

**CHARACTERISATION AND FLOWABILITY OF TITANIUM GRADE 5
ALLOY POWDERS**

**A thesis submitted in fulfillment of the requirements for the degree Magister
Technologiae: Mechanical Engineering**

in the Faculty of Engineering and Technology

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SEPTEMBER 2013

Declaration

I Mr. Patrick Kiola Nziu, declare that this thesis is my original work and that it has not been presented to any other university or institution for similar or any other degree award.

.....

Signature

17/09/2013

Date

Publication

A section of thesis has been accepted for publication in the Journal of Engineering, Design and Technology, manuscript ID JEDT-05-2013-0036 entitled “Characterization of titanium powder: A review on current status on flowability”.

Acknowledgement

Since the time I commenced working on this project to this final manuscript, I have continuously sought advice suggestions, data and financial support from numerous sources. For this, I am greatly indebted to a number of people for the success of this project.

First of all I express my thanks and gratitude to God, for giving me the strength and sanity to finish this project report.

My greatest debts are to my family for their encouragement, materials and financial support. I also give thanks to my colleagues for their contribution. Special thanks go to my supervisors Prof LM Masu, Prof P Mendonidis and Dr D Labuschagne for their brilliant suggestions, guidance and constructive criticism without which the project objectives could not have been achieved. The author also wishes to thank Mr Andries Uys, Mr Gerrie Booysen, Mr Johan Els, Dr Machio, Ms L Mahlatji and Mr Marius for their contribution towards this research, and Prof. Deon de Beer for providing research funds from Titanium Centre of Competence through Hub and Spokes.

Lastly the author pays gratitude to Aerosud, CUT, CSIR and Vaal University of Technology for their support during this research.

Dedication

To my family, friends and relatives.

Abstract

Flowability is one of the essential physical characteristics considered during the use of any powder in a manufacturing process. However, very little research on flowability of titanium powder has been conducted. To this end, this study dealt with global market survey of titanium powder manufacturers and suppliers. In addition, the effects of various physical parameters such as particle size, shape, chemical analysis, density and soundness on flowability of titanium grade 5 alloys powder in additive manufacturing application were investigated.

Twelve powder samples of titanium alloy grade 5 (Ti6Al4V) were sourced, tested and analyzed using various methods. The choice of the characterization method used depended on its accuracy, equipment availability and application. Particle size and shape were characterized using laser diffraction and scanning electron microscope techniques, respectively. Quantitative and crystallographic analyses were done to determine the chemical composition as well as alpha and beta phases. Shear cell and dynamic tests were performed to determine bulk density, stability, flow energy and flowability where as particle density was performed by a pycnometer. Research on potential manufacturers was conducted using questionnaires.

It was established that high cost of titanium powder is partly driven by titanium powder firms that are not willing to disclose information about the product. It was observed that powder flowability is affected by particle size, shape, chemical composition, density and soundness. The particle density was found to be a function of chemical composition that is the alloying elements and impurities present in the powder. It was noted that bulk density, porosity, cohesion and agglomeration were affected by particle size. Soundness of the powder was also found to improve with sphericity of the particles. Among the physical parameters studied, particle size had the highest effect on powder flowability. The highest flowability was noted at particle size of 41 μm .

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Chapter One: Introduction

1.1 Background of the study

Over the years, various manufacturing processes have been used to fabricate products and parts for industrial, domestic and other uses. These processes include casting, molding, forming, machining, joining and more recently additive manufacturing. Each process uses a distinctive technique starting with different forms of raw materials such as billets, bar, plate, sheet, hollows, extrusions, wire, strips, powder, foil etc. to the final products produced with varying application range (Ozugwu and Wang, 1995).

The current study focused on additive manufacturing (AM) processes, previously referred to as rapid prototyping (Fathi and Dickens, 2012), which is a process of joining materials layer upon layer to fabricate objects from 3D model data (Lim *et al.*, 2012) in form of continuous slices (Paul and Anand, 2012). AM process produces parts with complex shape, having net or near net shape which require limited finishing processes or none (Bolzoni *et al.*, 2012b), thus only small amounts of material waste is produced (Pohlman *et al.*, 2012). The produced parts, have good mechanical properties such as tensile strength, near full density, porosity and stiff moduli of elasticity, etc., all of which are enhanced by sintering processes (Essen *et al.*, 2009). However, the drawbacks of AM process are limited maximum part size and low manufacturing speed in comparison to the conventional methods (Vayre *et al.*, 2012).

The powder comprising spherically shaped metallic powders from titanium, titanium alloy, stainless steel, aluminium oxide, silicon carbide, bronze, nickel, cobalt, chromium (Paul and Anand, 2012) as well as non metallic powders such as plastics, wax, papers, glass, polymer among others have been used as feedstock materials (Mostafa *et al.*, 2009) in AM processes. However, titanium and its alloys are gaining wider industrial application (Ricceri and Matteazzi, 2003) due to their superior properties in comparison to other alternative metals. These properties include high specific strength (strength to weight ratio), toughness, low thermal expansion, light weight, non magnetic, low modulus of elasticity, high fracture and corrosion resistant among others (Ozugwu and Wang, 1997)

Some of the specific characteristics of these powders are flowability, compressibility, compactability and sinterability, among others. However, flowability is one of the essential physical characteristics considered during the use of any powder in a manufacturing process (Pohman *et al.*, 2012), since it affects the quality of the final products (Liu *et al.*, 2008). It is usually affected by various physical parameters such as particle size, shape, chemical composition, density, soundness, moisture content, surface roughness (Liu *et al.*, 2008; Matsusaka *et al.*, 2012) etc. These physical parameters are also used in powder characterization (Freeman *et al.*, 2009). However, flowability studies have only been conducted on pharmaceutical powders such as Ibuprofen and other powders, namely, alumina, soda, limestone, cement, dolomite, aluminum oxide trihydrate, coal and clay (Cagli *et al.*, 2007; Marcu *et al.*, 2012). As such, very little research has been conducted on titanium powder, actually using less accurate methods such angle of repose and flowmeters (Marcu *et al.*, 2012; Pohman *et al.*, 2012). In addition, there is lack of credible international titanium powder suppliers' reference database where titanium powder can be procured conveniently.

1.2 Purpose of study

The purpose of the study was to develop a credible international supplier reference database for titanium grade 5 alloy powders complete with product specifications, characteristics and their respective prices. Consequently, a list of companies trading in titanium powder was created. Powder verification was done through precise chemical and crystallographic analysis of powders sourced from international suppliers to ascertain the quality of the powder. In addition, the effect of physical characteristics on powder flowability in additive manufacturing processes was analysed and evaluated to determine the best flow characteristics.

1.3 Significance of the study

Publishing a comprehensive study on the existing global powder supply chain may provide impetus to all titanium research and development activities. Consolidation of procurement through the Titanium Centre of Competence is a realistic expectation and is considered a research enabler and accelerator for this field of application, innovation and research.

1.4 Problem Statement

Currently, there is very little credible and available data in form of a catalogue or directory comparing titanium powder products against known recognised manufacturing processes and meeting standards, quality, product range and price.

In the absence of clear guidelines, it is extremely costly (Froes, 2000) and difficult to correctly select powders with the appropriate characteristics for a particular application. It stands to reason that ascertaining whether the powder supplied was correctly chosen, ordered and delivered is not objectively possible without reliable specifications.

In practice, the procurement of typical gas atomized titanium powder for the additive manufacturing process is single sourced from the original equipment manufacturer with limited possibility of recycling. Since there is no well researched titanium powder specifications, most users are reluctant to buy the commodity from alternative suppliers due to the fact that the impact on the final product and equipment is not quantified. Due to lack of effective competition in the market, the prices of titanium powder has remained high, thus increasing the cost of production for additive manufacturing products.

The premium in cost of titanium powders drives the selling price for titanium products produced by additive manufacturing processes. Effective market penetration is limited because the selling price is two to five times higher (Poondla *et al.*, 2009) when compared with similar products from alternative processes.

Lastly, very little research on flowability of titanium powder has been conducted, despite being one of the essential physical characteristics considered during the use of any powder in manufacturing process.

1.5 Objectives

The main objective of this study was to determine the effects of various physical characteristics such as particle size, morphology, chemical composition, density and soundness on flowability of titanium grade 5 alloy powders in additive manufacturing. In addition, worldwide market survey of titanium powder manufacturers and suppliers was conducted.

In this study, twelve samples of titanium grade 5 alloy powders from various suppliers were characterized on major physical parameters which affect flowability. The choice of the equipment used for characterization was based on its accuracy, availability and application. In addition, research on potential manufacturers and suppliers was conducted using two sets of questionnaires and sent via email to possible identified Companies.

The layout of this thesis is presented in Table 1 hereunder:

Table 1: Thesis layout

S/No.	Chapter	Name
1	One	Introduction
2	Two	Literature Review
3	Three	Methodology
4	Four	Results and Discussions
5	Five	Conclusions
6	-	References
7	-	Appendix

Chapter Two: Literature Review

2.1 Titanium metal: Characteristics and uses.

Titanium is a relatively new engineering material (Bolzoni *et al.*, 2012) and is the ninth most abundant element in the earth crust (Cheng *et al.*, 2011). Due to its highly reactive nature, titanium exists in the form of compounds such as rutile (TiO_2), ilmenite ($\text{FeO} \cdot \text{TiO}_2$), leucosene ($\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2$) etc, in rocks, beach sand, sea water, ash coal deposits, etc (Cheng *et al.*, 2011), usually referred to as titanium ores. Titanium metal is extracted from these titanium ore compounds by metallothermic reduction processes (Toru *et al.*, 2004), and refined by chemical leaching and vacuum melting techniques to remove impurities.

Titanium is an allotropic element and has five naturally occurring isotopes, ^{46}Ti through ^{50}Ti , with ^{48}Ti being the most abundant (73.8%) (Encyclopaedia Britannica, 2006). It is alloyed with other metallic elements such as iron, aluminium, vanadium, molybdenum etc, to form titanium alloys.

Titanium and its alloys are classified into 31 grades (ASTM, 2006) with grades 1 to 4 being referred to as commercially pure (unalloyed) titanium while the rest are alloys with different properties (Donachie, 1988; Encyclopaedia Britannica, 2006). These grades are further categorized into four broad groups namely; commercially pure alloys, alpha and near alpha alloys, alpha-beta alloys and beta alloys (Ezugwu and Wang, 1997). They are briefly described here-under;

- i. The commercially pure alloys contain small amounts of oxygen and iron and are not heat treatable since they are single phase alloys (Ezugwu and Wang, 1997). They have excellent corrosion resistance but are low in strength.
- ii. Alpha alloys are single phase alloys since they do not contain any beta alloying elements. Ti5Al2.5Sn is the only true alpha alloy. Alternatively, near alpha alloys have small amounts of beta phases, up to 2 % in their matrix and therefore, are heat treatable (Ezugwu and Wang, 1997). They are good at weldability, notch toughness, corrosion and creep resistance.

- iii. The alpha and beta or dual phase alloys contain both alpha and beta phases. They are heat treatable and have superior ductility and strength properties when compared to their individual phases (Ezugwu and Wang, 1997). Titanium grade 5 alloy falls into this group.
- iv. The beta alloys have sufficient percentage of beta stabilizing elements and small amounts of alpha phases making them heat treatable (Ezugwu and Wang, 1997). They are good at cold forming and offer high strength up to 700°C.

The titanium alloy grades discussed above are further illustrated in form of three dimensional phase diagram as shown in Figure 1.

