) can be quantified as:
\[ \varepsilon = 0.2 \left( \frac{a}{R} \right) \] \hspace{2cm} \text{Eqn. 3.11}

The stress and hardness can be expressed as:

\[ P_m = H = 3\sigma \] \hspace{2cm} \text{Eqn. 3.12}

Ten different indentations were performed on each sample using applied load of 5 mN, loading and unloading rate of 30 mN/min, and pause of 1200 s. Then the average hardness of each sample was calculated.

Young’s modulus or modulus of elasticity is another property that can be determined from a tensile test. It is proportionality constant between stress and strain. It is also indicate material stiffness. Because of this attribute, the modulus of elasticity remains an important engineering property and normally comes to mind where stiffness is relevant especially in the design of columns and beams. The Young’s modulus of deposited samples are obtained using the Anton Paar indentation testing equipment using a load of 5 mN, loading and unloading rate of 30 mN/min and pause of 1200 s.

### 3.7.3 Creep test

The creep test is used to determine continuous change in the deformation of material at elevated temperature. This test is carried out at a stress below the yield strength of the material. The test is essential in the design of machine components that will be subjected to elevated temperatures. The safe operating life of components are determined through good understanding of their creep strain, which guarantee that the extreme deformation of components does not take place during the components service life (Harrison et al. 2014). It is important to also note that creep also occurs at room temperature in some materials. Creep rate of a material is the measure of the rate of
deformation and represented with a slope of a line in creep strain versus time curve (Illinois Institute of Technology 2013) as shown in Figure: 3.7.

![Creep strain vs Time curve](image)

Figure: 3.7: Creep strain vs Time curve (Illinois Institute of Technology 2013)

The different stages of creep are shown in the creep strain versus time curve above. There is usually an instantaneous elastic elongation as the load is firstly applied after which a primary stage where slip and work hardening occurs most especially in most oriented grains. A steady state creep occurs at the secondary stage where deformation continues at a relatively constant rate. In some instance, the creep rate may continue to decrease at slow rate at this stage for a long period. However, if the stress is high enough, the tertiary stage set in. At this stage, the creep rate accelerates until the material breaks or ruptures. Basically, the creep rate of a material reduces as the grain size increases (Illinois Institute of Technology 2013; Avner 2005).

Creep is regarded as the relative change of indentation depth at constant test force. In this particular work, using the Anton Paar instrumentation machine earlier mentioned,
the creep experienced by samples at ambient temperature are measured during pause at maximum force and calculated from the graph of indentation depth-time plots. The indentation creep, $C_{II}$ is obtained from the relationship in equation 3.13.

$$C_{II} = \frac{h_2 - h_1}{h_1} \quad \text{Eqn. 3.13}$$

Where the parameters are defined in Figure: 3.8 Anton Paar.

![Figure: 3.8: Evaluating Indentation creep](image)

### 3.7.4 Wear

Wear may be regarded as unintended deterioration that results from environment or use (Avner 2005). Sliding wear characteristics is one of the main factors of concern in manufacturing components (Ogunlana & Akinlabi 2016). For most metal products, the surface deterioration is one of the most important factors that need to be investigated to determine the quality of such metal products. This surface deterioration is one of the most important factors that tend to reduce the performance and the life of the machine.
components. This deteriorating effect resulting from wear makes the importance of wear resistance paramount in determining the quality of metal products.

The surface removal or displacement of metallic particles from a metal may result from:

- Contact with another metal, which is normally termed as metallic or adhesive wear
- Contact with either metallic or non-metallic abrasives, which is termed abrasion; or
- Contact with moving gases or liquids that is normally referred to as erosion. This is normally associated with some type of corrosion.

Ways and actions by which wear can be checkmated are: to prevent metal-to-metal contact, by increasing the hardness, in order to prevent indentation from occurring, and improving toughness and surface smoothness. Wear can be prevented by using different methods and materials. Selecting materials and processes, to be used to prevent wear, requires a proper understanding of applicability, limitations, the cost involved and the service conditions of the material. Some of the methods that can be used to prevent wear include: metal spraying, anodizing, electroplating, diffusion and selective heat treatment. The wear resistance of materials can be determined by using standard tests. The equipment used in testing wear resistance is normally designed to simulate real service conditions. For tests with fixed a specimen, the wear rate reduces with number of times the ball passes over same track; because of the degradation of abrasives (Axén et al. 2000).

For wear tests to be carried out, the Anton Paar (version 7.3.13) standard tribometer was used to carry out the pin-on-disc reciprocating wear test. The tribometer uses a 6
mm diameter stainless steel ball. Before the test, the weight of each sample is measured by using a digital measuring scale. After the test, the test samples were re-measured to determine the amount of wear loss. The test was carried out with a load of 10 N over a time period of 600 seconds; and the acquisition rate (the frequency) was maintained at 100 Hz. The coefficient of friction of each sample was generated from the test. The wear loss and the wear rate of the samples were calculated by using the Equation 3.14 and Equation 3.15 (Qu & Truhan 2006). The wear volume and the wear rate can also be obtained from Equation 3.16 and Equation 3.17 (Ogunlana & Akinlabi 2016). From the calculated result, the wear volume and the wear rate of each deposited sample can be established.

\[ W_l = L_k \left[ \frac{W}{2R_p} \sin^{-1}\left( \frac{W}{2R_p} \right) - \frac{W}{2}\left( R_p - W_d \right) \right] + \frac{\pi}{3} W_d^2 \left( 3R_p - W_d \right) \quad \text{......... Eqn. 3.14} \]

\[ W_d = R_p - \sqrt{R_p^2 - \frac{W^2}{4}} \quad \text{.............................................................. Eqn. 3.15} \]

Where, \( W_l \) is the wear loss; \( W_d \) is the wear depth; \( L_k \) is the stroke length; \( R_p \) is the pitch radius and \( W \) is the wear scar width.

\[ \frac{V}{S} = K \left( \frac{F_N}{H} \right) \quad \text{................................................................. Eqn. 3.16} \]

\[ K = \frac{V}{F_N+S} \quad \text{................................................................. Eqn. 3.17} \]

Where, \( V \) is the wear volume (mm\(^3\)); \( S \) is the sliding distance (mm); \( K \) is the wear rate (mm\(^3\)/Nm); \( F_N \) is load applied (N); and \( H \) is the hardness of the material (Hv).

3.7.5 Corrosion and electrochemical testing

Generally, the interaction between a material and the environment leading to the material destruction is termed as corrosion. The interaction may be in the form of
chemical, electrochemical or metallurgical. Base on the electrochemical principle, corrosion is regarded as an electrochemical process that results in part or the total transformation of a metal into an ionic state (Avner 2005).

Generally, corrosion occurs when there is an electrical flow in an electrolyte in which a metal surface has been exposed. The electrolyte may be in the form of just ordinary water, salt water or a concentration of acidic or alkaline solution. The presence of electrodes (cathode and anode) that may be of dissimilar metals or separate areas on same metal complete the electric circuit for corrosion to take place. Ordinarily, connection between the cathode and the anode is made possible by simple contact but can also be achievable through a metallic bridge. However, electrical flow can only occur though the existence of potential difference between the electrodes.

Over the years, corrosion has often been classified into various types. Uniform corrosion is said to have resulted, when all metal surface have been attacked equally or at same level of corrosion. However, such level of attack is not common as it is very rare to see metal surface being corroded evenly. Pitting is a type of corrosion that is regarded as non-uniform corrosion that does emerge from inhomogeneity in metal as a result of coring, inclusions and distorted zones. The inhomogeneity creates potential differences and localized spots which results to the creation of deep isolated holes. Cavitation corrosion result from crevities and the collapsing action of bubbles within liquid. Vibration motion between surfaces and liquid causes a surface to be subjected to continuous loads. This motion creates high stresses, which causes bubbles to be formed and collapse, thereby creating huge impact stresses which result in the removal of particles from surfaces leading to the creation of deep pits and depressions. Another
type is crevice corrosion which can also be regarded as accelerated attack which occurs between the boundaries of two metals that have been introduced into a corrosive environment. Fretting corrosion is a surface damage resulting from vibration. The vibration results in the robbing or striking at the boundaries of highly loaded or close fit surfaces.

Intergranular corrosion is a type of non-uniform corrosion that resulted from potential difference between grain boundaries and other parts of an alloy. These differs from stress corrosion, as stress corrosion occurs in an environment when metals has internal tensile stresses caused by cold working or when they have been stressed externally. These may results to cracks in the form of intergranular, triangular or a mixture of both. The stresses that will result in stress corrosion highly depend on the structure of base metal and the corrosive medium. Other form of corrosion is galvanic corrosion which results when two metals surfaces in contact are expose to a corrosive medium.

A Potentiostat DY2300 was used to conduct an electro chemical test to figure out the corrosion resistance of the TiAl deposited samples in 3.5 % NaCl solution. The tests were conducted on well prepared surfaces parallel to the build direction such as the sample shown in Figure: 3.6 (c). The experimental set up is shown in Figure: 3.9. The terminal in black colour from the Potentiostat is connected to the sample to be tested and immersed in the solution. The white terminal is connected to a reference electrode. At this point the open circuit potential (OCP) is determined in one hour. After which the counter electrode (in red) was introduced into the system to determine the polarization by setting the system to linear sweep voltammetry (LSV) and initial potential for OCP
lower limit (OCP-0.25) and OCP higher limit (OCP+0.25) were inputted to run the experimental process. At the end of the process, the atomic weight and atomic density (calculated using the values from Table: 3.7, equation 3.18 and equation 3.19) and the surface area of tested sample were inputted to generate the corrosion rate results of tested samples.

Table: 3.7: Titanium aluminide Powder constituent’s elements and percentages compositions.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Elements</th>
<th>Atomic weight of elements</th>
<th>Density of elements (g/cm^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Percentage composition (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>58.8</td>
<td>47.86</td>
<td>4.506</td>
</tr>
<tr>
<td>Aluminium (Al)</td>
<td>34.0</td>
<td>26.981</td>
<td>2.70</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>2.6</td>
<td>51.996</td>
<td>7.19</td>
</tr>
<tr>
<td>Niobium (Nb)</td>
<td>4.6</td>
<td>92.906</td>
<td>8.57</td>
</tr>
</tbody>
</table>

\[
AW_{Total} = \left(\frac{PC_{of\ Ti}}{100}\times AW_{of\ Ti}\right) + \left(\frac{PC_{of\ Al}}{100}\times AW_{of\ Al}\right) + \left(\frac{PC_{of\ Cr}}{100}\times AW_{of\ Cr}\right) + \left(\frac{PC_{of\ Nb}}{100}\times AW_{of\ Nb}\right)
\]

…………………………………. eqn. 3.18

Where, \( AW_{Total} \) is the Total atomic weight of titanium aluminide; \( AW \) is the Atomic weight of the element and \( PC \) is the percentage composition of the element.

\[
DT_{Total} = \left(\frac{PC_{of\ Ti}}{100}\times D_{of\ Ti}\right) + \left(\frac{PC_{of\ Al}}{100}\times D_{of\ Al}\right) + \left(\frac{PC_{of\ Cr}}{100}\times D_{of\ Cr}\right) + \left(\frac{PC_{of\ Nb}}{100}\times D_{of\ Nb}\right)
\]

…………………………………. eqn. 3.19
Where, \( D_{Total} \) is the Total density of titanium aluminide; and \( D \) is the density of the element; and \( PC \) is the percentage composition of the element.

3.8 MODELLING AND SIMULATION OF EXHAUST VALVE

Modelling and simulation of engineering components helps to give an idea on how engineering components react in a certain environment, or when they are subjected to specific loads. Simulations to study the ability and the strength of the components and structures have often been utilized to improve or optimise engineering components and structures, as witnessed in the literature (Gawale & Shelke 2016; Dahlan et al. 2017; Abdulkarim et al. 2017; Yahaya & Abdulrahman 2018).
The valve system controls the timing in the opening and closing of the intake and the exhaust stroke (Dahlan et al. 2017). The exhaust valve is regarded as an important component of an internal combustion engine; since it provides the path from which the exhaust gases produced in the combustion chamber are expelled (Gawale & Shelke 2016). The exhaust valve is often subjected to different kinds of stresses (like axial stresses due to the exhaust gas pressure, thermal stresses because of the high temperature in the combustion chamber; and cyclic stresses because of the return spring load) during the engine's operation.

There are mainly two varieties of steel (martensitic and austenitic) used in production (Carley 2015). The difference between the two lies in the micro-structures of the steels; and how other elements in the alloys interact when cast and cooled as its affect the hardness, strength and corrosion resistance of the steel. In Martensitic steel, the steel is quenched very fast from its molten state to solidify to a needle-like (acicular) grain structure. This structure makes the alloy hard and brittle. Reheating and cooling of the steel alloy rearranges the structure to give steels that are less hard and brittle. The hardness at room temperature (35 to 55 HR), improves the strength and the wear-resistance of such steels, thereby making them preferred for engine valves. However, temperature increase reduces the hardness and the strength of martensitic steels. This makes them to be mainly used as intake valves; since exhaust valves operate at about 650 to 790 °C or even higher.

The austenitic steel alloys (like 21-2N and 21-4N) are mostly used as exhaust valves. The austenitic alloy steels are much stronger at high temperatures, at which parts like exhaust valves work. High strength nickel-chromium-iron alloys, stainless
steel, carbon-steel alloys and titanium are materials that can be utilized for valve applications. Titanium is mostly seen as a superior valve-alloy material, due to its good strength-to-weight ratio and its durability close to that of stainless steel. However, titanium valves are more expensive (Carley 2015).

In this work, exhaust valves were modelled according to specifications obtained in Autozone, as shown in Figure: 3.10, and simulated for both buckling and thermal analysis by using a customised material developed from the mechanical properties obtained from tests carried out on deposited samples. The simulation result with Ti-4822-4 deposited material is compared with another titanium alloy material (Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si) in the software-data base, in order to determine how suitable the deposited material is for such high-temperature applications.

Figure: 3.10: Valve design (Autozone n.d.)
3.9 SUMMARY

A thorough research to manufacture TiAl-Ti composites via the laser-metal deposition technique using TiAl powder shielded by a gas and deposited in a melt-pool of pure titanium substrate has been carried out. This provides us with the ability to fabricate and examine the micro-structure and the mechanical properties of the composite produced, with the aim of establishing the influence of preheating temperatures and the processing parameters on the properties of the composite. This chapter has presented the experimental technique and set-ups that have been utilized for this study. The metallographic test performed included: SEM/EDX, XRD, as well as the optical microscopy (OP) test. The mechanical tests conducted included wear and hardness (nano and micro), creep, the modulus of elasticity, and lastly the electrochemical (corrosion) test. The results of the tests carried out are presented in Chapter Four. This Chapter Four also highlights the importance of modelling and the simulation of engineering components, as well as and the role played by materials in engineering applications, especially high-temperature applications and components, such as the exhaust valve.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 INTRODUCTION

In this chapter, the outcomes from the work conducted have been broken down into several sections, just as in the preceding chapter. The first section outlines some of the physical characteristics of the deposited samples. The second section discusses the microhardness results and the trend in the deposited samples. The third section discusses the microstructure and EDX results for the deposited samples. In the fourth section, the analysis of the XRD results obtained was discussed. Wear test outcomes and corrosion results were discussed in the fifth section. The final section discusses the outcome of Nano-indentation experiments carried out to further determine the hardness of the deposited material and their mechanical properties, as regards the modulus of elasticity, stiffness and creep.

4.1 PHYSICAL DESCRIPTION OF THE DEPOSITED SAMPLES

This section looked at the physical characteristics of the deposited samples. The physical characteristics, as regards the shape of the samples, the height of samples, as well as any visible cracks, and (or) burning or discolouration that may be observed on the deposited samples. The deposits (shown in Figure: 4.1, Figure: 4.2 and Figure: 4.3) were fabricated by depositing the titanium aluminide powder onto a pure titanium (CP-Ti) substrate by varying the various parameters, as highlighted earlier in Chapter 3.

From Figure: 4.1, it was noted that as the laser power increases, there was a corresponding increase in the heat-affected area on the substrate, which can be clearly
identified by the discoloration around the areas of the deposit. A similar scenario was also noted in Figure: 4.2 and partially in Figure: 4.3. The increase in the laser power and decrease in the scanning speed causes a progressive increase in discolouration (surface burning) in the deposits, as can be clearly seen. This can arguably occur because an increase in the laser power, or a decrease in the scanning speed has led to a corresponding increase in the input energy in the deposition process.

Looking at the depositions closely with the naked eye, some of the depositions displayed visible cracks. For the unpreheated samples, there are reductions in the cracks that can be seen as the laser power increases in samples (like UA1, UA2 and UA3). As the scanning speed increases, the amount of visible cracks seen becomes more prominent in samples UB2, UB3 and UB4. As the powder-flow rate increases, cracks were increase; and these could be observed in samples UC3, UC4 and UC5.
Similar occurrences were seen on the heating bed of the preheated samples. Cracks seen on samples reduce as the laser power increases; and they are also reduced as the scanning speed reduces. Visible cracks were seen on H1 and H3. However, for the laser-preheated samples, only sample LA1 clearly showed visible cracks on inspection.

Cracks in the deposited samples are normally attributed to the high amount of thermally induced stress created during the deposition process (Perevoshchikova et al. 2017). The reason for the crack trend observed can be linked to the fact that as the input energy (ratio of laser power to scanning speed) increases, the crack frequency also decreases (Liu & Dupont 2004). This is because the cooling rate is inversely proportional to the heat input from the laser (Kou 1987). As such, the reduced crack frequency noted at higher laser power can be attributed to the cooling rate of the deposits. An increase in the crack susceptibility of the deposits is more likely to happen at higher cooling rates.

The cooling rate at the lower laser power is normally greater than that at higher laser power. This is because, at high laser power, more melt pool is produced, which takes more time to solidify. This larger melt pool is also what is responsible for the increase in the height of the deposition. A smaller melt pool created at the lower laser power, easily undergoes rapid solidification; and therefore, this responsible for the cracks. Most of the work carried out on laser deposition, focused more on the need to provide additional heating system to achieve crack-free deposits (Sharman et al. 2018). Therefore, a way of eliminating or drastically reducing the cracks in a deposition process would be by careful regulation of the process parameters, and by preheating to
reduce the temperature gradient between the substrate and the deposits in the deposition process.

Figure: 4.2: (a) Samples deposited with laser preheating (b) Schematic diagram of marked samples with laser preheating

Figure: 4.3: (a) Samples deposited with heating bed preheating (b) Schematic diagram of marked samples with heating bed preheating
The outcome of the deposits’ height after measurement with a digital caliper revealed largely that any increase in the laser power, decrease in scanning speed or an increase in the powder-flow rate led to a corresponding increase in the height of the deposits. This can also be linked to the fact, as earlier explained, that as the laser power increases or the scanning speed decreases, more melt pool is created by the laser, which later solidified; and this translates to a consistent increase in the height of the deposit. An increase in the powder-flow rate, allows for more powder to be fed into the process, which also translates to the slight increase in the height observed.

The results of the height and the microhardness of the deposits were analyzed in a design expert 6.0.8 environment, as earlier mentioned in Chapter 3. Table: 4.1, Table: 4.5 and Table: 4.9 give the heights and the microhardness values of the deposited samples.

Table: 4.1: Outcome of processing parameters on heights and Microhardness of unpreheated samples

<table>
<thead>
<tr>
<th>Sample serial order</th>
<th>Factor 1 A: Laser power (W)</th>
<th>Factor 2 B: Scanning speed (mm/s)</th>
<th>Factor 3 C: Powder flow rate (g/min)</th>
<th>Response 1 Microhardness (Hv)</th>
<th>Response 2 Deposit height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>3.17</td>
<td>4.09</td>
<td>441.26</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>350</td>
<td>3.17</td>
<td>4.09</td>
<td>451.3</td>
<td>4.5</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>3.17</td>
<td>4.09</td>
<td>463.66</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>450</td>
<td>3.17</td>
<td>4.09</td>
<td>460.27</td>
<td>6.3</td>
</tr>
<tr>
<td>5</td>
<td>500</td>
<td>3.17</td>
<td>4.09</td>
<td>475.99</td>
<td>6.6</td>
</tr>
<tr>
<td>6</td>
<td>400</td>
<td>3.17</td>
<td>4.09</td>
<td>463.66</td>
<td>4.9</td>
</tr>
<tr>
<td>7</td>
<td>400</td>
<td>4.23</td>
<td>4.09</td>
<td>409.72</td>
<td>4.6</td>
</tr>
<tr>
<td>8</td>
<td>400</td>
<td>5.29</td>
<td>4.09</td>
<td>435.72</td>
<td>3.9</td>
</tr>
<tr>
<td>9</td>
<td>400</td>
<td>6.35</td>
<td>4.09</td>
<td>492.04</td>
<td>3.6</td>
</tr>
<tr>
<td>10</td>
<td>400</td>
<td>7.41</td>
<td>4.09</td>
<td>499.26</td>
<td>3.3</td>
</tr>
<tr>
<td>11</td>
<td>400</td>
<td>4.23</td>
<td>4.09</td>
<td>409.72</td>
<td>4.6</td>
</tr>
<tr>
<td>12</td>
<td>400</td>
<td>4.23</td>
<td>4.85</td>
<td>518.81</td>
<td>5.8</td>
</tr>
<tr>
<td>13</td>
<td>400</td>
<td>4.23</td>
<td>5.67</td>
<td>538.36</td>
<td>5.6</td>
</tr>
<tr>
<td>14</td>
<td>400</td>
<td>4.23</td>
<td>6.38</td>
<td>542.48</td>
<td>5.3</td>
</tr>
<tr>
<td>15</td>
<td>400</td>
<td>4.23</td>
<td>7.12</td>
<td>526.22</td>
<td>5.1</td>
</tr>
</tbody>
</table>
4.1.1 Analysis of unpreheated deposited samples with regard to Deposition height

The analysis of variance (ANOVA) for the height of the un-preheated samples is presented in Table: 4.2. The model F value of 23.88 indicates that the model is significant. There is only a 0.01% chance that a “Model F-Value” this huge could occur due to noise. Values of “Prob > F” less than 0.05, shows that the model terms are significant. In this particular case, A, B and C are all significant model terms. Values greater than 0.1, indicate that the model terms are not significant.

The coefficient of determinant in Table: 4.3, “R-squared” represents the coefficient of determination, which can range between 0 and 1. The “Pred R-squared” of 0.7712 is in reasonable agreement with the “Adj R-squared” of 0.8306. “Adeq precision” measures the signal-to-noise ratio. A ratio greater than 4 is normally desirable. The ratio of 16.971 shows an adequate signal; and the model can be used to navigate the design space.

Table: 4.4 gives estimates of the coefficient at the 95% confidence level. The final equation of the model in terms of coded factors is presented in Equation 4.1

\[
Deposit\ height = 4.62 + (1.4 \times A) - (1.02 \times B) + (0.40 \times C) \ldots \ldots \ldots \ldots \ldots \ldots \ldots eqn. \ 4.1
\]

Where, \(A\) is the Laser power, \(B\) is the laser scanning; and \(C\) is the powder flow rate.
Table: 4.2: Analysis of variance (ANOVA) table for the height of the un-preheated samples

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>11.04</td>
<td>3</td>
<td>3.68</td>
<td>23.88</td>
<td>&lt; 0.0001 Significant</td>
</tr>
<tr>
<td>A-Laser power</td>
<td>4.90</td>
<td>1</td>
<td>4.90</td>
<td>31.80</td>
<td>&lt; 0.0002</td>
</tr>
<tr>
<td>B-Scanning Speed</td>
<td>5.2</td>
<td>1</td>
<td>5.2</td>
<td>33.76</td>
<td>0.0001</td>
</tr>
<tr>
<td>C-Powder flow rate</td>
<td>0.94</td>
<td>1</td>
<td>0.94</td>
<td>6.08</td>
<td>0.0314</td>
</tr>
<tr>
<td>Residual</td>
<td>1.69</td>
<td>11</td>
<td>0.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>1.69</td>
<td>9</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>12.73</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table: 4.3: Coefficient of determinant for height of the un-preheated samples

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>R-Squared</th>
<th>0.8669</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>4.87</td>
<td>0.8306</td>
</tr>
<tr>
<td>C.V.</td>
<td>8.07</td>
<td>0.7712</td>
</tr>
<tr>
<td>PRESS</td>
<td>2.91</td>
<td>16.971</td>
</tr>
</tbody>
</table>

Table: 4.4: Estimates of the coefficient for the height of the un-preheated sample

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient Estimate</th>
<th>DF</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>4.62</td>
<td>1</td>
<td>0.17</td>
<td>4.24</td>
<td>5.00</td>
<td></td>
</tr>
<tr>
<td>A-Laser power</td>
<td>1.40</td>
<td>1</td>
<td>0.25</td>
<td>0.85</td>
<td>1.95</td>
<td>1</td>
</tr>
<tr>
<td>B-Scanning speed</td>
<td>-1.02</td>
<td>1</td>
<td>0.18</td>
<td>-1.41</td>
<td>-0.63</td>
<td>1</td>
</tr>
<tr>
<td>C-Powder flow rate</td>
<td>0.40</td>
<td>1</td>
<td>0.16</td>
<td>0.043</td>
<td>0.75</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure: 4.4 shows the graphical analysis of the residuals. The residuals are randomly distributed, which is quite desirable. A graph of the predicted deposit height-to-actual experimental deposit height is shown in Figure: 4.5. The model also shows well-distributed data, with some of the data in agreement with one another.
Figure: 4.4: Graph of normal plot of residuals

Figure: 4.5: Graph of predicted against actual experimental data
The surface plot of the deposits height against the laser power and the scanning speed is shown in Figure: 4.6. Also, the surface plot of the deposit height against the scanning speed and the powder-flow rate is shown in Figure: 4.7. The surface plots show the strong interaction between the deposit height, the laser power, and the scanning speed and powder-flow rate.