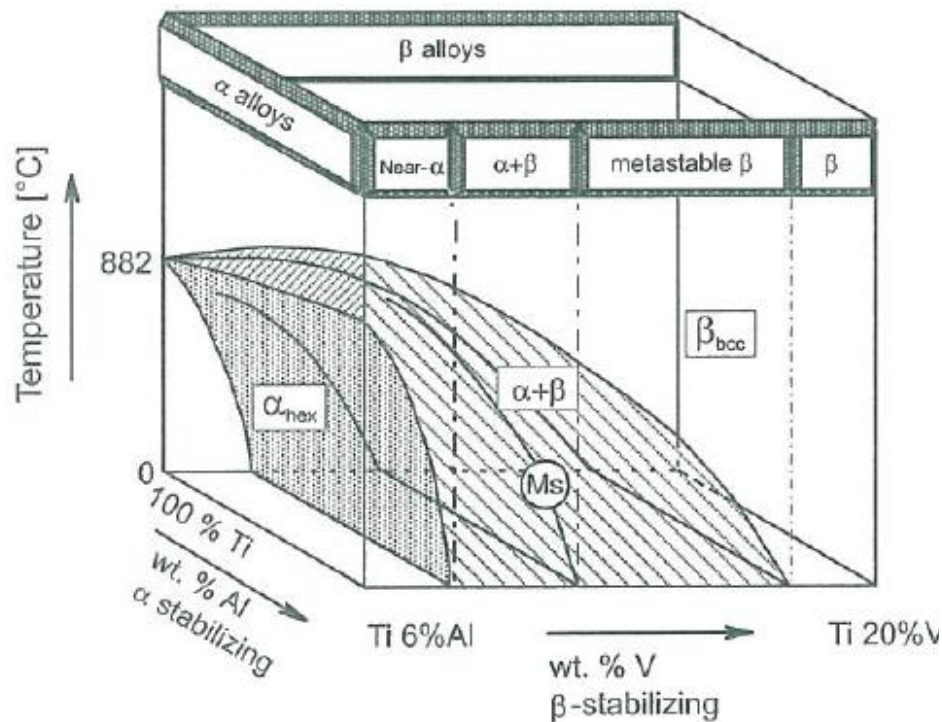


Figure 1: Three dimensional titanium alloy phase diagram (Leyens and Peters, 2003)

There are various types of titanium alloys phase diagrams. However, titanium-aluminium phase diagram shown in Figure 2 and ternary phase diagram shown in Figure 3 are the most commonly used phase diagrams in the heat treatment of titanium alloys. Titanium-aluminium phase diagram

consists of several intermetallic phases namely; α Ti, β Ti, α_2 Ti₃Al, γ TiAl, TiAl₂ and TiAl₃. Each intermetallic phase has unique physical properties and therefore suitable for different applications (Leyens and Peters, 2003).

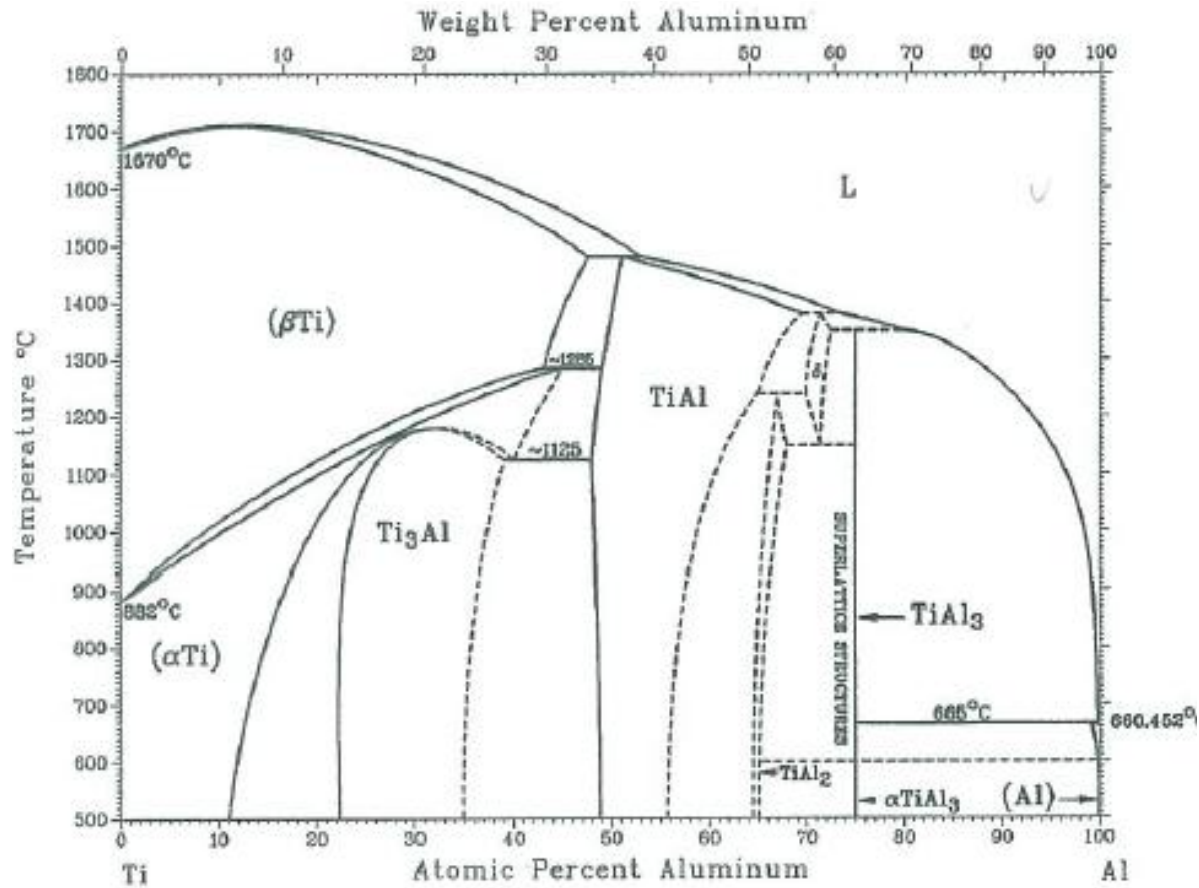


Figure 2: Titanium-Aluminium phase diagram (Leyens and Peters, 2003)

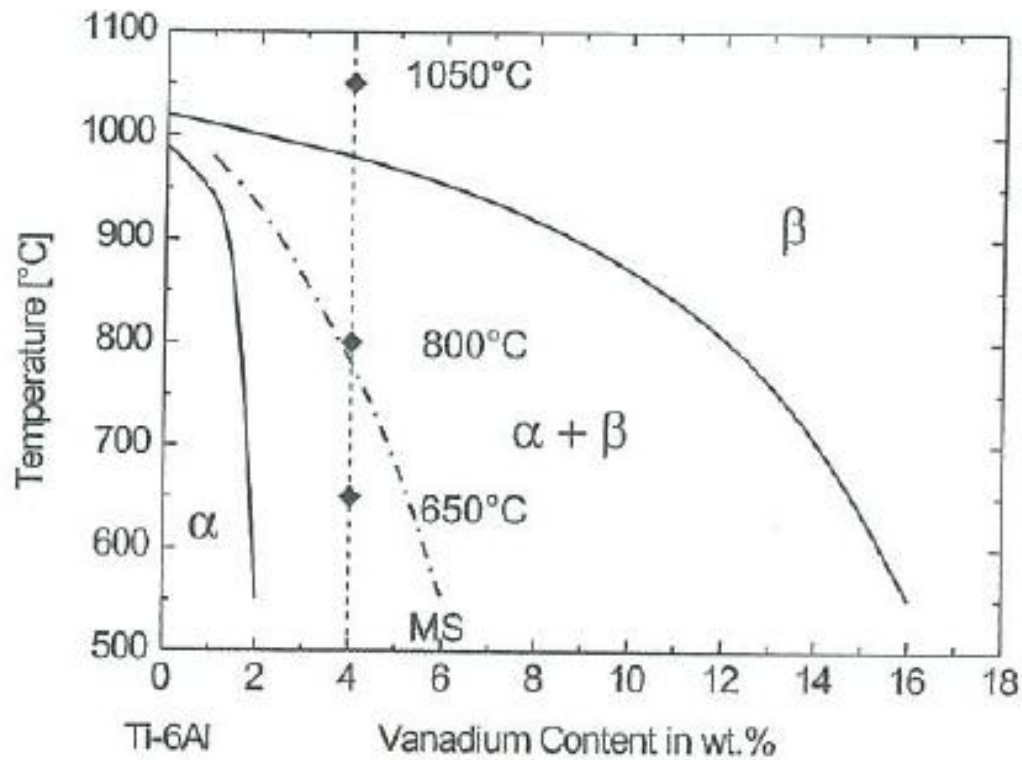


Figure 3: Ternary phase diagram Ti-6Al-V (Leyens and Peters, 2003)

The microstructure of titanium alloys is mainly influenced by the nature of thermo-mechanical treatment used such as heat treatment, deformation, recrystallization, aging and annealing. There are two common types of microstructures namely; lamellar and equiaxed. These microstructures depend on the size and arrangement of α and β phases (Leyens and Peters, 2003). Lamellar microstructure is generated by cooling from the beta phase, thus its structure depends on the cooling rate. Slow cooling rate results in coarse microstructures while rapid quenching leads to martensitic transformation of β forming fine needle like microstructures (Leyens and Peters,

2003). On the other hand, equiaxed microstructure occurs as a result of recrystallization which depends on the degree of deformation of α and β phases (Leyens and Peters, 2003).

Thermo-mechanical treatment of titanium alloy microstructure improves fracture toughness, fatigue and creep strength but reduces residual stress developed during fabrication. In addition, it produces an optimum combination of ductility, machinability, dimensional and structural stability (Leyens and Peters, 2003).

Titanium and titanium alloys are gaining wider industrial application (Ricceri and Matteazzi, 2003) due to their superior properties in comparison to stainless steel, cobalt, chromium alloys, commercially pure niobium and tantalum (Breme *et al.*, 2003). These properties are high specific strength (strength to weight ratio), toughness, low thermal expansion, light weight, non magnetic, non radio opaque, low modulus of elasticity, high fracture and corrosion resistant among others (Ozugwu and Wang, 1997). Major uses of titanium and its alloys in the industry are in:

- i. Aerospace industry to fabricate parts of jet engines and structural assembly. In jet engines they are used in fabrication of fan blades, compressor blades, rotors, discs, hubs and inlet guides vanes while in structural assembly they are used in forged wing structures, fasteners, springs, hydraulic tubing, engine nacelles, airframe and landing system (James and Edgar, 2003).
- ii. Chemical processing equipment, where they are used to manufacture titanium vessels, heat exchanger tanks, agitators, coolers and piping system since they are resistant to aggressive compounds such as nitric acid, organic acids, chlorine dioxide, inhibited reducing acids and hydrogen sulfide (Ozugwu and Wang, 1997).
- iii. Petroleum refining industry, where they are used to fabricate scrubbers, vessels, plate and frame exchangers as well as in shell and tube exchangers due to their high corrosion resistant against hydrogen sulphide and carbon dioxide.
- iv. Nuclear plants, where they are used to fabricate steam generating tubes and tube plates for both pressurized water reactors (PWR) and boiling water reactors (BWR) since they are able to withstand the operating conditions unlike copper tubes that crack due to hot spots allowing

radioactive matter to escape to the atmosphere (Ozugwu and Wang, 1997), hence enhancing the environmental safety.