As the laser power increases, or the scanning speed decreases, the deposits’ height increases. Likewise, the increase in the powder flow rate, also led to a considerable increase in the height of deposits. The trends witnessed in the increase in the height of the deposits is mainly due to the greater melt pool created, which allows it to trap more powder, as the laser-power increases, the scanning speed decreases and the powder-flow rate increases.

Figure: 4.6: Surface plot of Deposits height against laser power and scanning speed
Figure: 4.7: Surface plot of Deposits height against scanning speed and powder-flow rate

Table: 4.5: Outcome of the processing parameters on heights and the Microhardness of the laser-preheated samples.

<table>
<thead>
<tr>
<th>Sample serial order</th>
<th>Factor 1 A: Laser power (W)</th>
<th>Factor 2 B: Scanning speed (mm/s)</th>
<th>Factor 3 C: Powder flow rate (g/min)</th>
<th>Response 1 Microhardness (Hv)</th>
<th>Response 2 Deposit height (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>10.58</td>
<td>4.09</td>
<td>425.09</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>10.58</td>
<td>4.09</td>
<td>382.23</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>10.58</td>
<td>4.09</td>
<td>380.48</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>500</td>
<td>10.58</td>
<td>4.09</td>
<td>381.44</td>
<td>5.4</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
<td>10.58</td>
<td>4.09</td>
<td>373.11</td>
<td>6.2</td>
</tr>
<tr>
<td>6</td>
<td>300</td>
<td>10.58</td>
<td>4.09</td>
<td>382.23</td>
<td>2.6</td>
</tr>
<tr>
<td>7</td>
<td>300</td>
<td>9.52</td>
<td>4.09</td>
<td>391.08</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>300</td>
<td>8.46</td>
<td>4.09</td>
<td>382.7</td>
<td>3.7</td>
</tr>
<tr>
<td>9</td>
<td>300</td>
<td>7.41</td>
<td>4.09</td>
<td>388.58</td>
<td>4.4</td>
</tr>
<tr>
<td>10</td>
<td>300</td>
<td>6.38</td>
<td>4.09</td>
<td>364.31</td>
<td>5.2</td>
</tr>
<tr>
<td>11</td>
<td>300</td>
<td>10.58</td>
<td>3.49</td>
<td>395.75</td>
<td>2.3</td>
</tr>
<tr>
<td>12</td>
<td>300</td>
<td>10.58</td>
<td>4.09</td>
<td>382.23</td>
<td>2.6</td>
</tr>
<tr>
<td>13</td>
<td>300</td>
<td>10.58</td>
<td>4.85</td>
<td>390.96</td>
<td>3.9</td>
</tr>
<tr>
<td>14</td>
<td>300</td>
<td>10.58</td>
<td>5.67</td>
<td>390.01</td>
<td>4.2</td>
</tr>
<tr>
<td>15</td>
<td>300</td>
<td>10.58</td>
<td>6.38</td>
<td>387.52</td>
<td>4.8</td>
</tr>
</tbody>
</table>
4.1.2 Analysis of laser preheated deposited samples as regards Deposition height

The analysis of variance (ANOVA) for the height of the laser-preheated samples is presented in

Table: 4.6. The model F value of 162.95 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" this huge could occur due to noise. Values of "Prob > F" less than 0.05, show that the model terms are significant. As such, in this case, A, B and C are all significant model terms and values greater than 0.1; and this indicates that the model terms are not significant.

The coefficient of determinant in Table: 4.7, “R-squared” represents the coefficient of determination, which can range between 0 and 1. The “Pred R-squared” of 0.9568 is in reasonable agreement with the “Adj R-squared” value of 0.972. This is because the difference between the two values is less than 0.2 (Mahamood et al. 2015). For “Adeq Precision,” which measures the signal-to-noise ratio, a ratio greater than 4 is normally desirable. An “Adeq Precision” of 42.616 shows an adequate signal and the model can be used to navigate design space. Table: 4.8 gives the estimates of coefficient at the 95% confidence level. The final equation of the model in terms of coded factors is presented in Equation 4.2

\[
Deposit \ height = 5.93 + (2.48 \times A) - (1.21 \times B) + (1.41 \times C) \quad ................. \ eqn. \ 4.2
\]

Where, A is Laser power, B is laser scanning and C is the powder-flow rate.
Table: 4.6: Analysis of variance (ANOVA) table for height of the laser-preheated samples

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob&gt;F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>24.80</td>
<td>3</td>
<td>8.27</td>
<td>162.95</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>A</td>
<td>19.11</td>
<td>1</td>
<td>19.11</td>
<td>376.77</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>B</td>
<td>7.72</td>
<td>1</td>
<td>7.72</td>
<td>152.18</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>C</td>
<td>6.74</td>
<td>1</td>
<td>6.74</td>
<td>132.83</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Residual</td>
<td>0.56</td>
<td>11</td>
<td>0.051</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>0.56</td>
<td>9</td>
<td>0.062</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>25.36</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table: 4.7: Coefficient of determinant for height of preheated samples

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>R-Squared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.23</td>
</tr>
<tr>
<td>C.V.</td>
<td>6.02</td>
</tr>
<tr>
<td>PRESS</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Table: 4.8: Estimates of coefficient of height of preheated samples

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient Estimate</th>
<th>DF</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>5.93</td>
<td>1</td>
<td>0.12</td>
<td>5.66</td>
<td>6.21</td>
<td></td>
</tr>
<tr>
<td>A-Laser power</td>
<td>2.48</td>
<td>1</td>
<td>0.13</td>
<td>2.20</td>
<td>2.76</td>
<td>1.07</td>
</tr>
<tr>
<td>B-Scanning speed</td>
<td>-1.21</td>
<td>1</td>
<td>0.098</td>
<td>-1.42</td>
<td>-0.99</td>
<td>1.10</td>
</tr>
<tr>
<td>C-Powder flow rate</td>
<td>1.41</td>
<td>1</td>
<td>0.12</td>
<td>1.14</td>
<td>1.68</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Figure: 4.8 gives a graphical representation of the distribution of the residuals.

The residuals are randomly distributed. Graph of the predicted deposits’ height to actual
experimental deposits’ height is shown in Figure: 4.9. The model also shows a well-distributed data, with most of the data in agreement with one another.

![Normal Plot of Residuals](image)

Figure: 4.8: Graph of normal plot of residuals
The surface plot of the deposits’ height against laser power and scanning speed is shown in Figure: 4.10. Also, the surface plot of the deposits’ height against the scanning speed and the powder-flow rate is shown in Figure: 4.11. The surface plots also show a close interaction between the deposits’ height, laser power, scanning speed and powder-flow rate. The increase in laser power, decrease in scanning speed, or increase in the powder-flow rate is directly proportional to the deposits' height.
Figure: 4.10: Surface plot of deposits' height against laser power and scanning speed

Figure: 4.11: Surface plot of deposits' height against scanning speed and powder-flow rate
4.1.3 Analysis of heating bed preheated deposited samples as regards Deposition height

The relationship between deposits height to deposition parameters, like laser power and scanning speed, shows a linear relationship. In this case, as represented in Table: 4.9, with scanning speed kept at 3.17 mm/s and a powder-flow at 2.77 g/min; and laser power increased from 400W (sample H1) to 450W (sample H2), the height of the deposit increases from 1.6 mm to 2.1 mm. Similarly, using the same varied laser power and powder flow and reducing the scanning speed from 3.17 mm/s to 2.65 mm/s, the height of the deposit increased from 2.3mm in sample H3 to 2.7 mm in sample H4. This relationship also agrees with the earlier reason given under unpreheated sample depositions that as the laser power increases or the scanning speed decreases, more melt pool is created by the laser, which later solidified; and results to a consistent increase in the height of the deposit. Figure: 4.12 gives the graphical representation of the relationship.

Table: 4.9: Outcomes of processing parameters on heights and Microhardness on heating bed preheated samples.
4.2 MICROHARDNESS OF THE DEPOSITED SAMPLES

Much has been said on the role played by the process parameters on the microhardness of the laser-deposited materials. This section gives the analysis of the effect of laser power, scanning speed, powder-flow rate and the preheating on the microhardness of deposited samples. Referring back to Table: 4.1, Table: 4.5 and Table: 4.9, the microhardness of the deposited samples in the un-preheated, laser and heating-bed preheated stages have been itemized respectively. Analysis of these is presented below.
4.2.1 Analysis of unpreheated deposited samples as regards deposition micro-hardness

For the unpreheated deposition sample analysis, the analysis of variance (ANOVA) for the microhardness is presented in Table: 4.10. The model F value of 6.80 indicates that the model is significant. There is only a 0.74% chance that a “Model F-Value” this huge could occur due to noise. Values of “Prob > F” less than 0.05, show that the model terms are significant. In this case, C is a very significant model term.

The coefficient of determinant in Table: 4.11, “R-squared” represents the coefficient of determination, which can range between 0 and 1. The “R-squared” value of this model is 0.6496. The “Pred R-squared” of 0.3827 is in reasonable agreement with the “Adj R-squared” of 0.5541. “Adeq precision” ratio of 9.060 shows an adequate signal; and the model can be used to navigate design space. An estimate of the coefficient at the 95% confidence level is given in Table: 4.12. The final equation of the model in terms of coded factors is presented in Equation 4.3

\[ \text{Microhardness} = 504.99 + (35.23 \times A) + (5.47 \times B) + (45.30 \times C) \] ....... eqn. 4.3

Where, A is Laser power, B is laser scanning and C is the powder-flow rate.

Table: 4.10: Analysis of variance (ANOVA) table for the microhardness of un-preheated samples

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>15398.58</td>
<td>3</td>
<td>5132.86</td>
<td>6.80</td>
<td>0.0074</td>
</tr>
<tr>
<td>A</td>
<td>3102.53</td>
<td>1</td>
<td>3102.53</td>
<td>4.11</td>
<td>0.0676</td>
</tr>
<tr>
<td>B</td>
<td>149.50</td>
<td>1</td>
<td>149.50</td>
<td>0.20</td>
<td>0.6650</td>
</tr>
<tr>
<td>C</td>
<td>12146.56</td>
<td>1</td>
<td>12146.56</td>
<td>16.09</td>
<td>0.0020</td>
</tr>
<tr>
<td>Residual</td>
<td>8304.67</td>
<td>11</td>
<td>754.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>8304.67</td>
<td>9</td>
<td>922.74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>23703.25</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table: 4.11: Coefficient of determinant for the microhardness of the un-preheated samples

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>27.48</th>
<th>R-Squared</th>
<th>0.6496</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>472.22</td>
<td>Adj R-Squared</td>
<td>0.5541</td>
</tr>
<tr>
<td>C.V.</td>
<td>5.82</td>
<td>Pred R-Squared</td>
<td>0.3827</td>
</tr>
<tr>
<td>PRESS</td>
<td>14632.75</td>
<td>Adeq Precision</td>
<td>9.060</td>
</tr>
</tbody>
</table>

Table: 4.12: Estimates of the coefficient of the microhardness of the un-preheated samples

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient Estimate</th>
<th>DF</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>504.99</td>
<td>1</td>
<td>12.01</td>
<td>478.56</td>
<td>531.41</td>
<td></td>
</tr>
<tr>
<td>A-Laser power</td>
<td>35.23</td>
<td>1</td>
<td>17.38</td>
<td>-3.02</td>
<td>73.48</td>
<td>1.0</td>
</tr>
<tr>
<td>B-Scanning speed</td>
<td>5.47</td>
<td>1</td>
<td>12.29</td>
<td>-21.58</td>
<td>32.51</td>
<td>1.0</td>
</tr>
<tr>
<td>C-Powder flow rate</td>
<td>45.30</td>
<td>1</td>
<td>11.29</td>
<td>20.44</td>
<td>70.15</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure: 4.13 shows the graphical analysis of the residuals. The residuals are randomly distributed, which is quite desirable. A graph of the predicted deposits’ microhardness to the actual experimental deposits microhardness is shown in Figure: 4.14. The model also shows a well-distributed data, with some of the data in agreement with one another.
Figure: 4.13: Graph of normal plot of residuals

Figure: 4.14: Graph of predicted against actual experimental data
The surface plot of deposits’ microhardness against laser power and scanning speed, is shown in Figure: 4.15. Also, the surface plot of the deposits’ microhardness against scanning speed and powder flow-rate is shown in Figure: 4.16. The surface plots show the relationship between the deposits’ microhardness against laser power, scanning speed and the powder-flow rate.

As the laser power and the scanning speed increases, there is a resultant increase in the microhardness. However, there is a decrease in microhardness from sample UB1 at 3.17 mm/s (463.66 Hv) to sample UB2 at 4.23 mm/s (409.72Hv) and the linear increment was observed to sample UB5 at 7.41 mm/s (499.26 Hv) as the scanning speed increased. The increase in microhardness of the samples must have been due to the fast rate of cooling taking place in the deposition process; and the environment and between the melt pool and the unpreheated substrate. Likewise, the increase in the powder-flow rate, also led to an overall increase in the microhardness of the deposits from sample UC1 at 4.09 g/min (409.72 Hv) to sample UC4 at 6.38 g/min (542.48 Hv) and a slight decrease in sample UC5 at 7.12 g/min (526.22 Hv).

However, the overall microhardness of the samples increased tremendously when compared with the microhardness of the substrate (177.5 Hv). The microhardness of the deposited samples, with an unpreheated substrate, is about two to three times greater than that of the substrate.
Figure: 4.15: Surface plot of Microhardness against laser power and scanning speed

Figure: 4.16: Surface plot of microhardness against scanning speed and powder-flow rate
4.2.2 Analysis of laser preheated deposited samples as regards Deposition microhardness

The analysis of variance (ANOVA) for microhardness of the laser-preheated samples is presented in Table: 4.13. The model F value of 3.89 implies there is a 4.06% chance that a “Model F-Value” this large could occur due to noise. The Values of “Prob > F” less than 0.05, show that the model terms are significant. But in this case, A and B are significant model terms; and values greater than 0.1, indicate that the model terms are not significant.

The coefficient of determinant in Table: 4.14, “R-squared” (0.5147) represents the coefficient of determination, which can range between 0 and 1. The “Pred R-squared” of -0.0190 implies that the overall mean is a better predictor of response. “Adeq Precision” ratio of 6.369 indicates an adequate signal and the model can be used to navigate design space.

Table: 4.15 gives the estimates of coefficient at the 95% confidence level. The final equation of the model in terms of the coded factors is presented in Equation 4.4

\[ \text{Microhardness} = 369.45 - (17.45 \times A) + (10.51 \times B) - (8.58 \times C) \quad \ldots \ldots \text{eqn. 4.4} \]

Where, A is Laser power, B is laser scanning and C is the powder-flow rate.
Table: 4.13: Analysis of variance (ANOVA) table for microhardness of laser-preheated samples

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1313.95</td>
<td>3</td>
<td>437.98</td>
<td>3.89</td>
<td>0.0406</td>
</tr>
<tr>
<td>A</td>
<td>947.82</td>
<td>1</td>
<td>947.82</td>
<td>8.42</td>
<td>0.0144</td>
</tr>
<tr>
<td>B</td>
<td>586.61</td>
<td>1</td>
<td>586.61</td>
<td>5.21</td>
<td>0.0434</td>
</tr>
<tr>
<td>C</td>
<td>248.44</td>
<td>1</td>
<td>248.44</td>
<td>2.21</td>
<td>0.1656</td>
</tr>
<tr>
<td>Residual</td>
<td>1238.91</td>
<td>11</td>
<td>112.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>1238.91</td>
<td>9</td>
<td>137.66</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
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<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>2552.87</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table: 4.14: Coefficient of determinant for microhardness of laser-preheated samples

<table>
<thead>
<tr>
<th>Std. Dev.</th>
<th>10.61</th>
<th>R-Squared</th>
<th>0.5147</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>385.69</td>
<td>Adj R-Squared</td>
<td>0.3823</td>
</tr>
<tr>
<td>C.V.</td>
<td>2.75</td>
<td>Pred R-Squared</td>
<td>-</td>
</tr>
<tr>
<td>PRESS</td>
<td>2601.30</td>
<td>Adeq Precision</td>
<td>6.369</td>
</tr>
</tbody>
</table>

Table: 4.15: Estimates of coefficient of microhardness of preheated samples

<table>
<thead>
<tr>
<th>Factor</th>
<th>Coefficient Estimate</th>
<th>DF</th>
<th>Standard Error</th>
<th>95% CI Low</th>
<th>95% CI High</th>
<th>VIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intercept</td>
<td>369.45</td>
<td>1</td>
<td>5.83</td>
<td>356.63</td>
<td>382.27</td>
<td></td>
</tr>
<tr>
<td>A-Laser power</td>
<td>-17.45</td>
<td>1</td>
<td>6.02</td>
<td>-30.69</td>
<td>-4.21</td>
<td>1.07</td>
</tr>
<tr>
<td>B-Scanning speed</td>
<td>10.51</td>
<td>1</td>
<td>4.60</td>
<td>0.37</td>
<td>20.64</td>
<td>1.10</td>
</tr>
<tr>
<td>C-Powder flow rate</td>
<td>-8.58</td>
<td>1</td>
<td>5.77</td>
<td>-21.28</td>
<td>4.13</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Figure: 4.17 shows the graphical analysis of the residuals. The residuals are randomly distributed, which is desirable. A graph of the predicted deposits' microhardness to actual experimental deposits' microhardness is shown in Figure: 4.18.
Figure: 4.17: Graph of normal plot of residuals

Figure: 4.18: Graph of predicted against actual experimental data
Figure: 4.19: Surface plot of Microhardness against laser power and scanning speed

Figure: 4.20: Surface plot of Microhardness against scanning speed and powder-flow rate
The surface plot of deposits’ microhardness against laser power and scanning speed is shown in Figure: 4.19. Also, the surface plot of the deposits’ microhardness against scanning speed and powder-flow rate is shown in Figure: 4.16.

The plots show an overall relationship that; as the laser power increases and scanning speed decreases, there is a corresponding decrease in the microhardness. The decrease in microhardness of the samples must have been due to the slow cooling rate that took place in the solidification process; as the preheated substrate is not able to absorb much heat as is normally assumed with an unpreheated substrate. The Increase in the powder-flow rate, led to an overall decrease in the microhardness of the deposits.

In summary, the laser-preheated deposited samples displayed a desirable increase in the microhardness as to that of the substrate (177.5 Hv). The microhardness of the deposited samples, with an unpreheated substrate, is about two to three times greater than that of the substrate.

4.2.3 Analysis of heating bed preheated deposited samples as regards Deposition microhardness

The deposits microhardness to the deposition parameters (laser power and scanning speed) gives an interesting outcome. As represented in Table: 4.9, with scanning speed kept at 3.17 mm/s and powder flow at 2.77 g/min and laser power increased from 400W (sample H1) to 450W (Sample H2), the microhardness of the deposit slightly decreases from 562.6 Hv to 559.5 Hv. Similarly, when using the same varied laser power and powder flow; and reducing the scanning speed from 3.17 mm/s
to 2.65 mm/s, the microhardness of the deposit increased from 519.06 Hv in sample H3 to 549.09 Hv in sample H4.

In summary, the change in the deposition parameters leads to a change in the microhardness of the deposits. This relationship observed in depositions was obtained via heating-bed preheated substrate; and it also agrees with the reason given under laser preheated depositions. Figure: 4.21 gives the graphical representation of the relationship.

![Figure 4.21: Pictorial representation of the microhardness of the samples](image)

Laser deposition of Ti-4822-4 titanium aluminide powder, by using laser-engineered net shaping (LENS) technique shows that it is possible to achieve
depositions with microhardness values above 500 Hv. However, achieving high microhardness might be prone to cracks due to residual stress development during such processes. As such, proper measure must be put in place to control the process.

4.2.4 Microhardness trend in deposits

The microhardness profiling from top of the deposits down to the substrates revealed similar trends. It was observed that the top of the deposits show high microhardness values. As the indentations move down into the deposits, the microhardness values decreases and as the indentations approaches the fusion zone (FZ), the microhardness rises to peak values at the interface between the deposit and the substrate. And microhardness value reduces as the indentations goes into the substrate. Figure: 4.22, Figure: 4.23 and Figure: 4.24 show the microhardness profiling plot of samples deposited without, with laser and heating bed preheated substrates.
Figure: 4.22: Microhardness profiling for deposits produced under unpreheated substrate at (a) Different laser power (b) different scanning speed and (c) different powder flow rate

In figure 4.22 (a), the microhardness profiling show that there is a decrease in the microhardness of samples to a close steady state where the microhardness of samples were fluctuating around 400 to 450 Hv and on getting to the fusion/interface region microhardness increases due to fast cooling rate taking place at such region and finally decreases as the indentation moves into the substrate. However, the trend seen in figure 4.22 (a), (b) and (c) show that the microhardness witnessed in most of the samples where higher at the top of the deposit than at the fusion/interface zone and sample UC1 deposited at 400 W, 4.23 mm/s and 4.09 g/min showing the least microhardness trend. The trend witnessed indicated that the cooling rates at the top of the deposits are higher than what is witnessed at the fusion/interface region.
The trend of microhardness profiling for samples deposited with a laser-preheated substrate, as shown in Figure: 4.23 (a), (b) and (c), revealed a different trend from those of samples deposited without the preheated substrate. The microhardness values at the top of the deposits are lower, when compared with that observed for the un-preheated substrate depositions; and the microhardness values at top of the deposits are lower than what is witnessed at the fusion/interface region. These
characteristics can be linked to the reduction in the temperature gradient at which the laser-preheated substrate depositions are achieved (Sharman et al. 2018).

The microhardness profiling achieved under heating bed preheated substrate shown in Figure: 4.24 is higher than that achieved with laser preheated substrates. The microhardness profiling also shows a gradual decrease and increase; and no serious deviations were observed from the top of the substrate to the interface/fusion region before the gradual microhardness decreases into the substrate.

![Microhardness profiling for deposits produced under heating bed preheated substrate.](image)

Figure: 4.24: Microhardness profiling for deposits produced under heating bed preheated substrate.

The high microhardness trend observed in the samples at lower laser power are due to the smaller melt pool produced on the surface of the substrate, which cause rapid cooling. This was responsible for the high microhardness witnessed at the heat-affected zones, were the formation of the acicular martensitic microstructure is witnessed (Liu & Dupont 2004). This martensite microstructure is known to be very hard (Mahamood et al. 2015). A slow cooling rate would normally result in the formation of a Widmastätten microstructure that would be relatively soft; and this is the cause of the
lower microhardness value recorded at higher laser powers. In general, with the high microhardness exhibited by the deposited samples, it is expected that the deposited samples will display excellent wear resistances (Liu & Dupont 2003). The trends in microhardness observed are further discussed in section 4.3, establishing the relationship between microstructure and microhardness.

4.3 MICROSTRUCTURE AND EDS ANALYSIS

4.3.1 Sample Microstructural analysis

The morphology of Ti-4822-4 titanium aluminide powder shown in Figure: 4.25 is an un-equiaxed spherical in shape particles with tiny dust particles agglomerated sparingly onto the larger spherically shaped particles. This powder has been selected for the deposition process as it is a profound knowledge that the shape of such powder makes it mostly preferable in laser-deposition process because of its ability to absorb the laser beam better (Schade et al. 2014).
The microstructures of the deposited samples were observed under the microscope; both at low and high magnifications. Some of the samples revealed lateral cracks (mainly around the fusion zone) and longitudinal cracks running from the bottom of the substrate right to the top of the deposits. However, as the energy density increases (laser power increase or scanning speed decrease), the cracks reduce and no cracks were seen running from the substrate to the top of the deposit in samples like LA5 (deposited at 600 W, 4.09 g/min and 10.58 mm/s) and H4 (deposited at 450 W, 2.77 g/min and 2.65 mm/s).

Cracks in the deposited samples can be linked to the high amount of thermal-induced stress created during the deposition processes (Perevoshchikova et al. 2017). Liu and Dupont (2004) explained that the crack frequency reduces; as the input energy increases. This argument is justified; because the cooling rate is inversely proportional
to the heat input from the laser (Kou 1987); and depositions done at lower-energy inputs tend to cool faster, thereby causing thermally induce stresses that tend to initiate cracks.

At high laser power, more melt pool is created, which takes more time to solidify, unlike the little melt pool produced at a lower laser power that quickly undergoes rapid solidification. The micrographs (optical magnification 50X) of the deposited samples on unpreheated, laser preheated and heating bed preheated substrates are presented in Figure: 4.26, Figure: 4.27 and Figure: 4.28 respectively.

Generally, the microstructures, as presented when using optical microscope, are characterized with \( \alpha_2 \)-Ti\(_3\)Al and flowery \( \gamma \)-TiAl grain structures; but they vary in concentrations due to the manufacturing route and the cooling rate (Porter et al. 2009). To understand the microstructures better, the samples were studied by using the SEM.
Figure 4.26: Micrographic Images of samples deposited without a preheated substrate
The microstructures of the deposited sample on a substrate preheated by a heating bed (in Figure: 4.28) at 50X magnification. These were characterised by randomly distributed dendrites. However, the primary dendritic arms were more predominant. In some of the samples characterized with cracks, it is believed that acicular structures observed between the interface of the substrate and the deposit (fusion zone) may have been responsible for the micro-parallel cracks witnessed.
Figure: 4.28: Micrographic Images of samples deposited with a heating bed preheated substrate

Figure: 4.29, Figure: 4.30 and Figure: 4.31 present the SEM micrographs (at 6kX magnifications) of samples deposited on un-preheated, laser-preheated and heating bed preheated substrates, respectively.
Figure 4.29: SEM Images of samples deposited without any preheated substrate
Sample LB5
Figure: 4.30: SEM Images of samples deposited with laser-preheated substrate

Sample LC5

Sample H1
Figure: 4.31: SEM Images of samples deposited with heating bed preheated substrate

Sample H2
From the results presented in Figure: 4.29, Figure: 4.30 and Figure: 4.31, it can be seen that the cooling rate and the manufacturing method actually lead to the production of materials exhibiting different micro-structures.