- v. Marine industry, where they are used to fabricate submarine ball valves, fire pumps, heat exchangers, hull materials for deep sea submersibles, water jet propulsion systems, propellers and propeller shafts, exhaust stack liners, naval armor, under water manipulators, high strength fasteners, yatch fittings, shipboard cooling and piping systems due to their high strength and corrosion resistance (Ozugwu and Wang, 1997).
- vi. Architectural applications, where they are used to fabricate roofs due to their high strength, light weight, and low thermal expansion (Ozugwu and Wang, 1997).
- vii. Automotive and motorcycle industry, where they are used to manufacture connecting rods, wrist pins, valves, valve retainers, springs, rocker arm and camshafts because of their good heat resistant, light weight, durability and better performance (Froes, 2000).
- viii. Military hardware, where they are used for the manufacture of body vests, heavy duty body armor, helmets for military, police and security forces due to their ballistic properties as well as high strength to weight ratio (Ozugwu and Wang, 1997).
- ix. Biomedical application, where they are used to make hard body tissues such as artificial hip joints and surgical implants (Ozugwu and Wang, 1997) by joining the bones and tissues since they possess good mechanical properties (such as bioadhesion and biocompatibility) that are similar to the human bone (Barbucci, 2002). The Young's modulus of titanium (110 Gpa) is almost ten times higher than that of the bone (10 – 30 Gpa) (Long and Rack, 1988). This mismatch leads to the formation of stress shielding which reduces both the bone healing and modeling, thus causing an unreliable bone implant. Nevertheless, stress shielding is overcome by reducing the implant young's modulus of elasticity (Oh *et al.*, 2003). This is achieved by altering the implant porosity level through introduction of pores (Oh *et al.*, 2003). Two methods are used to introduce pores in titanium implants namely solid and liquid state methods (Banhart, 2001). Since titanium is highly reactive and has high melting point the solid state method which uses foam is preferred. The foam solid state processes that are commonly used include gas entrapment (Murray and Dunand, 2003), space holder (Wen *et al.*, 2001, 2002; Jee *et al.*, 2000), pressing and sintering methods (Oh *et al.*, 2003). The above processes produce an open cellular structure (Karlsson *et al.*, 2000) having a low modulus of elasticity of 5.3 Gpa (Oh *et al.*, 2003) which is compatible with human bone. Implants with

rough surfaces usually encourage the bone growth into the pores. This allows the stress to be transferred from the implant to the bone (Oh *et al.*, 2003) thus providing an excellent anchorage. However, the implants produced by foam solid state technology have low compressive strength compared to human cortical bones (human bones found in arms and legs) (Oh *et al.*, 2003).

- x. Other applications include the manufacture of pulp and paper, electrochemical anodes (cathode protection), brazing alloys, nuclear waste storage (Ozugwu and Wang, 1997) and sports equipment such as softball bats and golf club heads (Froes, 2000) among other uses.

Titanium and its alloys are sold in the market mostly in the cast or wrought form as billet, bar, plate, sheet, strip, hollows, extrusions, wire, powder etc. (Ezugwu and Wang, 1997). Conventional machining operation such as turning, milling, reaming, drilling, tapping, sawing and grinding are cumbersome and challenging (Pohlman *et al.*, 2012) due to chipping and premature tool failure (Ezugwu and Wang, 1997). This occurs as a result of the tendency of titanium metal to weld onto the cutting tool, and the presence of high interface temperatures and stresses between the tool and the work piece (Ezugwu and Wang, 1997) during machining. In this regard, powder metallurgy and additive manufacturing processes (Harby *et al.*, 2007) of titanium powder are recommended for use (Pohlman *et al.*, 2012) while utilizing the advantages of powder forming process.

2.2 Titanium powder production

Pure titanium powder is produced by the Armstrong Process (Pohlman *et al.*, 2012) where titanium tetrachloride (TiCl_4) is injected into a flowing stream of liquid sodium (Na^+) producing a two phase mixture of Ti powder and the by-product of sodium chloride (NaCl). Titanium alloy powder is produced mainly by either the blended elemental or the pre-alloying techniques, followed by powder consolidation (Froes, 2002).

Traditionally, titanium production is through the Kroll process which involves chlorination of TiO_2 ore at high temperatures in the presence of carbon and then reacting the resulting TiCl_4 with magnesium to produce titanium sponge (Toru *et al.*, 2004). In the blended elemental approach the sponge fines are blended together, then hot isostatic pressed and sintered to near full density (Grenier *et al.*, 1998; Froes, 2000).

Various processes are used in the production of prealloyed titanium powder such as titanium Ti₆Al₄V Grade 5 (Bolzoni *et al.*, 2012a), which include;

- i. The Hydride- De-Hydride process (HDH) where raw material in the form of solid scrap, billet or machined turnings are cleaned of impurities then hydrogenated to produce brittle material which is ground in the presence of inert argon gas (Vinicius *et al.*, 2001).
- ii. The Plasma Electrode Process (PREP) where Ti grade 5 alloy in the form of a rotating bar is arced with gas plasma (Froes, 2000). As the bar rotates the molten metal is centrifugally flung off, cooled and collected (Vinicius *et al.*, 2001).
- iii. The Titanium Gas Atomisation (TGA) process where melting of titanium metal is done in a vacuum induction skull melted in a water cooled crucible (Fritz *et al.*, 2011). The molten metal is collected and atomized with a stream of high pressure inert gas (Vinicius *et al.*, 2001).
- iv. The Plasma Atomization (PA) process which employs 3 inert gas plasma jets to atomise titanium wire to form powders (Froes, 2000; Fritz *et al.*, 2011).

All of the above production processes produce spherically shaped particles except for the HDH process that produces angular shaped particles. Spherically shaped particles can achieve full density, thus the parts produced have no porosity or void defects and are good in weldability ((Froes, 2000).

2.3 Titanium components production

Various powder consolidation methods are used to produce final additive manufacturing products, *inter alia*:

- i. Metal injection or powder injection moulding (MIM), where the metal powder is mixed with polymer binder to form the feed stock that is injected into the mould (Froes, 2000) after which debinding is done, followed by vacuum sintering (Sidambe *et al.*, 2012).
- ii. Direct powder rolling process (DPR), where powder produced by elemental processes is used in fabrication of both single and composite multilayered sheet and plates (Harby *et al.*, 2007).

- iii. Spray forming process, where powder is put into a deleva-type nozzle and expanded until it reaches a supersonic flow speed of 300 – 1200 m/s, and then sprayed into a rotating mould to produce monolithic shapes (Froes, 2000). In addition, this technique is also used for coating and bonding together of different materials (Froes, 2000).
- iv. Hot isostatic pressing (HIP), where powders are consolidated close to their densities by using high temperature and pressure (Bolzoni *et al.*, 2012b; Froes, 2000).
- v. Spark plasma sintering (SPS), which consolidates powders close to their maximum densities (Grigoryev and Olevsky, 2012) by application of resistive heating and pressure (Choi *et al.*, 2007).

Research has shown that for a manufacturing industry to be more efficient in its production operation (Harby *et al.*, 2007) it has to embark on the use of sound prototype components preferably from additive manufacturing processes (Harby *et al.*, 2007) because they are easy to manufacture.

2.4 Additive Manufacturing

Additive Manufacturing (AM), previously referred to as rapid prototyping (Fathi and Dickens, 2012), is a process of joining materials layer upon layer to fabricate objects from 3D model data (Lim *et al.*, 2012) in form of continuous slices (Paul and Anand, 2012). All AM processes follow the following development stages (Harby *et al.*, 2007);

- i. Concept- product requirements to satisfy the need are first identified.
- ii. Preliminary design- the product requirements are made into a computer CAD program that performs design checks such as stress analysis, fit, form and function.
- iii. Preliminary prototype fabrication- AM products are produced easily since the CAD has an ability to modify and create new prototypes without using a highly skilled operator. It also saves a lot of time unlike manual machining which makes prototypes out of metal or wood.
- iv. Short run production- AM technology is used to produce several prototypes or rapid tooling machines like jigs and fixtures which make work easier and faster.
- v. Final production- involves the manufacturing of hard tooling moulds and dies.

These development stages can be represented in an AM cycle as shown in Figure 4:

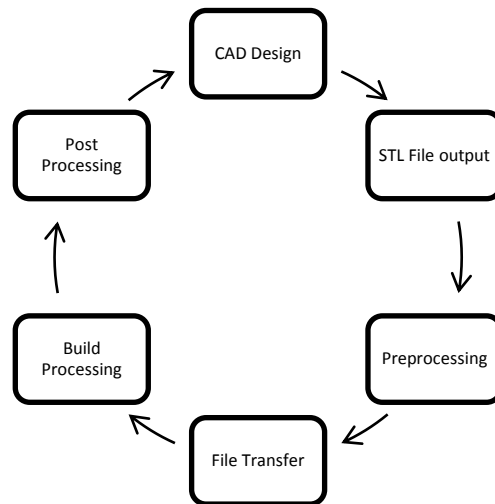


Figure 4: The AM Cycle (Harby *et al.*, 2007).

Metallic powders from titanium, titanium alloy, stainless steel, aluminium oxide, silicon carbide, bronze, nickel, cobalt, chromium (Paul and Anand, 2012) as well as non metallic powders such as plastics, wax, papers, glass, polymer among others have been used as feedstock materials (Mostafa *et al.*, 2009) in AM processes.

The AM process produces parts with complex shapes, having net or near net shape which require minimal finishing processes or none (Bolzoni *et al.*, 2012b), thus only small amounts of material waste is encountered (Pohlman *et al.*, 2012). The produced parts, also have good mechanical properties such as tensile strength, near full density, low porosity and stiff moduli of elasticity, etc., all of which are enhanced by sintering processes (Essen *et al.*, 2009). However, the drawbacks of AM process are limited maximum part size and low manufacturing speed.

The primary methods of AM process are as follows (Harby *et al.*, 2007);

- i. Fused Deposition Modeling (FDM)
- ii. Laminated Object Modeling (LOM)
- iii. Stereolithography Apparatus (SLA)
- iv. Selective Laser Sintering (SLS)
- v. Laser Engineered Net Shaping (LENS)

2.4.1 Fused Deposition Modelling (FDM)

This process involves laying down the material in layers. Production of parts is through extrusion in the form of thermoplastic material beads to form layers that harden immediately as they leave the nozzle. The arrangement is such that a filament made of plastic or a metal wire is unwound from a coil and directs the feedstock to a heated extrusion nozzle. The heated nozzle melts the feedstock and also controls its flow rate (Sarat *et al.*, 2012) into the mould. The nozzle is hydraulically adjusted such that it can move in horizontal and vertical directions using a computer aided manufacturing (CAM) software package that converts STL files into quick slice (QS) format (Mostafa *et al.*, 2009). During the manufacturing process supports are made from water soluble material that are later dissolved with specialized mechanical agitation equipment that uses heated sodium hydroxide solution. Some of the feedstock materials used in this process are investment casting wax, acrylonitrile, butadiene styrene ABS plastic, medical grade ABS thermoplastic and elastomers (Mostafa *et al.*, 2009).

FDM process produces parts with good strength properties due to its stable operating temperature. For example, Figure 5 shows a space shuttle that was built using this process, although it is believed that it could have taken 10 – 20 hours to build while using manual machining (Harby *et al.*, 2007). The major drawback being that the build up speed is slow and it is not able to produce thin vertical columns (Harby *et al.*, 2007).

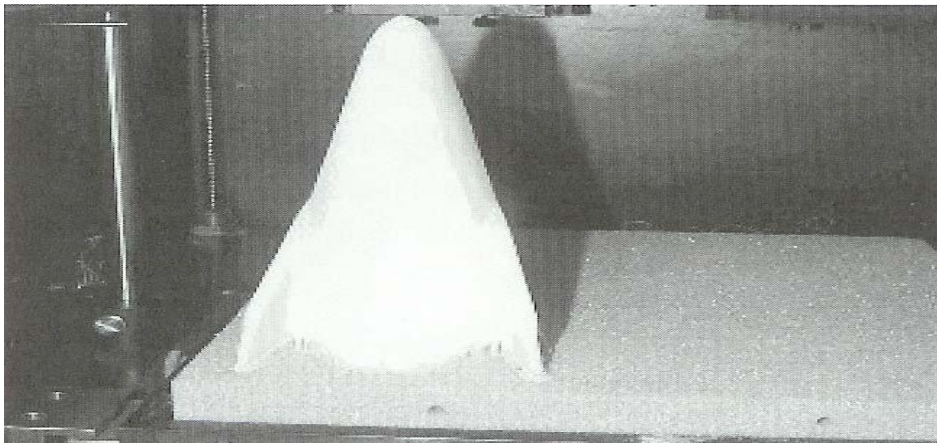


Figure 5: Fused Deposition Created Space Shuttle Model (Harby *et al.*, 2007).