For samples fabricated without a preheated substrate, Sample UA1 (deposited at 300 W, 3.174 mm/s and 4.09 g/min), UB5 (deposited at 400 W, 7.406 mm/s and 4.09 g/min) and UC5 (deposited at 400 W, 4.232 mm/s and 7.12 g/min) all exhibit a combination of equiaxed and lamellar forms of microstructures. However, sample UA5 (deposited at 500 W, 3.174 mm/s and 4.09 g/min) shows more of the lamellar microstructure. Samples UA1, UB5 and UC5 also show the presence of pores. Sample UB5 and UC5 also present white-spot particles that might be TiAl material that might not have been melted, indicating thereby that the heat input was not enough to fully melt the material.

Fabricated samples with a laser-preheated substrate also revealed different microstructures. Sample LA2 (deposited at 300 W, 10.58 mm/s and 4.09 g/min) displayed a duplex and uneven distributed γ and γ+α₂ lamellar structures. Sample LA4 (deposited at 500 W, 10.58 mm/s and 4.09 g/min) also revealed a duplex microstructure, but with larger lamellar spacing when compared with sample LA2. Sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min) and LB3 (deposited at 300 W, 8.464 mm/s and 4.09 g/min) displayed a fully fine lamellar structure, with Widmastätten needles distributed randomly. These Widmastätten colonies are also seen in samples UA1, UA5, UC5, LB3 and LB5, but in different amounts.

The different quantities in which the Widmastätten colonies are found are attributed to the amount of Al in the TiAl material (Ramanujan 2000). Sample LB5
(deposited at 300 W, 6.348 mm/s and 4.09 g/min) and LC5 (deposited at 300 W, 10.58 mm/s and 6.38 g/min) also displayed a duplex structure of γ grain and γ+α₂ lamellar structures. However, the lamellar structure is more prominent in sample LC5 than sample LB5 which, may have arisen from rapid cooling. The deposited samples displayed smaller grain sizes, ranging from 9.58 µm in sample LA1 to 8.87 µm in sample LA5. The grain sizes and the microstructures of the samples confirm the reason why the samples microhardness values were lower than in those samples deposited on an un-preheated and a heating bed preheated substrate; as the grain sizes witnessed in the other methods were larger.

For the samples fabricated with a heating bed preheated substrate; as presented in Figure: 4.31, both sample H1 (deposited at 400 W, 3.174 mm/s and 2.7 g/min) and H2 (deposited at 450 W, 3.174 mm/s and 2.7 g/min) displayed duplex structures with a white-coloured dendritic structure. The amount of the dendrites structures decreases as the heat input increases from 90.02 J/mm² in sample H1 to 101.27 J/mm² in sample H2. Fine grain sizes where noted for the deposited samples with sample H1 having an average grain size of 10.64 µm, 8.15 µm in H2, H3 and H5 with about 11.26 and 11.02 µm. The small grain sizes obtained agree with the work of Wang et al. (2002), that grain sizes must be within the range of 10-30 µm for the material to show sufficient ductility. The reduction in grain sizes of sample H2 and H4 must have emerged due to the lower cooling rate in samples; as the energy input (laser power) increases. The microstructure observed in the samples is also responsible for the trend witnessed in the samples tested microhardness.
The amount and sizes of the pores in some of the samples decreases, as the laser power increases, or the scanning speed decreases. These occur because the cooling rate is high at lower laser powers; and the melt pool produced is not sufficient to dissolve the entrapped gas. At higher laser power, the larger part of the gases are able to find their way out, because of the elastic nature of the surface; while some other proportions of the gases remain trapped, when no room is further available for escape; and the pores are responsible for weight reduction in the deposited samples (Erinosho 2015).

4.3.2 Electron dispersive spectroscopy (EDS) analysis

The EDS results for the deposited samples on the un-preheated, laser preheated and heating bed preheated substrates have been presented in Figure: 4.32, Figure: 4.33 and Figure: 4.34 respectively.
From the EDS resulting spectrum obtained, all the samples indicate the presence of Ti, Al, Cr and Nb, but in different amounts. For sample UA1, the spectrum peak of Al is higher than that of Ti. However, Ti is also present as a trace element, with Cr and Nb at lower peaks. Sample UA5 showed equal and roughly equal amounts of spectrum peaks of Ti and Al. Sample UB5 shows a similar trend of equal amounts of Ti and Al spectrum peaks; while the sample UC5 followed the trend of sample UA1, with an Al spectrum peak higher than that of Ti.

Samples deposited with laser preheated substrate also showed a similar distinctive trend. Sample LA2 displayed similar spectrum peaks witnessed in sample UA5 and UB5, but with slightly higher peaks of the trace elements. Sample LA4, similar to LB3, even though the spectrums were not as pronounced as other spectrums, the Al peaks were higher than those of Ti. Equal spectrum peaks of Ti and Al were recorded for samples LA5, LB5 and LC5. However, the spectrum peaks of the trace elements seen in LA5 were similar to those of sample LA2, and higher than that of sample LA4. The spectrum peaks traces (Ti, Nb and Cr) in sample LB5 were similar to those of LC5.
In heating bed preheated deposited samples, samples H1 and H2 gave similarly equal spectrum peaks of Ti and Al. The composition of the white dendritic structures present in sample Hi and H2 were also examined in spectrum 2; and it was confirmed that the structures were made up of all the elements (Ti, Al, Cr and Nb), with similar compositional peaks, like those of the peaks obtained in spectrum 1 for H1 and H2.

All these characteristics of the elemental composition account for the type of microstructures witnessed in the deposited samples.
Sample LC5
Figure: 4.33: Electron dispersive spectroscopy of samples with laser preheated substrate

Sample H1

Sample H1
4.4 X-RAY DIFFRACTION (XRD) PHASE ANALYSIS

X-ray diffraction was carried out on the deposited samples, in order to identify the phases present. Figure: 4.35 and Figure: 4.36 show the diffractogram observed at different laser powers, scanning speeds and powder-flow rates of deposits fabricated on a laser-preheated substrate. The scanning mode was continuous, and in the range of 5° to 90°. A K-beta filter with 40 kV and 30 mA analytical set-ups were utilized.

4.4.1 XRD of samples deposited on laser preheated substrate

Figure: 4.35 presents the diffractogram of the samples deposited with different laser power. Generally, the XRD analysis shows predominantly, the two main phases of γ-TiAl and α₂-Ti₃Al, except for sample LA5 deposited at 600 W laser power that has only the γ-TiAl phase. For samples LA2, LA3 and LA4, the major peaks of phases (γ-TiAl
and $\alpha_2$-Ti$_3$Al) are observed at $2\Theta = 38.61^0$, $38.74^0$ and $39.36^0$, respectively. The other peaks of Ti$_3$Al, TiAl, and in the combined form (Ti$_3$Al, TiAl) were noted as $2\Theta$ increases, but with lower peaks. The peaks of sample LA5 were not as intense as seen in samples LA2, LA3 and LA4. However, this is of one single $\gamma$-TiAl phase seen at $2\Theta = 39.62^0$, $42.32^0$, $66.49^0$ and $80.1^0$.

[Graphs showing diffraction patterns for samples LA2, LA3, LA4, and LA5]

Figure: 4.35: Diffractogram of deposits produced at different laser power on a laser-preheated substrate
Samples deposited at different scanning speeds (LB2 and LB3) and powder-flow rates (LC3 and LC4), as shown in Figure: 4.36, show similar peak trends, as those noted in LA2, LA3 and LA4. However, they show single γ-TiAl phases, such as the one witnessed in sample LA5. Major peaks were also observed at similar $2\Theta = 38.66^\circ$, $39.1^\circ$, $39.01^\circ$ and $38.98^\circ$ for LB2, LB3, LC3 and LC4, respectively. The phases with low peaks were also noted towards increasing $2\Theta$.

Figure: 4.36: Diffractogram of deposits produced at different laser scanning speeds (Sample LB2 and LB3) and powder-flow rates (Sample LC3 and LC4) on a laser-preheated substrate.
From the observations noted, it may be said that the increase in laser power, the reduction in scanning rate and the increase in powder-flow rates leads to a total transformation from $\gamma$-TiAl/$\alpha_2$-Ti$_3$Al to $\gamma$-TiAl. This might have been so; because, the cooling rate decrease will usually cause $\alpha$ to $\gamma$ transformation; as the formation of $\gamma$-grains can be witnessed at a very low cooling rate (Cheng & Loretto 1998).

4.4.2 Phase comparison of samples deposited on unpreheated, laser preheated and heating-bed preheated substrate

The diffractogram of sample H2 and sample UA4 (in Figure: 4.37 and Figure: 4.38) deposited with similar energy input of 101.3 J/mm$^2$ but different processing methods, displayed different phases in contrast from what was seen in the laser-preheated deposited samples. For sample H2, the highest peaks for phases $\gamma$-TiAl and $\alpha_2$-Ti$_3$Al were witnessed at $2\theta = 38.92^0$, similar to those of samples LA2, LA3 and LA4.

However, there is an emergence of a new weak phase (TiAl$_3$) found either alone or in combined form with TiAl and Ti$_3$Al. It is seen before the highest peak; and again as $2\theta$ increases its position to $41.14^0$, $64.9^0$, $72.05^0$, $76.38^0$ and $79.7^0$.

In Figure: 4.38, showing UA4 diffractogram, the highest peak was also observed similar to other samples at $2\theta = 38.97^0$, showing a combination of Ti$_3$Al$_2$ and TiAl$_2$ phase and with the Ti$_3$Al phase present, as a trace at $2\theta = 31.51^0$ and as $2\theta$ increases.

Earlier reported in literatures was the formation of an intermetallic phase $\delta$-Ti2Al and $\gamma$-Ti3Al by Ence & Margolin (1961) and debunked by Tsujimoto & Adachi (1966) that the intermediate phase occurred as a result of transformation from the peritectoid $\beta + \alpha_2 \rightarrow \alpha$ phase that may have occurred due to the presence of oxygen and nitrogen; as they tend to increase the $\beta$-transition temperature.
The new phase witnessed in H2 (TiAl₃) and UA4 (TiAl₂ and Ti₃Al₂) may have occurred due to the solubility of Al in Ti, and the cooling rate during the solidification process. TiAl₂ and superlattice TiAl₃ structure do occur at high contents of wt.% Al (Basuki et al. 2016); and this may also have contributed to the emergence of the phases seen in sample H2 (deposited at 450 W, 3.174 mm/s and 2.7 g/min) and UA4 (deposited at 450 W, 3.174 mm/s and 4.09 g/min).

The emergence of different phases in all the deposited samples has also demonstrated that the γ-TiAl has the tendency of producing different microstructures that may have emanated from the composition of the alloy, the processing route, the solidification path, and the post-processing heat-treatment (Kim & Kim 2018).

Figure: 4.37: Diffractogram of sample H2
4.5 WEAR AND CORROSION BEHAVIOUR

This section presents the wear and corrosion results, and the analysis of the test samples. The section noted result variations and comparisons on how the process parameters and the method of production (unheated, laser preheated and heating bed preheated substrates) affects the outcome of the wear-and-corrosion behaviour of the deposited samples.

4.5.1 Wear-Rate Analysis

The wear experienced in samples was that of the abrasive type, characterized by the wear debris that resulted from the rubbing of samples with a steel ball. Some areas exhibited surface smearing that may have been as a result of the heat produced during the dry-wear experiment. This observation indicated that the wear observed in samples must have been a combination of adhesive and abrasive wear. Figure: 4.39 shows the
wear-track of the deposited sample. The wear rate of deposited samples with laser preheating was between $1.38 \times 10^{-4}$ mm$^3$/Nm in samples LA3 (deposited at 400 W, 10.58 mm/s and 4.09 g/min) to $6.74 \times 10^{-5}$ mm$^3$/Nm in sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min).

The decrease in wear rate, as observed in sample LA5, as compared with sample LA3, might be attributed to the microstructure of LA5, its hardness, and its ductility. The wear rates of the deposited samples with heating-bed preheating, gave a slight increase in the wear rate from $8.57 \times 10^{-5}$ mm$^3$/Nm to $8.68 \times 10^{-5}$ mm$^3$/Nm as the laser power is increased from 350 W in sample UA2 to 400 W, in sample UA3. Sample H2 gave a lower wear rate of $1.51 \times 10^{-4}$ mm$^3$/Nm, compared with that of sample H1 with a wear rate of $2.53 \times 10^{-4}$ mm$^3$/Nm.