2.4.2 Laminated Object Modelling (LOM)

This is a rapid prototyping method where parts are fabricated from either paper, plastic or composites (Harby *et al.*, 2007) using STL files prototype modellers. The principle of operation is illustrated in Figure 6. The material roll is cut into small layers by laser. The layers are then added to the layer below until aided by a hatched pattern to form a solid laminated block (Aravind and Sanjay, 2001).

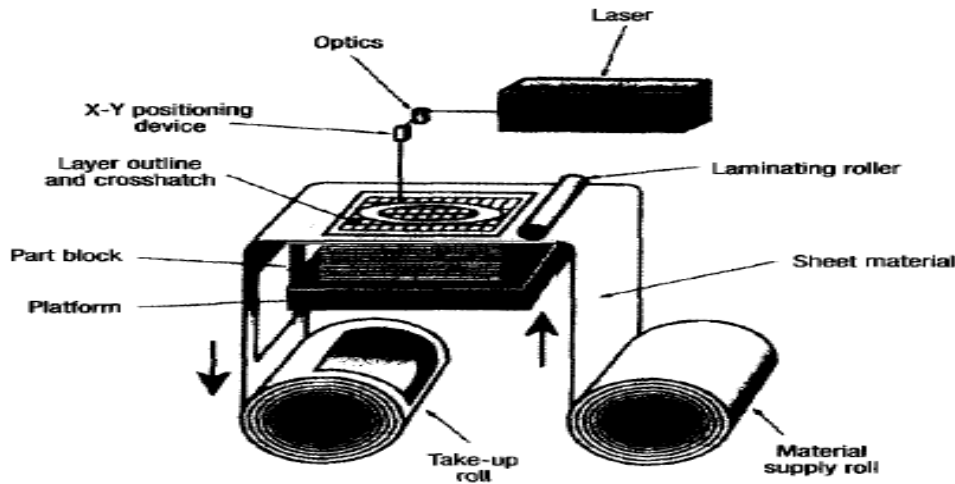


Figure 6: Laminating Object Modeling (Aravind and Sanjay, 2001).

The advantages of this process are that parts produced have high degree of accuracy, high speed development, cheap raw materials and easy to use (Mueller and Kochen, 1999). The major drawbacks are bad smell fumes from hot adhesive, high risk of fire due to burning of materials with a laser to remove any unwanted cross-hatches (Mueller and Kochen, 1999).

2.4.4 Stereolithography (SLA)

In this process, curing of a photosensitive resin is done by an initializing laser by converting the liquid resin into a solid (photopolymerization) (Paul and Anand, 2012). The prototypes produced are thermoset (one time use, non reusable) which consist of acrylates and epoxyresins materials (Gripma *et al.*, 2010). The principle of operation is illustrated in Figure 7. Parts are produced using a computer aided design (CAD) files using a special software package from 3D system (SLA slice) that converts the final usage file into a STL modeling file. After tracing of the

pattern, the SLA's elevator platform moves down to a distance equal to a single layer thickness (Gripma *et al.*, 2010). Fresh resin is then applied to the cross section using a blade and tracing of a new layer is done joining the previous layers thus producing a 3D part. Upon completion of the building process excessive resin is removed by dipping the parts in a chemical bath and then cured in an ultraviolet oven (Harby *et al.*, 2007).

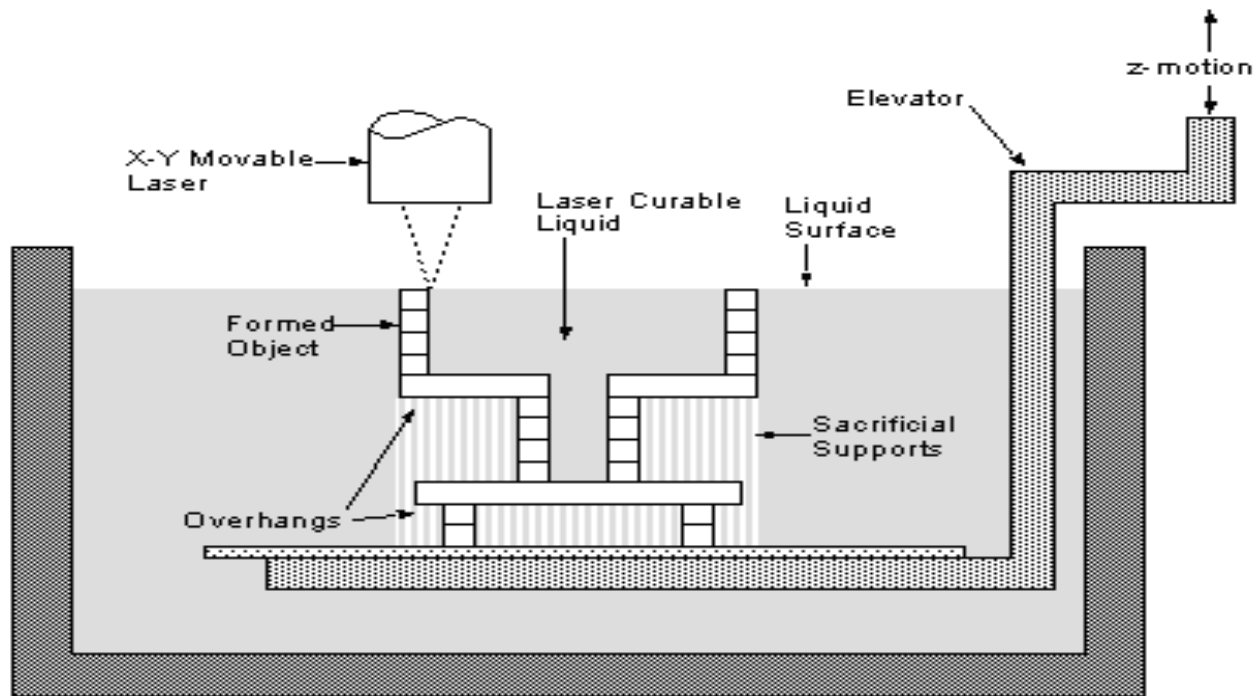


Figure 7: Stereolithography Apparatus(Harby *et al.*, 2007).

The advantages of this process are high production rate, ability to produce large part size, production of strong parts that are used as master patterns for injection and blow moulding (Harby *et al.*, 2007). The major drawback is that the process has a high initial capital cost (Harby *et al.*, 2007).

2.4.4 Selective laser sintering (SLS)

In this process, a high power laser such as carbon dioxide is used to fuse small powder particles of plastic, metal, ceramic or glass to form a three dimensional shape (Harby *et al.*, 2007). The bulk powder material is first preheated by the SLS machine to a temperature below its melting point, so that it is melted easily by the laser.

By scanning the cross section generated from a 3D digital description (usually from a CAD file or scan data), the powdered material is selectively fused by laser on the powder bed surface (Paul and Anand, 2012). After the process completion, bed powder cross section is lowered and a new layer of powder is applied on its top and the above process is repeated until the desired component is obtained.

The general construction of SLS is shown in Figure 8.

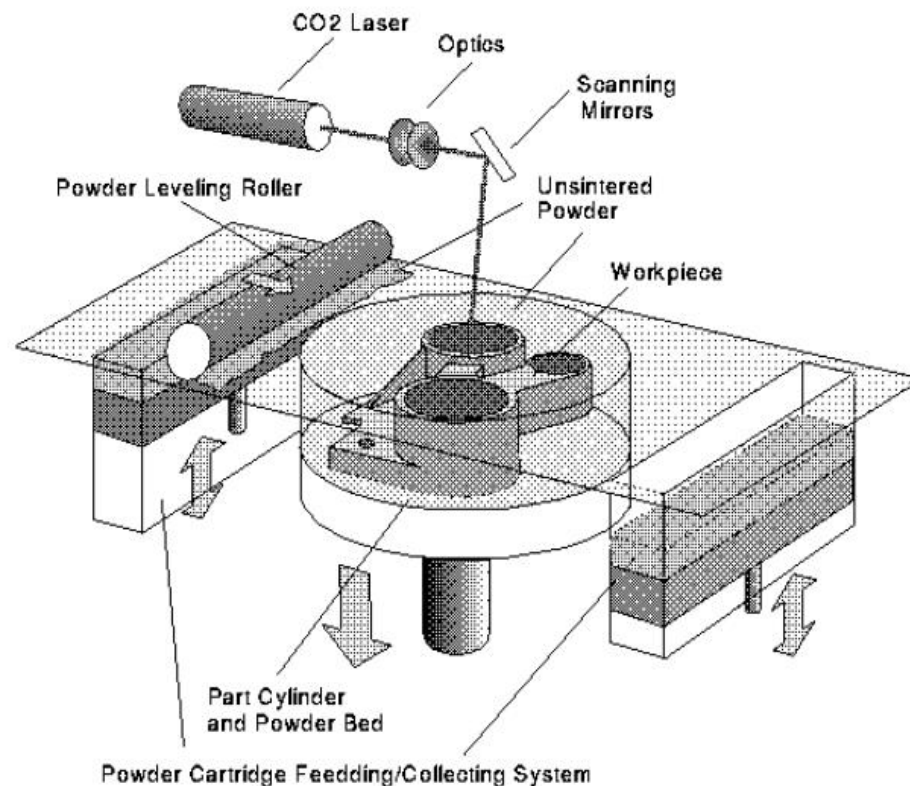


Figure 8. Selective laser sintering (Harby et al., 2007).

In this process components are produced by SLS equipment using either single or two components method. In single component method only the outer particle surface is melted by the laser hence fusing the unmelted cores to each other as well as the previous layer e.g direct metal laser sintering. While in the two component powder method either a powder mixture or a coated powder is used. This process produces a wide range of products from polymers (nylon and polystyrene), metal powder (steel and titanium), alloy mixtures, composites and green sand (Paul and Anand, 2012).

The advantages of SLS are;

- i. Parts produced by this process are able to achieve full density,
- ii. Complex shapes are produced with help of digital CAD data,
- iii. No support structures are required as in SLA and FDM processes.
- iv. High productivity is attained since large number of parts can be packed in the same powder bed.

2.4.5 3D Printing

This process is similar to SLS except that instead of laser, an inkjet printer cartridge injects a liquid binder on to the powder thus binding the deposited powder together to form a complete prototype. However, 3D printed components are weaker compared to the sintered parts produced by SLS, but give a good physical fit and form prototype (Harby *et al.*, 2007). The 3D printing process layout is shown in Figure 9.

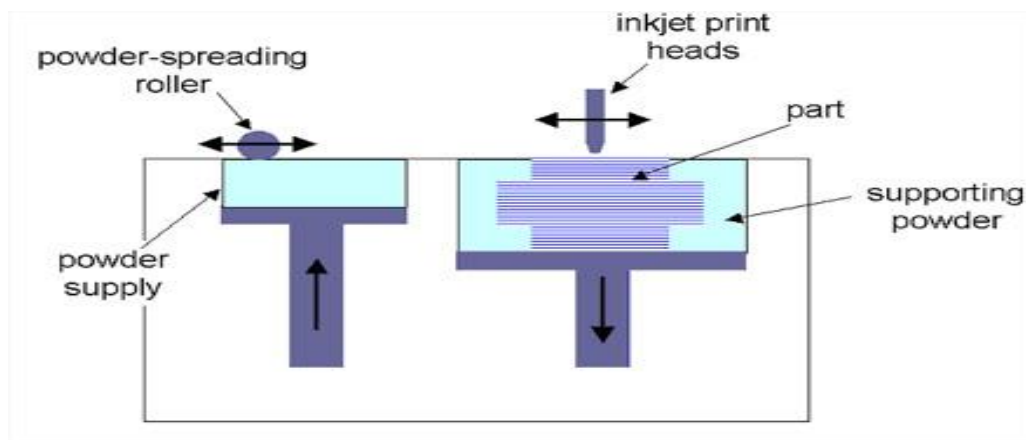


Figure 9: 3D printing process (Harby *et al.*, 2007).

Powder materials used are aluminium oxide, silicon carbide, silica or thin layer of zirconia. The only advantage with 3D printing method is that small size components are fabricated at a low cost and fast.

2.4.6 Comparison between SLA and SLS

In SLA process parts are produced by laser curing of actinic photo polymeric liquid while in SLS they are produced by laser powder sintering (Paul and Anand, 2012). Further comparison of parts produced by these two methods is as follows:

Accuracy

Parts produced by SLS are less accurate than SLA due to high shrinkage rate.

Stability

SLS components retain dimensional stability over a longer periods of time regardless of whether the parts are subjected to high temperatures, chemicals or humidity than SLA components.

Surface features

Parts produced by SLS method have rougher surface finishes than those produced by SLA.

Cost

Both SLS and SLA have high initial and operating costs.

Applications

The sizes of SLA products change with time and are only suitable for applications where strength is less important, while SLS parts are stable and maintain structural integrity over long periods of time.

2.4.7 Laser Engineered Net Shaping

This technique is used to fabricate metal parts from a computer aided design (CAD) solid model by injecting metal powder into a pool of molten metal formed by a focused high powered laser beam. The powder is melted by the laser beam by focusing it on a small area using one or more lenses (Amano and Rohatgi, 2011) in an inert atmosphere to avoid oxidation (Li et al., 2010).

The approach of this process is similar to 3D fabrication and forms solid components by layer additive method and the parts produced have near full density. The powders used are mainly alloys of titanium, aluminum, stainless steel and composites materials. Generally this process is used in repair and overhaul works, rapid prototyping, rapid manufacturing and medical applications.

The advantage of this process is that it produces strong functional metal components that are constructed easily from CAD with variety of metal powders. However, parts produced by this process have rough surface finish, therefore secondary finishing processes such as polishing are necessary.

From the literature reviewed, components produced by additive manufacturing processes such as 3D Printing technology are less commonly used in the manufacturing industry than alternative manufacturing process such as subtractive material methods, despite the advantages (Harby *et al.*, 2007). The low usages of additive manufacturing components is attributed to lack of reliable data (Harby *et al.*, 2007), particularly on some mechanical properties such as compressive strength (Harby *et al.*, 2007). Research on compressive strength properties of the components produced by additive manufacturing technology would give the much needed information on the effects of build orientation, cure time after initial part build and cure temperature (Harby *et al.*, 2007).

2.5 Titanium powder manufacturers

Since the main scope of this study is on titanium powder, the research also focused on titanium powder manufacturers. A review of metal powder producers published in 2005 by Capus M Joseph (Capus, 2005) showed that most of the Companies are in North America, United States of America, Europe and Japan. The rest are in Australia, Bahrain, Brazil, China, India and Russia. Out of 86 companies reviewed only 6 dealt with manufacture of titanium and its alloys among other metal powders (Capus, 2005). Most of the companies produced metal powders of iron, steel, copper, aluminum, magnesium and nickel alloys.

The above information was obtained through questionnaires and response letters from titanium powder manufacturers among other published sources (Capus, 2005) which included the

company profile, their contact address and production capacity, since it was considered confidential to list company by sales volume (Capus, 2005). Table 2 shows a list of some of the titanium powder manufacturers that are available.

Table 2: Titanium Powder Availability (Froes, 2000).

S/ No	Organization	Process	Type	Size	Price	Market Activity	General Comments
1	Pyrogenesis	Plasma atomization	Various	-45 >45	≈ 180 35-75	Powder available	High quality(low PIM grade is<45 microns
2	Starmet	PREP/REP	Various	Average 150	50-100 ≈200(PIM)	Powder available level about 1 ton/year but potential to increase	Sales of power “healthy” with increasing PIM inquires
3	Crucible research	GA	Various	-500 +45 -45	≈45(CP/64) ≈50(TiAl) 155(1000lbs) and 134(5000 lbs)	2-3 Tons/year market growing slowly	15 ton/year capability
4	Sumitomo Sitix	Ingot drip/ GA	CP 6-4 TiAl	-45 -150 -250 -250	40-50 (MIM) 20-30	1-3 Tons/month unstable market Powder available	“Tilop”(Ti low oxygen powder) capability to 15 ton/month formerly Osaka Ti
5	MER	PA	CP Alloys	1 to 15	60	R &D Stage	Produced on custom order basis
6	Affinity	GA	CP 6-4	Various size fractions from -230 to +43	20-48	Powder available with O ₂ , Fe lower than ASTM, B-265 requirement	Containerless process 200MT/year capability 1000MT in 2001
7	Affinity	HDH	CP	Various size Fractions from -140 to +25	8 - 12	R & D Stage	Low O ₂ 200mt/year capability

8	Metamorphic Metal Ltd	HDH	CP Ti, Ti-3Al-2.5V & Ti6Al4V	-250 for plasma - 149 for press/Sinter (P/S) -74 and -44 for PIM	20-50	Capacity@2 ton/month Custom lots/blends and low O ₂ powders available	Focus is on the development of new applications for P/S and PIM technology
9	Hyper Industries	HDH	6-4	-200	20-25	Powder available	Produced on order basis
10	ADMA Chips	HDH	CP 6-4	-45 -45	10 10	Samples available Samples available	
11	ADMA	BE	CP	-45	20	Powder available	
12	Reading Alloys	HDH	CP 6-4	-300 + 50 -300 +50	20-50 20-50	Powder available Powder available	Oxygen 0.3 wt% Max.-Angular Oxygen 0.25 wt % Max -Angular
13	Fray	Reverse Electrolytic	Various	To be defined	To be defined	Research base	Oxygen levels as desired

There are also other organizations that deal with titanium manufacturing namely, International Titanium Organizations (ITA), Titanium Information Group (TIG) and others. These are shown in Tables 3 and 4.

Table 3: Titanium powder manufacturers (TIG data sheet No.16, 2006).

S/No.	Company	Country	Powder type	Approximate cost/kg (€/kg)
1	AP & C	Canada	Plasma	500-1000
2	Bongen/Affinity	China/USA	GA	150-200
3	Bongen/Affinity	China/USA	HDH	25-150
4	Crucible	USA	GA	150-200
5	International Titanium powder	USA	Direction reduction	500-1000
6	Pioneer Metals & Technology	USA	PREP	500-1000
7	Pyrogenesis	Greece/Canada	Plasma	500-1000
8	Reading alloys	USA	HDH	25-150
9	Se-Jong	Korea	HDH	25-150
10.	Starmet (Formely Nuclear Metals)	USA	PREP	500-1000
11.	Sumitomo	Japan	GA	150-200
12.	TLS	Germany	GA	150-200
13.	TLS	Germany	HDH	25-150
14.	Toho	Japan	HDH	25-150
15.	Zunyi Titanium	China	HDH	25-150

Table 4: Titanium powder processors (TIG data sheet No.16, 2006).

S/No.	Company	Country	Process
1.	Bodycote HIP	UK	HIP
2.	Dynamet Technology	USA	Cold-Hip
3.	Hitachi	Japan	MIM
4.	ITB Precisiotechniek	Netherlands	MIM
5.	Neotech Services	Germany/USA	LENS
6.	PCC Advanced Forming Technology	USA	MIM
7.	QinetiQ	UK	MIM

2.6 The character and characterization of titanium powder

In Material Science, characterization is defined as the use of physical techniques to investigate the composition, internal structure and properties of materials (ASM, 1986). Various physical parameters such as particle size distribution, shape, chemical composition, density and soundness among others are used to characterize titanium powder (Freeman *et al.*, 2009). Moreover, these parameters also affect its flowability (Matsusaka *et al.*, 2012), which is one of the main aspects of this study.

2.6.1 Particle size distribution

Titanium powder production methods produce particles with various particle sizes i.e. BE 45-180 μm , HDH 50-300 μm , PREP 100-300 μm , TGA 50-350 μm and PA 0-200 μm particle size ranges (Oh *et al.*, 2003; Oliveira *et al.*, 2006). Grain size and shape affect the particle movement, permeability and angle of friction.

Particle size is measured in wet or dry conditions. In dry conditions methods such as sieving, optical microscopy, transmission electron microscopy and scanning electron microscopy are used (Otsuki *et al.*, 2010). In wet conditions interactive force apparatus and various laser source methods such as dynamic light scattering and laser diffraction are used (Tafesse *et al.*, 2012)

even though the latter is not suitable for use in a high particle concentration solution (Otsuki *et al.*, 2010). The above size determination methods are discussed here under:

- i. Sieving methods are carried out according to ASTM C136 where mesh screens of reducing sizes (Oliveira *et al.*, 2006) and mechanical shakers are used. Particle size range of 45 -710 μm can be determined by sieving (Pohlman *et al.*, 2012) in either dry or wet conditions. In practice, this method enables particles of various size ranges to be separated easily but its major drawback is that some powder sticks to the mesh holes preventing further separation (Liu, 2009). Table 5 shows a mesh size comparison chart for titanium powder currently being used by the manufacturers such as Timet Powder Metals.
- ii. Optical microscopy methods have been used to study the structure of powder and metals (Johari and Bhattacharyya, 1969), however they are limited in their use since they have small depth of focus, low magnification $\times 2000$, their resolution depends on wavelength of light used and, in addition, the specimens have to be polished (Johari and Bhattacharyya, 1969).
- iii. Transmission electron microscopy has high magnification of $\times 300,000$. It is usually used to study the effects of heating, cooling, deformation and oxidation when fitted with the necessary accessories (Johari and Bhattacharyya, 1969). However, the equipment is fairly costly and it requires great care and skill to operate (Johari and Bhattacharyya, 1969).

Table 5: Mesh Size Comparison Chart (Timet Powder Metals, 2012).

Mesh	Microns	Inches	Millimeters	Netafim Disk Ring Color	Object
3	6730	0.2650	6.730		
4	4760	0.1870	4.760		Gravel starts at 4.75 mm
5	4000	0.1570	4.000		
6	3360	0.1320	3.360		
7	2830	0.1110	2.830		
8	2380	0.0937	2.380		
10	2000	0.0787	2.000		
12	1680	0.0661	1.680		
14	1410	0.0555	1.410		
16	1190	0.0469	1.190		Eye of a Needle = 1,230 microns
18	1000	0.0394	1.000		
20	841	0.0331	0.841		
25	707	0.0280	0.707		
28	700	0.0280	0.700		
30	595	0.0232	0.595		
35	500	0.0197	0.500		
40	420	0.0165	0.420	Blue	
45	354	0.0138	0.354		
50	297	0.0117	0.297		
60	250	0.0098	0.250		
70	210	0.0083	0.210		
80	177	0.0070	0.177	Yellow	
100	149	0.0059	0.149		
120	125	0.0049	0.125	Red	
140	105	0.0041	0.105	Black	

	100	0.00394	0.100		Beach sand (100 – 2,000 microns)
170	88	0.0035	0.088		
200	74	0.0029	0.074		Portland cement
	70	0.00276	0.070	Brown	Average Human Hair (70 – 100)/Grain of salt
230	63	0.0024	0.063		
	55	0.00217	0.055	Green	
270	53	0.0021	0.053		
	50	0.00197	0.500		Remove visible particles from liquid
325	44	0.0017	0.044		Silt (10 – 75)
	40	0.00157	0.040	Purple	Lower limit of visibility (Naked Eye)
400	37	0.0015	0.037		Plant pollen
(550)*	25	0.00099	0.025		White blood cells/level to achieve “optical clarity” in a liquid
(625)	20	0.00079	0.020	Gray	
(1200)	12	0.0005	0.012		
(1250)	10	0.000394	0.010		Talcum powder/level to remove haze from liquid/fertilizer (10 – 1,000)/ mold spores (10 – 30 microns)
	7	0.000276	0.007		Red blood cells (8 – 12 microns)
(2500)	5	0.000197	0.005		Bacteria (0.5 – 20 microns)
(4800)	3	0.000118	0.003		
(5000)	2.5	0.000099	0.0025		Cigarette smoke & bacteria (Cocci) =2 microns
(12000)	1	0.0000394	0.001		Cryptosporidium (1 – 10 microns)
* Mesh numbers in parentheses are too small to exist as actual screen sizes. They are only estimations and are included for reference.					