The outcome of the experiment is, therefore, of the mixed results obtained as samples of the laser-preheated and heating-bed preheated substrate, which showed that an increase in the laser power resulted in a decrease in the wear rate. While for samples of the un-preheated substrate, the reverse is the case; as an increase in the laser power resulted in a slight increase in wear rate, thereby conforming to the argument that samples deposited at lower laser power or at higher scanning speeds appear to display lower wear rates (Balla et al. 2016; Ogunlana & Akinlabi 2016; Erinosho & Akinlabi 20016).

However, the wear-rate results obtained in all the samples were between $6.74 \times 10^{-5}$ mm$^3$/Nm in sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min) to $2.53 \times 10^{-4}$ mm$^3$/Nm in sample H1 (deposited at 400 W, 3.174 mm/s and 2.7 g/min). These
results seem to be more desirable than those obtained by Balla et al. (2016), with wear rates within the range of $4.3 \times 10^{-4}$ mm$^3$/Nm to $5.7 \times 10^{-4}$ mm$^3$/Nm.

![Micrograph of wear track of sample LA5](image)

Figure: 4.39: Micrograph of wear track of sample LA5

The plot of the coefficient of friction (COF) against the sliding time for the selected deposited samples is shown in appendix 3. The results of the wear rates of the deposited samples are tabulated in Table 2.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average Coefficient of friction (µ)</th>
<th>Wear volume (mm$^3$)</th>
<th>Wear rate (mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA3</td>
<td>0.053</td>
<td>0.0964</td>
<td>1.38*10$^{-4}$</td>
</tr>
<tr>
<td>LA5</td>
<td>0.169</td>
<td>0.0482</td>
<td>6.74*10$^{-5}$</td>
</tr>
<tr>
<td>UA2</td>
<td>0.284</td>
<td>0.0482</td>
<td>8.57*10$^{-5}$</td>
</tr>
<tr>
<td>UA3</td>
<td>0.171</td>
<td>0.0482</td>
<td>8.68*10$^{-5}$</td>
</tr>
<tr>
<td>H1</td>
<td>0.038</td>
<td>0.12</td>
<td>2.53*10$^{-4}$</td>
</tr>
<tr>
<td>H2</td>
<td>0.153</td>
<td>0.072</td>
<td>1.51*10$^{-4}$</td>
</tr>
</tbody>
</table>
Figure: 4.40 shows the trend in the wear volume and the wear rates of deposited samples; while Figure: 4.41 presents the percentage wear loss in the deposited samples. The trend in the figure revealed the graphical representation of how increases in energy density (in this case, laser power) have a direct effect on the wear rates of the deposited samples. The best wear performance was exhibited by sample (LA5) deposited with laser preheating. This might be attributed to the micro-structural features, as a result of the cooling rate.
The percentage wear loss in the deposited samples showed that samples H1 and H2 with 32.36% and 19.31% wear rate, are of a lower wear performance, when compared with sample LA5 having the lowest wear rate of 8.62%. The differences in the wear loss witnessed can be attributed to the wear-scar width and depth created by the test ball on the test samples. The wear depths of the samples with high wear performance are lower; since the wear-scar width and the depth play very important roles in evaluating the wear losses. From the results obtained; it can be said that the manufacturing method and the cooling rate both have a significant influence on the wear rates of the deposited samples. Better tribological performance displayed by the deposited samples can also be linked to the relatively fine microstructure caused by the rate of cooling (Balla et al. 2016).
4.5.2 Corrosion Rate Analysis

As earlier discussed in section three under the test for the corrosion rate of the samples, this section presents the results on the corrosion rates of the samples deposited on un-preheated, laser-preheated and heating-bed preheated substrates. All the corrosion experiments were conducted under normal aerated atmospheric conditions. The polarization curves of the corrosion rates of the deposited samples have been presented in Appendix 4.

4.5.2.1 Corrosion rates of deposited samples from an un-preheated substrate

With the anodic and cathodic branches of the polarization curves of the Tafel plots, results were obtained for the deposited samples on the un-preheated substrate. The testing provides a mixed result, as presented. Table: 4.17 presents the corrosion rate, the corrosion potential ($E_{corr}$) and the current density ($I_{corr}$). The lowest $I_{corr}$ of $6.384 \times 10^{-9}$ A was recorded for sample UA5 (deposited at 500 W, 3.174 mm/s and 4.09 g/min); and sample UA1 (deposited at 300 W, 3.174 mm/s and 4.09 g/min) gave the noblest $E_{corr}$ (-0.027 V) among the deposited samples on an un-preheated substrate with varying laser power. It is believed that lower $I_{corr}$ values and noble or higher $E_{corr}$ values are the most desirable for the high corrosion-resistance of alloys (Balla et al. 2016). From the corrosion rate results obtained, it is noted that these two samples (UA5 and UA1) had the lowest corrosion rates with sample UA5 (deposited at 500 W, 3.174 mm/s and 4.09 g/min), displaying the lowest values; while sample UA3 (deposited at 400 W, 3.174 mm/s and 4.09 g/min) showed the highest corrosion rate, as shown in the corrosion rate trend in Figure: 4.42.
Table: 4.17: Electro-chemical results obtained from the polarization tests of the deposited samples on an un-preheated substrate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion Rate X10^{-4} (mm/year)</th>
<th>E_{corr} (V)</th>
<th>I_{corr} (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UA1</td>
<td>5.3</td>
<td>-0.198</td>
<td>2.449 X 10^{-8}</td>
</tr>
<tr>
<td>UA2</td>
<td>7.9</td>
<td>-0.027</td>
<td>3.684 X 10^{-8}</td>
</tr>
<tr>
<td>UA3</td>
<td>99.8</td>
<td>-0.265</td>
<td>4.483 X 10^{-7}</td>
</tr>
<tr>
<td>UA4</td>
<td>12.6</td>
<td>-0.088</td>
<td>5.583 X 10^{-8}</td>
</tr>
<tr>
<td>UA5</td>
<td>2.6</td>
<td>-0.105</td>
<td>6.384 X 10^{-9}</td>
</tr>
</tbody>
</table>

Figure: 4.42: Trends in the corrosion rates of the deposited samples on an un-preheated substrate

4.5.2.2 Corrosion rates of the deposited samples from the laser-preheated substrate

With the anodic and cathodic branches of the polarization curves of the Tafel plots, the results were obtained for the deposited samples on the laser-preheated substrate. Table: 4.17 presents the corrosion rate, the corrosion potential (E_{corr}) and the
current density ($I_{\text{corr}}$). The lowest $I_{\text{corr}}$ of $1.8 \times 10^{-8}$ A was recorded for sample LA4 (deposited at 500 W, 10.58 mm/s and 4.09 g/min) and the same sample gave the highest reading $E_{\text{corr}}$ (-0.138 V) among the samples on the laser preheated substrate with varying laser power. Since it is agreed that lower $I_{\text{corr}}$ and noble or higher $E_{\text{corr}}$ values are the most desirable for the high-corrosion resistance of the alloys (Balla et al. 2016). As confirmation of the corrosion-rate results obtained, sample LA4 is the most preferred candidate to be the material with the highest corrosion resistance.

According to the corrosion-rate trend in the deposited samples, as shown in Figure: 4.43, the sample is closely followed by sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min) with LA3 (deposited at 400 W, 10.58 mm/s and 4.09 g/min) being the sample with the highest corrosion rate.

Table: 4.18: Electro-chemical results obtained from the polarization test of the deposited samples on a laser preheated substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion Rate $\times 10^{-4}$ (mm/year)</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$I_{\text{corr}}$ (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LA1</td>
<td>1192</td>
<td>-0.628</td>
<td>$2.744 \times 10^{-6}$</td>
</tr>
<tr>
<td>LA2</td>
<td>2967</td>
<td>-0.54</td>
<td>$1.061 \times 10^{-5}$</td>
</tr>
<tr>
<td>LA3</td>
<td>3720</td>
<td>-0.543</td>
<td>$8.378 \times 10^{-6}$</td>
</tr>
<tr>
<td>LA4</td>
<td>4.33</td>
<td>-0.138</td>
<td>$1.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>LA5</td>
<td>8.4</td>
<td>-0.235</td>
<td>$7.13 \times 10^{-8}$</td>
</tr>
</tbody>
</table>
4.5.2.3 Corrosion rates of deposited samples on heating-bed preheated substrate

The results were obtained for the deposited samples on a heating bed preheated substrate. These gave a mixed outcome. Table: 4.17 presents the corrosion rate, the corrosion potential ($E_{\text{corr}}$) and the current density ($I_{\text{corr}}$). The sample with the lowest $I_{\text{corr}}$ between sample H1 (deposited at 400 W, 3.174 mm/s and 2.77 g/min) and sample H2 (deposited at 450 W, 3.174 mm/s and 2.77 g/min) is the sample H1 with an $I_{\text{corr}}$ of $3.806 \times 10^{-8}$ A and with the noblest $E_{\text{corr}}$ (-0.106 V). This is what made it a better corrosion-resistance material than sample H2, H3 and H4. The sample with the lowest $I_{\text{corr}}$ between sample H3 (deposited at 400 W, 2.645 mm/s and 2.77 g/min) and sample H4 (deposited at 450 W, 2.645 mm/s and 2.77 g/min) is sample H4 with $I_{\text{corr}}$ of $4.636 \times 10^{-8}$ A. But the $E_{\text{corr}}$ (-0.073 V) of sample H3 is higher than that of sample H4. However,
sample H4 is of a better corrosion resistance to sample H3, according to the results obtained. Looking at all the four tested samples; sample H1 gave the best corrosion resistance; and this was immediately followed by sample H4. Figure: 4.44 gave the corrosion rate trend in the deposited samples on a heating bed preheated substrate.

Table: 4.19: Electro-chemical results obtained from the polarization test of the deposited samples on a heating bed preheated substrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Corrosion Rate X10⁻⁴ (mm/year)</th>
<th>E_corr (V)</th>
<th>I_corr (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>5.7</td>
<td>-0.106</td>
<td>3.806 X 10⁻⁸</td>
</tr>
<tr>
<td>H2</td>
<td>610</td>
<td>-0.326</td>
<td>3.442 X 10⁻⁷</td>
</tr>
<tr>
<td>H3</td>
<td>8</td>
<td>-0.073</td>
<td>4.719 X 10⁻⁸</td>
</tr>
<tr>
<td>H4</td>
<td>6.4</td>
<td>-0.1</td>
<td>4.636 X 10⁻⁸</td>
</tr>
</tbody>
</table>

Figure: 4.44: Trend in corrosion rate of deposited samples on a heating bed preheated substrate.
In general, even though the corrosion rates exhibited by the deposited samples on un-preheated, laser-preheated and heating-bed preheated substrates are seen to be small, sample UA5 (deposited at 500 W, 3.174 mm/s and 4.09 g/min) of unpreheated substrate gave the best corrosion resistance (2.6 x 10^{-4} mm/year). While samples LA4 (deposited at 500 W, 10.58 mm/s and 4.09 g/min) and H1 (deposited at 400 W, 3.174 mm/s and 2.7 g/min) with corrosion resistances of 8.4 x 10^{-4} mm/year and 5.7 x 10^{-4} mm/year remain the best among their peers.

The reason for the corrosion characteristics might be associated with the laser material interaction and the cooling rates that do play a tremendous role in the properties of the deposited materials.

4.6 NANO-INDENTATION

This section presents the nanoindentation test results carried out with the Anton Paar indentation testing equipment. With a load of 5 mN, loading and an unloading rate of 30 mN/min, pause of 1200 s and stiffness threshold of 150 µN/µm, the results, as regards the average hardness (in HV and MPa), stiffness, modulus of elasticity and creep are presented. Appendices 5a to 5f present the indentation test values of the test samples.

4.6.1 Material Property results of deposited samples

The material properties of the test samples are presented in Table: 4.20. The results in the table present the effect of laser parameter (laser power) and manufacturing procedure (laser preheated and heating bed preheated) on the material properties of the deposits. As shown in the table, the sample with the highest hardness (5095.96MPa and 471.94Hv) is sample H2 (deposited at 450 W,
3.174 mm/s and 2.7 g/min); and the sample with the least hardness (4077.51 MPa and 377.62 Hv) is sample LA3 (deposited at 400 W, 10.58 mm/s and 4.09 g/min). Sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min) with 104.2 GPa has the lowest indentation modulus. This is closely followed by sample LA3 (deposited at 400 W, 10.58 mm/s and 4.09 g/min) with 113.98 GPa and 150.94 GPa for sample H2 (deposited at 450 W, 3.174 mm/s and 2.7 g/min). The modulus of samples LA3 and LA5 fell within the range of titanium alloy of 105-120 GPa (Engineering ToolBox 2003) but the sample H2 modulus showed an improved material modulus.

However, the stiffness witnessed in some of the samples did not follow the exact trend witnessed in material hardness. This is because stiffness is the ability of a material to resist elastic deformation and not hardness, which is the property of a material to resist surface penetration by another solid body. As such, sample LA5 has the least value (0.129 mN/nm) and sample H2 has the highest (0.172 mN/nm) value. The stiffness values in test samples indicate that an applied uniaxial force, either tensile or compressive, would produce the larger deformation in the material, with the least stiffness (sample LA5) than the material with the highest stiffness (sample H2). The tendency of the deposited material (sample LA3) to move gradually or to permanently deform under the influence of the applied stresses is higher (0.191) than that of sample LA5 (0.133) and Sample H2 (0.106).

Sample H2 with lowest value indicates that the material will not easily deform under the influence of an applied load. However, the rate of deformation of any material depends on the material’s properties, the exposure temperature, exposure time and load applied. Difference in mechanical properties of samples are obtained based on the
kind of microstructure in the γ-based TiAl alloy, heat and thermo-mechanical treatment (Padilla et al. 2015). These mechanical properties are also determined by the aluminium content and the alloying elements (Cr and Nb) present in the alloy (Gebhard et al. 2009; Ramanujan 2000).

Table: 4.20: Material properties of the test samples

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Sample LA3</th>
<th>Sample LA5</th>
<th>Sample H2</th>
</tr>
</thead>
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<tr>
<td>Indentation hardness (MPa)</td>
<td>4077.51</td>
<td>4253.74</td>
<td>5095.96</td>
</tr>
<tr>
<td>Indentation hardness (HV)</td>
<td>377.623</td>
<td>393.942</td>
<td>471.94</td>
</tr>
<tr>
<td>Indentation modulus (GPa)</td>
<td>113.9803</td>
<td>104.2</td>
<td>150.942</td>
</tr>
<tr>
<td>Stiffness (mN/nm)</td>
<td>0.14069</td>
<td>0.12905</td>
<td>0.1722</td>
</tr>
<tr>
<td>Material creep at ambient temperature</td>
<td>0.191</td>
<td>0.133</td>
<td>0.106</td>
</tr>
</tbody>
</table>

4.6.2 Trend in displacement-time plot of the test samples

The trend in the displacement-time plot, shown in Figure: 4.45, indicates that maximum displacement (266.11 nm) is witnessed by sample LA3. Sample LA5 experienced the maximum displacement of 256.55 nm; and the minimum displacement (239.43 nm) was experienced by sample H2. This trend is reflected in the outcome of the material hardness and the modulus of the test samples. The material creep of the test samples, which is the comparative change in the indentation depth at a constant test force or load can be determined from the displacement-time curve.
4.6.3 **Trend in force-displacement plot of test samples**

The trend of the force-displacement curve for the test samples is shown in Figure: 4.46. The plot shows the continuous application of load, until the optimum load is reached. A hold period at maximum load is observed, from which hold period data at maximum load are used to evaluate the creep of the test samples discussed in section 4.6.2. Figure: 4.46 provides the loading, the hold and the unloading periods of the test samples. According to the figure, at maximum force, the displacement of the sample H2 at the hold period starts and stops early, compared to those of samples LA3 and LA5.
This also means that sample LA3 gave the highest displacement at the maximum force, which is why its material hardness value is lower than those of samples LA5 and H2.

![Force-displacement plot of test samples](image)

**Figure: 4.46: Force-displacement plot of test samples**

### 4.7 EXHAUST-VALVE MODELLING AND SIMULATION ANALYSIS

As earlier mentioned in Chapter Three, exhaust valves was modelled and simulated using Ti-4822-4 and Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si titanium alloys. The properties of Ti-4822-4 titanium aluminide were obtained from the tests that were carried out. The simulation was performed to have an idea of how well the valve
material would be able to cope under certain loading conditions (thermal and buckling) during engine operation by comparing the results with those of another set of simulated results, also obtained with titanium alloy material (Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si) in the software data base.

4.7.1 Thermal analysis and comparison of valves made up of the two titanium alloys

The modelled valve made of Ti-4822-4 titanium alloy is treated as a solid body with a density of 4150 kg/m3, weight of 0.914 N and with an elastic modulus of $1.1398 \times 10^{11}$ N/m$^2$. The valve material of Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si titanium alloy is of density 4650 kg/m3, weight 1.024 N and with elastic modulus of $1.23 \times 10^{11}$ N/m$^2$. The thermal study consisted of applying a temperature load of 750 °C (1382 °F) where radiation and convection are also expected to be taking place between the valve and the other components in the engine during operation. The meshed valve shown in Figure: 4.47 consists of 11551 nodes and 7136 elements.
The temperature, the resultant heat flux and the resultant temperature gradient results of the exhaust valve with both materials, indicate that the titanium alloy (Ti-4822-4) will perform well under such high temperature applications. Figure: 4.48 to Figure: 4.53 give the results of the temperature, the resultant heat flux and the resultant temperature gradient for both materials. According to the results, both materials show invariably no deformation to the applied temperature load. This indicates that the deposited material (Ti-4822-4) would comfortably do well under such high temperature conditions.
Figure: 4.48: Temperature reactant in exhaust valve with Ti-4822-4 material

Figure: 4.49: Resultant heat flux of exhaust valve with Ti-4822-4 material
Figure: 4.50: Resultant temperature gradient of exhaust valve with Ti-4822-4 material

Figure: 4.51: Temperature reactant in exhaust valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material
Figure: 4.52: Resultant heat flux in exhaust valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material

Figure: 4.53: Resultant temperature gradient in exhaust valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material
4.7.2 Buckling analysis and comparison of valve of the two titanium alloys

Axial stresses due to exhaust gas pressure and the valve spring that keeps the valve in its seat, might sometimes cause the valve to buckle. As a result of this, it is good when buckling analysis is exploited to determine how well a designed valve can withstand the stresses to which it will be subjected. In this case, the valve with Ti-4822-4 customised materials operating at 750 °C, is subjected to an assumed pressure (stress) 20 N/m². The buckling result is compared to that of the valve made with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material.

![Figure: Resultant amplitude on valve with Ti-4822-4 material](image-url)
Figure: 4.55: Resultant amplitude of valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material

The buckling analysis results presented in Figure: 4.54 and Figure: 4.55 for both titanium alloy materials show that the resultant amplitude plot for the valve with Ti-4822-4 material is between 0 to $2.035 \times 10^{-3}$, while that of the valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material is between 0 to $1.926 \times 10^{-3}$. These are negligible values; however, the resultant amplitude is more felt on the valve head and slightly at the valve neck, which is quite expected as the valve heat is directly subjected to the exhaust gas pressure, as it is expelled from the engine. The load factor of 24.148 of valve with Ti-4822-4 material is slightly higher than the load factor of 23.814 for the valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material. This indicates that the deposited material (Ti-4822-4) can well withstand the buckling stresses under high-temperature applications.

4.8 SUMMARY

To summarize this chapter, it is necessary to present and simplify the important outcomes of the selected test samples based on the characterizations done and the
analysis that resulted from the outcomes. Heights and the microhardness of the deposited samples in relation to the deposition parameters (laser power, scanning speed and powder-flow rate), as well as the deposition method on the un-preheated, laser-preheated and the heating-bed preheated substrates have been established by using the design expert 6.0.8. Micrographs with OP and SEM have also been presented. The results of the constituent material compositions plot and phase analysis, using EDX and XRD have also been presented. The wear-volume and the wear-rates results of the sliding wear test were presented. The results of the corrosion potential ($E_{corr}$), current density ($I_{corr}$) and the corrosion rates of the deposited samples were similarly presented and discussed.

The results based on the nano-indentation tests (on hardness, stiffness, modulus of elasticity and creep) carried out on the selected samples were presented and analyzed. And finally, the results on the thermal and buckling analysis carried out on a simulated exhaust valve were also presented. The last chapter (Chapter Five) presents the main conclusions of this research work.
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATION

5.0 INTRODUCTION

In concluding this research work, a summary of the material characterization, the results and the analysis are presented in this chapter. The summary encapsulates the deposition parameters utilized, method of deposited samples production (through un-preheated, laser-preheated and heating-bed preheated substrates), as well as the effects of deposition parameters and the preheating of substrates. From the analysis, some recommendations for future work were proffered.

5.1 CONCLUSIONS

The advent of laser-additive manufacturing technology has brought about sustainable production, repairs and the addition of extra-functional features on the existing components. Laser-additive manufacturing technology (laser-metal deposition) has now made it possible to fabricate components of titanium aluminide alloys, which are now gaining numerous applications in the aerospace, automobile, marine, medical, nuclear and energy industries.

The gamma-titanium aluminide alloys are structural materials now finding applications in areas, in which high strength and elevated temperature applications are desired. The ability to improve its properties and to produce either equiaxed, lamellar, duplex and pseudo-duplex structures (and in some cases with Widmastätten structures) makes the gamma-titanium aluminide alloy a material of engineering importance. These
characteristics or structures have caused the gamma-titanium alloy to greatly influence the chemical, physical and mechanical properties of such materials.

With the ability of gamma titanium aluminide alloy (Ti-4822-4) to compete with other high-strength structural materials in high strength and high temperature applications, the manufacturing process of production to obtain the best-quality components becomes an issue of paramount importance. This is because the manufacturing process, heat treatment and thermo-mechanical actions influence the quality of the structural materials. As such, an investigation has been carried out to deposit titanium aluminide alloy (Ti-4822-4) and to study the effects of the processing parameters and the manufacturing method on the deposits.

Three different manufacturing routes (using un-preheated, laser-preheated and heating-bed preheated substrates) have been utilized to deposit the TiAl alloy; while varying the deposition parameters (laser power, scanning speed and powder-flow rates). The deposited samples were characterized on the basis of their microhardness, microstructures, phase analysis, wear rates, corrosion rates and other mechanical properties (hardness, stiffness, Young’s modulus and creep) based on the nano-indentation experiments. The outcome of the characterization revealed interesting findings.

The lateral cracks seen at the fusion zone and the longitudinal cracks running from the surface of the substrates – right up to the top surface of the deposits disappears - as the laser power increases or the scanning speed decreases. This is attributed to the increase in the energy density of the deposited samples that causes
gradual cooling, thereby reducing the residual stresses that normally lead to cracks. The height measurement of the deposited samples also revealed that an increase in the laser power, a decrease in the scanning speed and an increase in the powder-flow rate causes more metallic powder to be trapped in the melt pool, thereby leading to a corresponding increase in the height of the deposited samples.

The Vicker's microhardness of the deposited samples on an un-preheated substrate, revealed that any increase in the laser power, or an increase in the scanning speed and an increase in the powder-flow rates all lead to an overall increase in the microhardness of the deposited samples. For samples deposited on the laser-preheated substrate, the overall Vicker's microhardness decreases, as the laser power increases; while the scanning speed decreases, as the powder-flow rate increases.

While for samples of the heating-bed preheated substrate, the Vicker's microhardness reduces from sample H1 (546.58 Hv) to H2 (536.42 Hv) as the laser power increases from 400 W to 450 W; while the scanning speed and the powder-flow rate are kept constant at 3.17 mm/s and 2.77 g/min. But at 400 W and 450 W, at a constant scanning speed of 2.65 mm/s and a powder-flow rate 2.77 g/min, the Vicker's microhardness of the sample H3 (549.48 Hv) increases to 559.88 Hv in sample H4.

The careful examination under the scanning-electron microscope, the deposited samples revealed fine clearly defined grains of duplex structures, showing feathery $\gamma$-TiAl and $\alpha_2$-Ti$_3$Al lamellar structures. The lamellar structures increase as the energy density (with respect to laser power and scanning speed) increases, with Widmanstätten colonies found within the lamellar structures, as well as being noticeable.
in samples like UC5 (deposited at 400 W, 4.232 mm/s and 7.12 g/min) and LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min). The increase in laser power, together with a decrease in the scanning speed and a reduction in powder-flow rate also results in a reduction in the density of the pores seen in the deposited samples. The increase in laser power in deposited samples with heating bed preheated substrate led to a reduction in the dense dendrite structures, seen in samples H1 and H3 at 400 W compared to that used in samples H2 and H4 at 450 W.

The energy dispersive spectroscopy (EDX) revealed a similar elemental composition spectrum for those deposited samples, without preheating and heating bed preheated substrates. The EDX spectrum of samples with a laser-preheated substrate revealed slightly different elemental composition with sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min) showing less and with a narrower energy spectrum. The X-ray diffraction (XRD) analysis of samples showed that γ-TiAl and α₂-Ti₃Al phases were the two phases found in sample LA1 (deposited at 200 W, 10.58 mm/s and 4.09 g/min), LA2 (deposited at 300 W, 10.58 mm/s and 4.09 g/min), LA3 (deposited at 400 W, 10.58 mm/s and 4.09 g/min) and LA4 (deposited at 500 W, 10.58 mm/s and 4.09 g/min).