- iv. Scanning electron microscope (SEM) (Figure 10) is used to study surfaces of metal, plastic, ceramic and biological materials such as blood, tissue or live insects (Johari and Bhattacharyya, 1969). The specimens are usually prepared for non conductive materials by depositing a thin layer of carbon, gold, tantalum, etc., coating to avoid specimens charging. It has a large depth of focus of about 300 times that of optical microscope. The images are formed by scanning (Johari and Bhattacharyya, 1969) and size distribution analysis is by digitally programmed software. The advantage of SEM is high magnification range, easy manipulation and no special specimen preparation needed (Johari and Bhattacharyya, 1969).

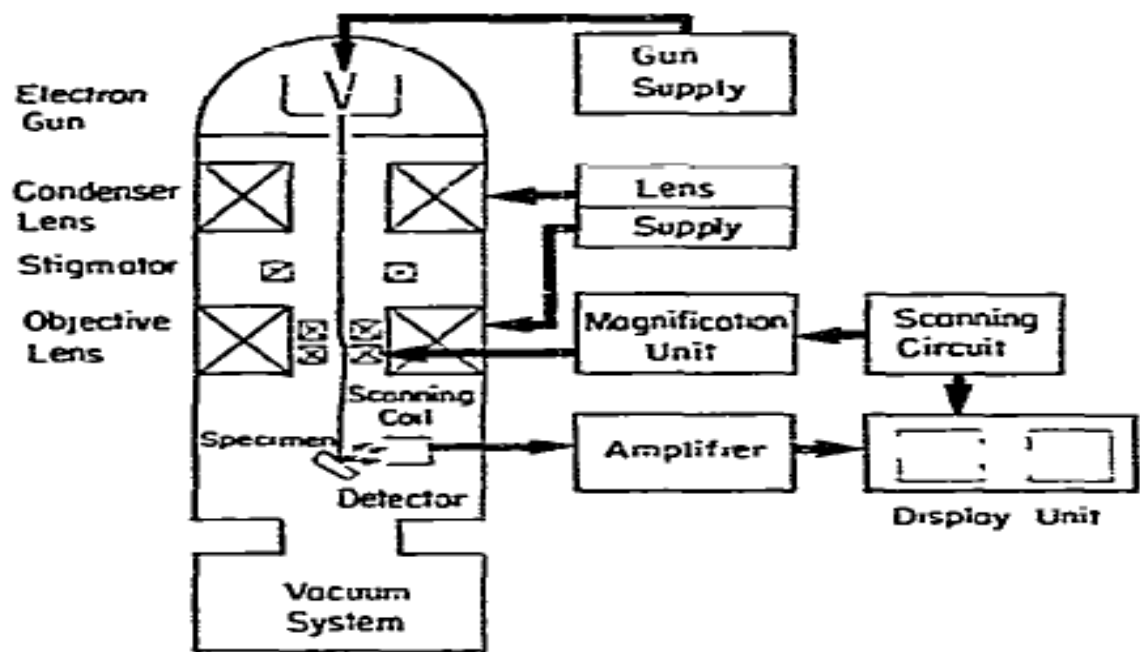


Figure 10: Scanning electron microscope (Johari and Bhattacharyya, 1969).

- v. Laser diffraction and scattering method uses principles of Fraunhofer diffraction and Mie scattering theory (Takeshi, 2001) to measure particle size distribution using particle diameter and diffraction/scattering pattern relationship (Takeshi, 2001). The operation principle of the laser diffraction method is shown in Figure 11. The particle size distribution is determined from two different light intensity distributions in which one is generated by the particles while the other, is determined using theoretical scattered light intensity using either Fraunhofer diffraction or Mie scattering method for particles whose diameter are known (Takeshi, 2001).

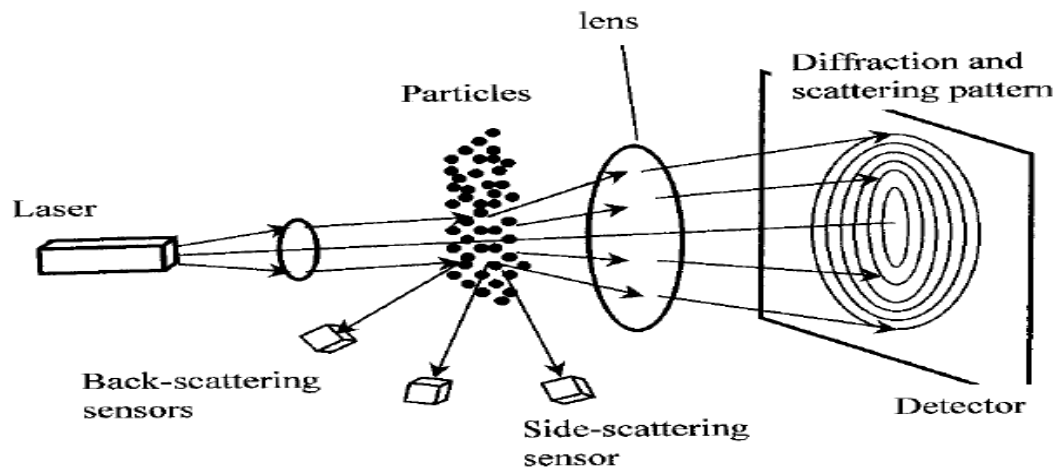


Figure 11: Laser diffraction and scattering method (Takeshi, 2001).

This technique is based on the principle that particles passing through a laser beam will scatter the light rays at angles related to the particle sizes, where larger particles will scatter light at narrower angles with higher intensity than smaller particles (Liu *et al.*, 2008) which scatter at wider angles with low intensity (Liu *et al.*, 2008). The sizes obtained represent the volumetric diameter (Liu *et al.*, 2008) of the particle which are represented in form of a cumulative frequency curve. Parameters D10, D50 and D90 are used to represent the particle size range diameters, with D10 representing the smallest, D50 the average size and D90 the maximum particle diameter (Krantz *et al.*, 2009; Marcu *et al.*, 2012). However, this technique assumes that particles are spherical in shape hence it is not suitable for non spherical (Takeshi, 2001) particles. In addition, elongated or agglomerated powder particles which are difficult to break by sonication are measured as one large particle leading to inaccurate particle size range readings (Otsuki *et al.*, 2010).

- vi. In the Interactive Force Apparatus (IFA) method (Otsuki *et al.*, 2012) particle size distribution in the size range of 147-471nm are determined. The operation principle of IFA method is shown in Figure 12. The process involves suspending the particles in a functional fluid (aqueous, non aqueous solution or organic solvent) under magnetic or electric field thus determining the extent of particle dispersion and coagulation (Otsuki *et al.*, 2010). It consists of main body (electric balance, hemisphere and flate plate), control unit (computer, piezo-stage controller and voltage supplier) and detecting part (multi-meter and oscilloscope).

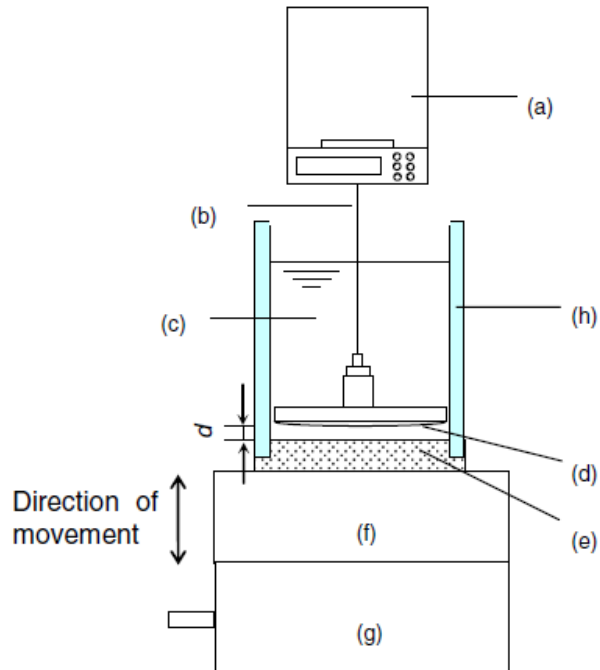


Figure 12: Interactive force apparatus (Otsuki et al., 2010; 2012).

where

- a. Electric balance
- b. Platinum wire
- c. Sample solution
- d. Hemisphere (Gold-coated)
- e. Flat brass (Brass)
- f. Piezo-stage
- g. Z stage
- h. Glass cell

When the electric field is applied between the gold coated hemisphere and flat plates the dielectric particles move towards the direction of electric field in the area between the two plates. This causes particles to experience both repulsive and attractive forces due to the change of particle structure. The cycle of these forces are referred to as interactive force (F_{Sphere}) and are calculated using equation (1). The values of interactive forces obtained in the above test are plotted graphically against the distance between the hemisphere and flat plate to determine both the particle size and the degree of agglomeration (Otsuki *et al.*, 2010):

$$\frac{F_{\text{Sphere}}}{R} = 2\pi W_{\text{Plane}} \quad (1)$$

where

F_{Sphere} - Interactive force between hemisphere and the flat plate

W_{plane} - Interactive free energy

R - Curvature radius of the glass hemisphere

Recent studies show that particle size distribution is mostly being determined by laser diffraction method (Bolzoni *et al.*, 2012a), because of its ability to determine particle sizes less than 1 μm and also gives more accurate results than the other discussed methods, when using equipment models such as Malvern master sizer analysette (Nanotec), BT-9300H or Coulter Laser particle analyser fitted with sonication and diffoculant that breaks up agglomerates and elongations (Esen *et al.*, 2009).

2.6.1.1 Particle shape and size

Particle shape and size are described by three axes namely length (a-axis), width (b-axis) and thickness (c- axis). Length is taken to be the maximum caliper dimension while the thickness is the orthogonal dimensions to the a-axis or b -axis (Tafesse *et al.*, 2012). The ratio between the width and the length is referred to as aspect ratio (AR) (Liu *et al.*, 2008). The two main methods used to measure particle axes are the manual technique and image analysis method. In the manual technique each particle is measured by hand with the help of a Danish box or a caliper, though the method is cumbersome (Tafesse *et al.*, 2012). In the image analysis method also

referred to as digital sieving uses computers where particles images are analyzed by already programmed software that interprets quantitative data from digital images. The process involves four basic steps, namely;

- i. Image acquisition where images are taken using scanners or digital cameras.
- ii. Thresholding where boundaries of the object are determined from the image background using binary image (the object is represented by a white color while black represents the background) (Tafesse *et al.*, 2012).
- iii. Image processing where the calculations of different parameters are done. However, it should be noted that most algorithms in commercial image analysis software are predetermined, therefore, the user can not make any alterations in case of errors.
- iv. The obtained data is tabulated on a Microsoft excel sheet or other statistical programs for further evaluation.

The equipment setup is shown in Figure 13. The images are taken either in static or dynamic state. In the static state, the camera is positioned in orthogonal direction while the plexiglass holder containing the particle is rotated whilst in dynamic system a moving conveyor belt conveys the particle towards a synchronized camera placed in orthogonal position. However, in order to capture all the three axes, 2 to 3 cameras are used (Tafesse *et al.*, 2012).