XRD analysis of sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min), LB2 (deposited at 300 W, 9.522 mm/s and 4.09 g/min), LB3 (deposited at 300 W, 8.464 mm/s and 4.09 g/min), LC3 (deposited at 300 W, 10.58 mm/s and 4.85 g/min) and LC5 (deposited at 300 W, 10.58 mm/s and 6.38 g/min) all gave an intermetallic single-phase γ-TiAl compound. The XRD analysis of sample UA4 gave three different phases of TiAl₂, Ti₃Al and Ti₃Al₂; while that of sample H2 gave Ti₃Al, TiAl and TiAl₃ phases.
The emergence of these phases can be attributed to the manufacturing process and the rate of cooling that took place in the deposited samples. The structures, phases and elemental composition of the processed TiAl alloy are responsible for the mechanical properties displayed by the deposited samples.

The tribology test carried out on the samples showed that test samples displayed minimal wear rates. However, sample UA2 (deposited at 350 W, 3.174 mm/s and 4.09 g/min) has the lowest wear rate of 8.57x10^{-5} mm³/Nm while sample H1 (deposited at 400 W, 3.174 mm/s and 2.7 g/min) had the highest wear rate of 2.53x10^{-4} mm³/Nm. The relationship between the laser power and the wear rate showed that the wear rate increases; as laser power increases in samples of unpreheated substrate; while in samples of the laser-preheated and the heating-bed preheated substrate, revealed that the wear rate decreases, as the laser power increases.

The corrosion rates displayed by the samples showed minimal corrosion rates with the lowest corrosion rate recorded for sample UA5 (deposited at 500 W, 3.174 mm/s and 4.09 g/min) at 2.6x10^{-4} mm/year, sample LA4 (deposited at 500 W, 10.58 mm/s and 4.09 g/min) at 4.33x10^{-4} mm/year and sample H4 (deposited at 450 W, 2.645 mm/s and 2.7 g/min) at 6.4x10^{-4} mm/year.

The nano-indentation analysis carried out on the selected test samples revealed that sample H2 (deposited at 450 W, 3.174 mm/s and 2.7 g/min) has the highest hardness and modulus of 5095.96 MPa and 150.94 GPa and sample LA5 (deposited at 600 W, 10.58 mm/s and 4.09 g/min) with the least hardness of 4253.74 MPa. The test also revealed the highest material stiffness of 0.1722 mN/nm in sample H2 and the least
material stiffness of 0.1291 mN/nm in sample LA5. The stiffness value means that sample LA5 compared to sample H2, would easily be deformed; when subjected to uniaxial load. The creep referred to as comparative change in indentation depth at constant test load, revealed that sample LA3 has the highest value of 0.191; and sample H2 with the minimal value of 0.106.

The modelled valve simulated under thermal and buckling conditions using SOLIDWORKS 2017, indicated that the deposited material (Ti-4822-4) would do well under such high temperature application and gave a load factor of 24.148 as compared to valve with Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si material that gave a load factor 23.814.

In conclusion, the study has clearly demonstrated the effect of the manufacturing method and the deposition parameters on the manufactured TiAl alloy. The study revealed that it is possible to improve the properties of gamma TiAl alloy through careful selection of the manufacturing process and the laser-deposition parameters. Hardness of alloy has been improved by two to three times the value of CP-Ti microhardness of 178.5 Hv. The study also revealed that the intermetallic duplex structure has improved creep resistance, strength, stiffness, wear rate and corrosion rate; and this is what makes them suitable for high-strength structural and elevated temperature applications.
5.2 RECOMMENDATIONS

Possible future works in this regard are highlighted below:

- Wear and corrosion analysis can further be studied under artificial sea water or any corrosive medium at a higher temperature.
- Design and simulation of engine components with the determined results, using a sophisticated simulation tool. This would provide better insight into the material's behaviour and safety.
- A prototype of such engine components can then be fabricated through the laser-metal deposition technique; and this could then be subjected to physical, mechanical, and non-destructive testing.
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### APPENDICES

Appendix 1: CP-Ti test certificate.

![Material Test Certificate](https://example.com/appendix1_certificate.jpg)

We hereby certify that the materials above have been manufactured and tested in accordance with the specification stated—all materials comply with the specification.

**Note**
1. Visual Inspection: passed
2. Dimensional Inspection: acceptable
3. Packing in plywood case.

**MANAGER OF Q.C. DEPT.**
Appendix 2: Ti-4822-4 material test certificate

Certificate of Analysis & Certificate of Conformity

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All elements measured in weight percent unless otherwise specified. Sampling Method per ASTM B215.

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**Hall Flow per ASTM B213**

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**Microtrac**

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**Qualification Tests**

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**Sieve per ASTM B214**

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Spec ranges shown above in italics are target or nominal specifications only.
* indicates test is not required for routine acceptance.

By Abdulrahman, Kamardeen Olajide: 217037413
Certificate of Analysis & Certificate of Conformity

Product Name: T1-4822-4
Customer: WEARTECH
Ship Date:

Praxair Spec: 038014-BK
Shipping Order #: 70923945
Item Number: 038014-2K
Customer PO #: POA50502
Lot Number: 7
Quantity: 2
UM: KG

All elements measured in weight percent unless otherwise specified. Sampling Method per ASTM B215.

Sieve per ASTM B214

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PLI INFORMATION:
The materials meet the following requirements: N. 4606 M Issue 2 Rev A, P1TF120 S1, C50TF96 S4, B50TF345 S1

CERT COMMENTS:

LOT COMMENTS:
PRAXAIR SURFACE TECH VENDOR #90506

COMMENTS:

DAR Date:
Approved for GE S-400 codes D, F, G, H, I, J, K, XD
The material test report has been generated by a certified S400 laboratory.

Statement of Conformity
Praxair Surface Technology certifies that processing, product testing, and inspection control of raw material and formulating procedures are in conformance with all applicable specifications, drawings, and/or standards. Complete test reports as required are on file. Powders do not have a shelf life & the expiration date of slurries is listed in the header above. Document validated per electronic signature.

PST: 171711  C-51027

Spec ranges shown above in italics are target or nominal specifications only.
* indicates test is not required for routine acceptance.

(317) 240-2650
Telefax (317) 240-2225
Toll-Free Telefax 1-800-234-4738 U.S.A
AS9100 Registered Quality System

Materials Testing Laboratory
This report is confidential and proprietary, and intended for the recipient of the product. If you receive in error you are prohibited from discussing, copying, distributing, or using any of the information. The test report shall not be reproduced except in full, without the written approval of the laboratory. Please contact our office for instructions. The recording of false, fictitious, fraudulent statements or entries on the certificate may be punished as a felony under federal law. All elements measured in percent unless otherwise specified. Founding is per ASTM E28.
Appendix 3: Friction Coefficient plot of deposited samples.

Sample UA2

Sample UA3

Sample LA3

Sample LA5

Sample H1

Sample H2
Appendix 4: Corrosion rates of Deposited samples from log[i(A)] against potential (V).

Tafel plot of Sample UA1

Tafel plot of Sample UA2

Tafel plot of Sample UA3

Tafel plot of Sample UA4

Tafel plot of Sample UA5
Tafel plot of Sample LA1

Tafel plot of Sample LA2

Tafel plot of Sample LA3

Tafel plot of Sample LA4

Tafel plot of Sample LA5

Tafel plot of CP-Ti
Appendix 5: Indentation test values of deposited samples
Appendix 5a: Indentation test values for sample LA3
Parameters
HIT (Mpa)
EIT (Gpa)
E* (Gpa)
HVIT (HV)
Fmax (mN)
hmax (nm)
S (mN/nm)
hc (nm)
hr (nm)
hp (nm)
m
Epsilon
R2
Ap (nm^2)
Welast
Wplast
Wtotal
Er (Gpa)

Indent 1 Indent 2 Indent 3 Indent 4 Indent 5 Indent 6 Indent 7 Indent 8 Indnet 9 Indnet 10 Avg. Values
3680.4 4154.6 4305.9 5653.5 4837.8 4161.2 4142.3 2979.9 3562.7 3296.8
4077.51
121.78 128.51 135.19 158.48 128.24 44.513
199.8 111.59 69.303 42.397
113.9803
131.36 138.62 145.82 170.94 138.32 48.014 215.51 120.37 74.752 45.731
122.9437
340.85 384.76 398.77 523.58 448.03 385.38 383.62 275.97 329.95 305.32
377.623
4.97
5.01
5.01
4.98
5
4.99
4.99
5.02
5.01
5
4.998
268.66 252.05
246.3 207.81 232.13 290.04
244.7 306.34 290.07 323.01
266.111
0.1598 0.1584 0.1627
0.163 0.1465 0.0589 0.2324 0.1649 0.0971 0.0632
0.14069
246.05 229.07 223.84 185.16 206.55 228.41 229.08 284.22 252.56 265.46
235.04
237.56 220.44 215.54 177.22 197.96 205.27 223.22 275.92 238.48 243.84
223.545
-11306.9 149.21 188.31 157.28 180.19 -4512.49 191.37 -13954.1 -20176.1 -5978.38 -5506.149
372.2725 3.2534 1.8856
1.652 1.5202 56.6519 2.4824 468.6948 396.7115 79.6018 138.47261
0.73
0.73
0.73
0.74
0.75
0.73
0.73
0.73
0.73
0.73
0.733
1.196
1
1
1
1
1.065
1
1.308
1.571
1.065
1.1205
1349668 1205294 1162508 881722.1 1034436 1199811 1205417 1684057 1405748 1517949 1264661.17
186.67 143.73 111.79 110.24 111.18
299.7 129.61 182.25 252.51 295.74
182.342
538.13 248.47 299.47 284.41 292.58 450.44 360.39 585.61 429.82 521.26
401.058
724.8 392.19 411.26 394.65 403.76 750.14
490 767.86 682.33 816.99
583.398
117.86 123.67 129.36 148.76 123.43 46.084 181.41 108.93 70.177 43.977
109.3658

Appendix 5b: Indentation test values for sample LA5
Parameters Indent 1 Indent 2 Indent 3 Indent 4 Indent 5 Indent 6 Indent 7 Indent 8 Indnet 9 Indnet 10 Avg. Values
HIT (Mpa)
3404.4 4905.3 4667.3 3757.5 4405.2 5433.9 3566.2 3979.7 4670.8 3747.1
4253.74
EIT (Gpa)
87.33 124.82 111.27 107.11 103.19 118.28
56.36 107.82 115.85 109.97
104.2
E* (Gpa)
94.196 134.63 120.02 115.53
111.3 127.58 60.791
116.3 124.96 118.62
112.3927
HVIT (HV)
315.28 454.28 432.24 347.99 407.97 503.24 330.27 368.56 432.57 347.02
393.942
Fmax (mN)
5.01
5.01
5
5
5.01
4.99
5
4.99
4.98
5.01
5
hmax (nm)
289.83 230.32
239.8 269.57 249.99 219.77 297.74 261.05 237.52 269.89
256.548
S (mN/nm)
0.1232
0.142 0.1312 0.1413 0.1262 0.1283 0.0798 0.1378 0.1357
0.145
0.12905
hc (nm)
260.26 204.68 211.58 243.84 220.55
190.3 252.16 234.76 210.86 244.62
227.361
hr (nm)
249.16 195.06
201.7 234.84
210.3
180.9 235.05 224.89 200.84 235.34
216.808
hp (nm)
-16199.6
44.46 176.94 187.38 185.65 164.96 -16094
-13.8 160.74 206.07 -3118.125
m
405.37 5.2716 1.6497
2.322 1.6211 1.4101 261.4484 7.6003 2.0936 1.8474
69.06342
Epsilon
0.73
0.73
0.74
0.73
0.74
0.76
0.73
0.73
0.73
0.73
0.735
R2
1.233
0.999
1
1
1
1
1.526
1
1
1
1.0758
Ap (nm^2)
1472494 1020906 1071016 1330641 1137297 917805.4 1402297 1253237 1065722 1337344 1200875.73
Welast
238.12 201.22 142.41 155.58 146.78 131.89 353.46
192.6 159.61 150.52
187.219
Wplast
282.12 290.94 367.36 361.96 315.36 339.04 380.15 347.96 375.16 371.85
343.19
Wtotal
520.24 492.17 509.77 517.64 462.14 470.93 733.61 540.56 534.77 522.36
530.419
Er (Gpa)
87.046 120.49 108.65 104.95 101.45
114.8 57.731 105.59 112.68
107.5
102.0887

By Abdulrahman, Kamardeen Olajide: 217037413

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### Appendix 5c: Indentation test values for sample H2

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<th>Indent 9</th>
<th>Indent 10</th>
<th>Avg. Values</th>
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<td>102.15</td>
<td>147.94</td>
<td>152.96</td>
<td>141.93</td>
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Appendix 6: Other metallographic equipment used in preparation and characterization of samples

Optical Microscope (OP)

Polishing Machine
Vicker's Micro-hardness tester

Anton Paar (version 7.3.13) standard tribometer
Anton Paar indentation (7.3.15) equipment enclosure