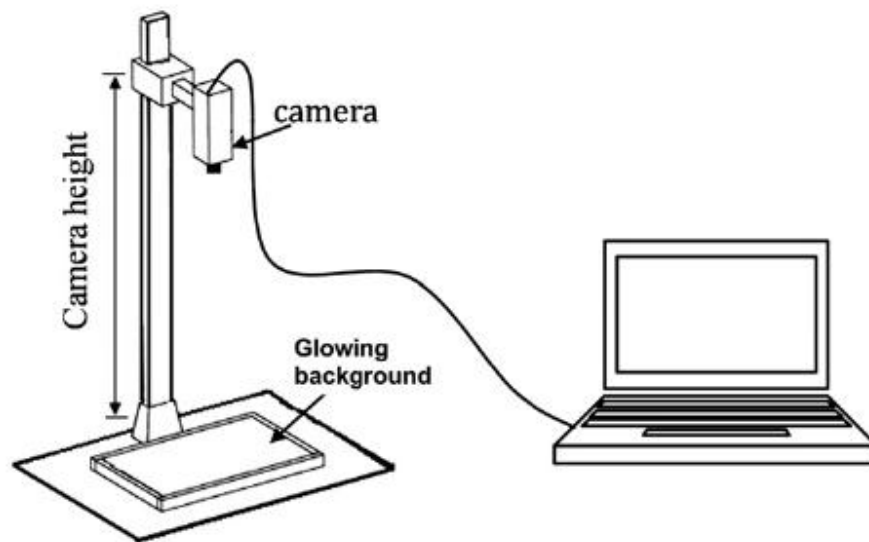


Figure 13: Digital sieving (Tafesse *et al.*, 2012).

2.6.2 Particle shape or morphology

The shape of a particle, whether natural or crushed, normally has a complex morphology and is not uniform (Tafesse *et al.*, 2012). Shape is described in three methods namely; form, roundness and surface textures although, in some studies, form has been termed as shape without any regard to roundness and surface texture (Tafesse *et al.*, 2012). These methods are briefly described below;

- i. Form depends on relative dimensions of the three axes of a particle and is usually expressed in particle axial ratios and can be plotted on Zingg or Sneed and Folk Diagrams. These axial ratios are classified into four groups as shown in Figure 14 namely; oblate (disk shaped or flat), equant (spherical), prolate (rod like or columnar) and bladed (flat and columnar) (Tafesse *et al.*, 2012).

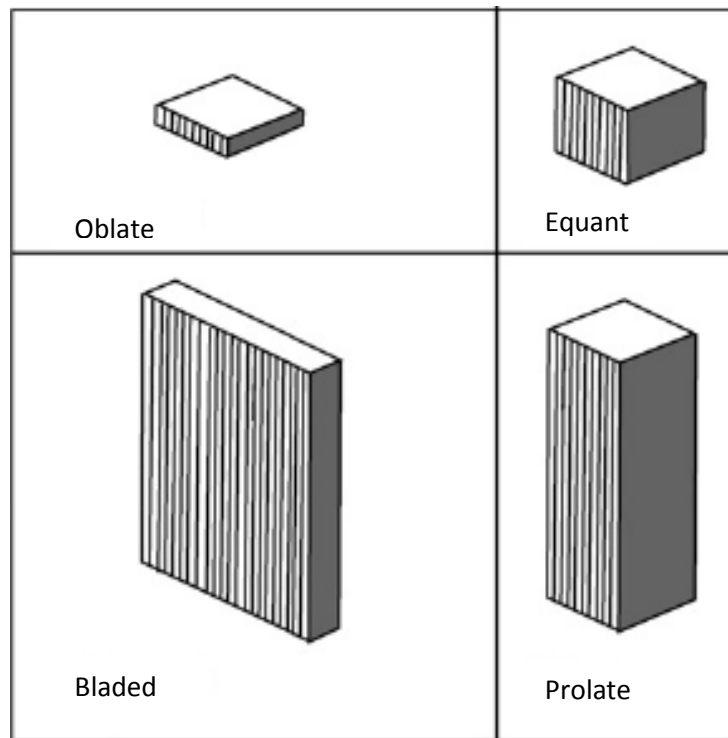


Figure 14: Classification of axial ratios (Tafesse *et al.*, 2012).

- ii. Roundness is the smoothness of a particle and it shows how the edges are curved (curvatures of the corners), usually defined by (Tafesse *et al.*, 2012):

$$P = \frac{\sum r_n}{R} \quad (2)$$

where

- P - roundness.
- r_n - average radii that can be fitted into all corners.
- R - radius of the largest inscribed circle.

It can also be determined through high magnification observation by (Pohlman *et al.*, 2012):

$$P = \frac{4A\pi}{K^2} \quad (3)$$

where

- P - roundness.
- A - area enclosed by the boundary of the particle.
- K - perimeter of the particle.

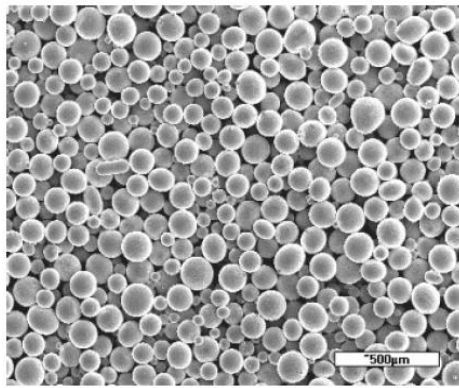
The value of roundness (P) is a ratio which ranges from 0 to 1. For a perfect circle the roundness ratio is 1, which decays exponentially as the area flattens (Pohlman *et al.*, 2012). However, in practice, particle roundness is determined by comparing a particle with standard silhouette charts or photographic images (Tafesse *et al.*, 2012).

- iii. Surface texture shows features or the outer physical appearance of a particle. It gives an indirect estimation of intuitive qualities such as roughness, smoothness or bumpiness (Irregularity of surface between corners). Surface texture gives information on transport mechanism and deposit setting of sediments (Tafesse *et al.*, 2012).

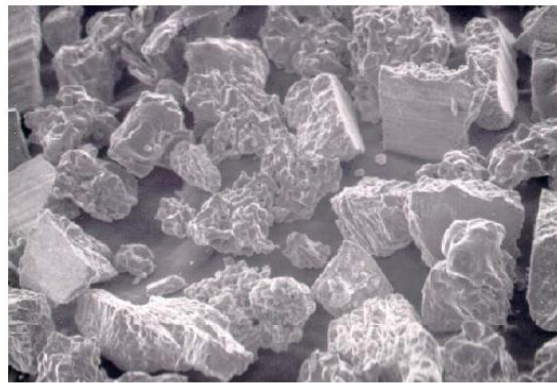
Both spherical and angular shaped titanium powders are readily available in the market and have wide industrial applications, however, other shapes like sponge fines, cylindrical, acicular, cubic, rounded, flake and coral also exist. Figure15 shows some of the most common particle shapes of titanium powders available in the market. The particle shape is determined using SEM (Pohlman *et al.*, 2012). This type of microscope also shows other particle properties such as grain boundaries, size and chemical composition when fitted with energy dispersive spectrometry (EDS) (Pohlman *et al.*, 2012).

Spherical shaped particle powders have better packing density, good flowability and a smoother macroscopic surface (Gai *et al.*, 2008). In addition, they have uniform pore distribution, good air permeability and are suitable for thermal spraying since they produce symmetrical and homogeneous layers (Gai *et al.*, 2008). The sphericity of the particle ϕ is given by the ratio of surface area of the equivalent volume sphere to the particle surface area (Liu *et al.*, 2008).

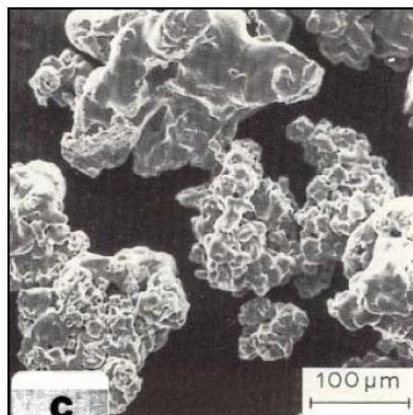
Angular particles, also referred to as ground particles, have irregular shape. Their characteristics are low fluidity index, low bulk and tap density, high degree of compression and high angle of repose (Gai *et al.*, 2008). In this regard, they have poor flow characteristics and are unsuitable for moulding processes such as injection, sintering and hot pressing (Gai *et al.*, 2008).



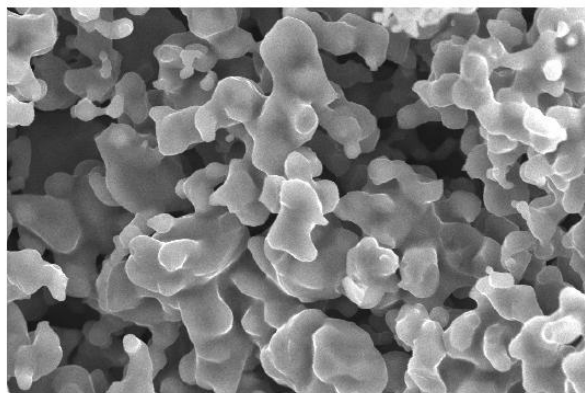
a) Spherical shape



b) Angular shape



c) Sponge fines



d) Fray reverse electrolytic powder

Figure 15: Examples of titanium powder shapes (Froes, 2000).

However, angular shaped particle powders are still being used to produce low tensile strength parts such as valves for production models of the Toyota Altezza family automobile, golf club heads and softball bats (Froes, 2000) despite their poor flow properties.

The properties of angular particles can be enhanced by spheroidization technology. This technology involves converting angular shaped particles to spherical shape (Gai *et al.*, 2008). It employs particle composite system (pcs) consisting of high speed rotary mixer fitted with blades in a ring shape chamber operated between 2000 to 8000 revolutions per minute and at a temperature of 45 to 75⁰C for a minimum of 20 minutes (Gai *et al.*, 2008). After these particles are sintered they possess mechanical properties superior to those obtained from original spherical powder (Gai *et al.*, 2008).

2.6.3 Chemical composition and crystal structure of titanium and titanium alloys

The titanium metal is an allotropic element that occurs in more than one crystallographic form. At room temperature titanium exists in hexagonal closed packed form, until it reaches 882 °C temperature when it transforms into body centred cubic form and remains fairly stable at this form regardless of increase in temperature (Ezugwu and Wang, 1997). However, an additional omega phase exists, which is thermodynamically stable at high pressures, but metastable at ambient pressures as shown in Figure 16. This omega phase is either hexagonal (ideal) or trigonal (distorted) and exists as a result of collapse of planes of atoms from the soft longitudinal acoustic phonon of the β phase (Leyens and Peters, 2003).

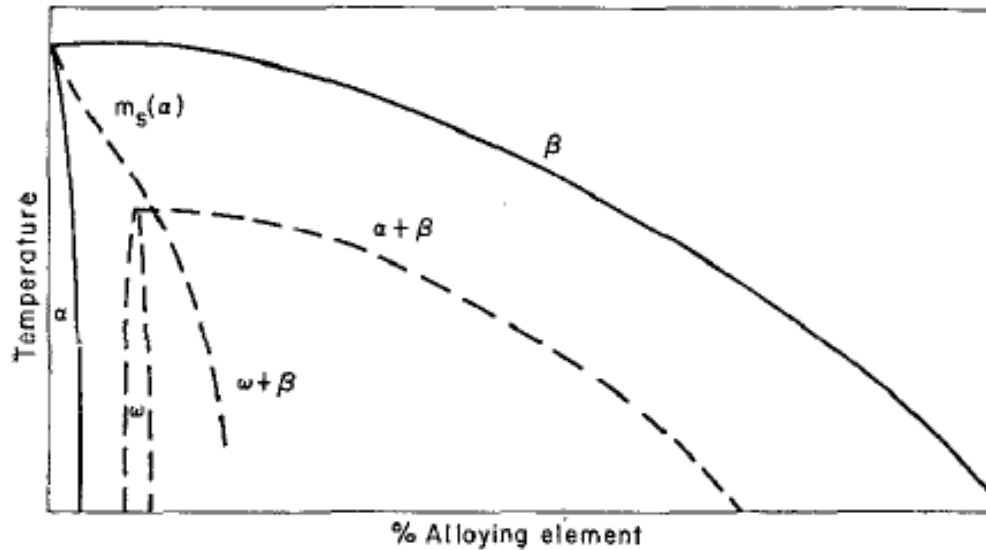


Figure 16 Metastable phase diagram for omega formation (Hickman, 1969)

The formation of alpha and beta phases in the titanium alloy depends on the amount of alloying additions present and the temperature at which the material is equilibrated. Alpha alloying elements stabilise the alpha phase (Leyens and Peters, 2003) by increasing the beta transus temperature. These elements include aluminium, oxygen, nitrogen, carbon, gallium, germanium, lanthanum and cerium (Leyens and Peters, 2003). However, aluminium is commonly used as the alloying element up to 8% content due to its low density. Oxygen and nitrogen are used to regulate titanium tensile strength, however in high quantities they cause embrittlement (formation of cracks), because they are completely soluble in titanium. The alpha phases have high modulus of elasticity, tensile and creep strength (Ezugwu and Wang, 1997).

Alternatively, some alloying elements stabilise the beta phases by lowering the beta transus temperature (Leyens and Peters, 2003). The elements are divided into two groups namely beta-isomorphous and beta-eutectoid. Beta-isomorphous are completely soluble in titanium and they include elements such as molybdenum, vanadium, tantalum, rhenium and niobium (Leyens and Peters, 2003). However, rhenium and tantalum have high particle density hence they are not preferred for use.

Beta-eutectoid elements are partially soluble in titanium and form intermetallic compounds by eutectoid decomposition of the beta phase. They include manganese, iron, chromium, cobalt,

nickel, copper, silicon, hydrogen and silver (Leyens and Peters, 2003). Chromium, iron and silicon are commonly used. Hydrogen, on the other hand, causes embrittlement effect by precipitating into hydrides, thus, its content in titanium alloy is minimised. Beta phases are easy to fabricate both in hot and cold working conditions because they have low modulus of elasticity and are corrosion resistant.

Tin, zirconium and Hafnium are considered as neutral elements since they do not have any effect on the transus temperature (Leyens and Peters, 2003). However when tin and zirconium dissolve in aluminium they cause hardening effect that stabilises the alpha phase.

The alpha and beta phases are determined crystallographically using X-ray Diffraction (XRD) by showing the elements peaks and positions, while the alloy composition is determined by X-ray fluorescence (XRF) spectrometry, however, oxygen, nitrogen and hydrogen contents are determined by combustion or fusion methods.

Figure 17 shows the XRD diffraction pattern for $\text{Ti}_6\text{Al}_4\text{V}$ titanium alloy determined using a $\text{CuK}\alpha$ X-ray source. The major peaks of titanium alloy occur at $\mp 35.4^\circ$, $\mp 38.6^\circ$ and $\mp 40.5^\circ$ for the alpha phase, and $\mp 39.7^\circ$ for beta phase. The main peak of aluminium coincides with second most intense peak of the titanium alpha phase (0002 at 38.4°), thus explaining the reason why the intensity of the main peak of alpha phase (101 at 40.1°) is relatively high (Bolzoni *et al.*, 2012a). The presence of aluminium/vanadium phase shows that $\text{Ti}_6\text{Al}_4\text{V}$ is not completely homogeneous compound (Bolzoni *et al.*, 2012a). This occurs when isomorphous beta elements present such as vanadium do not completely dissolve in titanium as expected, but combine with aluminium to form aluminium/vanadium phase (Bolzoni *et al.*, 2012a).

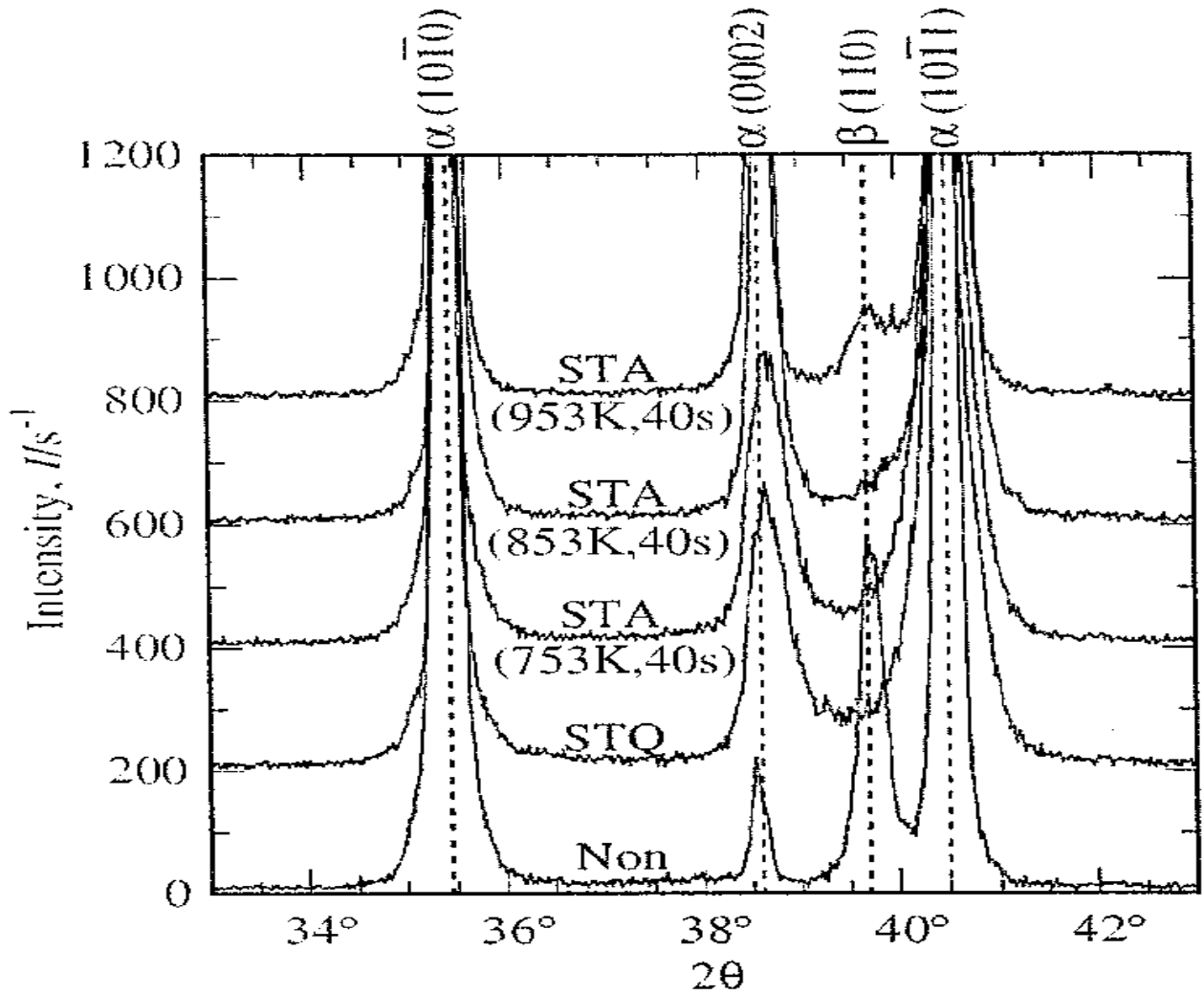


Figure 17: Titanium alloy pattern (Bolzoni et al., 2012a).

The particle density of titanium alloy depends on the particle densities of the alloying element present. Beta stabilizers and neutral alloying elements have higher particle densities than alpha stabilizers (Leyens and Peters, 2003) as shown in Table 6. However, since one of the advantages of the titanium alloy is low density, careful selection of alloying elements is required to maintain low density (Leyens and Peters, 2003).

Table 6: Densities of alloying elements in g/cm³ (Leyens and Peters, 2003).

Alpha elements		Beta elements				Neutral elements	
		Isomorphous		Eutectoid			
Aluminium	2.7	Molybdenum	10.22	Manganese	7.43	Zirconium	6.51
Oxygen	1.43	Vanadium	6.11	Iron	7.87	Hafnium	13.31
Nitrogen	1.25	Tantalum	16.65	Chromium	7.19	Tin	7.31
Carbon	2.26	Rhenium	21.04	Cobalt	8.9		
Gallium	5.91	Niobium	8.57	Nickel	8.9		
Germanium	5.32			Copper	8.96		
Lanthanum	6.15			Silicon	2.33		
Cerium	6.77			Hydrogen	0.09		
				Silver	10.5		

The American Society for Testing and Materials (ASTM) chemical analysis standard for cast and wrought titanium powder (ASTM F1108 and F1472 respectively) by percentage mass is given in Table 7.

Table 7: Titanium powder chemical analysis (ASTM, 2006).

Element	Al	V	Fe	Si	O	C	N	H
Ti 1 max	-	-	0.21	n.a	0.15	0.08	0.05	0.013
Ti 1 typical	-	-	0.05	< 0.01	0.11	0.01	0.04	0.005
Ti 2 max	-	-	0.25	n.a	0.25	0.08	0.05	0.013
Ti 2 typical	-	-	0.03	n.a	0.19	0.02	0.04	0.005
Ti 5 max	5.5 – 6.5	3.4 -4.5	0.25	n.a	0.13	0.08	0.05	0.012
Ti 5 typical	5.9	3.9	0.19	n.a	0.12	0.01	0.01	0.004

2.6.4 Density

Both bulk density and individual particle density are of importance in titanium powder characterisation. Particle density is the mass of a particle divided by its volume excluding open and closed pores and is not dependent on the degree of compaction (Abdullah and Geldart, 1999). Essentially, it is the density of the individual grains within the sample. If the grains/particles comprise several phases, the particle density is the average density of the phases present. The particle density is expressed as (Webb, 2001):

$$\rho_{\text{particle}} = \sum_{i=m}^{i=n} f_i \rho_i \quad (4)$$

where:

f_i = fraction of phase i in the particle

ρ_i = density of phase i.

The ASTM standard gives the particle density of titanium grade 5 alloys Ti6Al4V as 4.43 g/cm³ (Bolzoni *et al.*, 2012a). On the other hand bulk density is the ratio of the mass and the volume of a sample including open and closed pores and is dependent on the degree of compaction. The relationship between particle density and bulk density is given by (Webb, 2001):

$$\rho_{\text{bulk}} = (1 - n)\rho_{\text{particle}} \quad (5)$$

where:

n = porosity of the material/sample

ρ_{particle} = density of the particles

ρ_{bulk} = density of the bulk material/sample

The porosity of the material (n) is the ratio of open and closed porosity. It mainly depends on the particle size and shape, however, in a monosized batch the ratio decreases with an increase in the particle size (Liu *et al.*, 2008). It is determined by shear testing method or by weight measurements prior to and after dipping a compacted sample in a highly volatile solvent like xylol for 36 hours (Essen *et al.*, 2009).

Different values of bulk densities are obtained when the powder is measured in different states, for instance when settled, packed or compacted (Abdullah and Geldart, 1999) and, therefore, has no definite value for a particular powder (Abdullah and Geldart, 1999). Compaction involves morphological modification of the granules while packing involves rearranging the powder particles such that there is a reduction of interparticle voids without changing the original particle shape or dimensions (Canu *et al.*, 2003).

For powders, bulk density is determined by two major methods. One method is to measure the volume of a known mass of a powder sample by pouring it through a sieve into a graduated

cylinder while the other is to measure the mass of known volume of powder that has been passed through a volumeter into a measuring cup or vessel (Canu *et al.*, 2003).

Other common techniques used to measure bulk density include random loose packing and tapped densities. These techniques are briefly described as follows:

- i. There are two types of random loose packing densities namely aerated density and poured or apparent density (Canu *et al.*, 2003). In the aerated density measurement, the powder is left to settle down under the influence of gravity by means of a vibrating sieve or under fluidization as illustrated in Figure 18 (a) (Canu *et al.*, 2003) while, in poured density measurement, the powder is poured into a container gently.

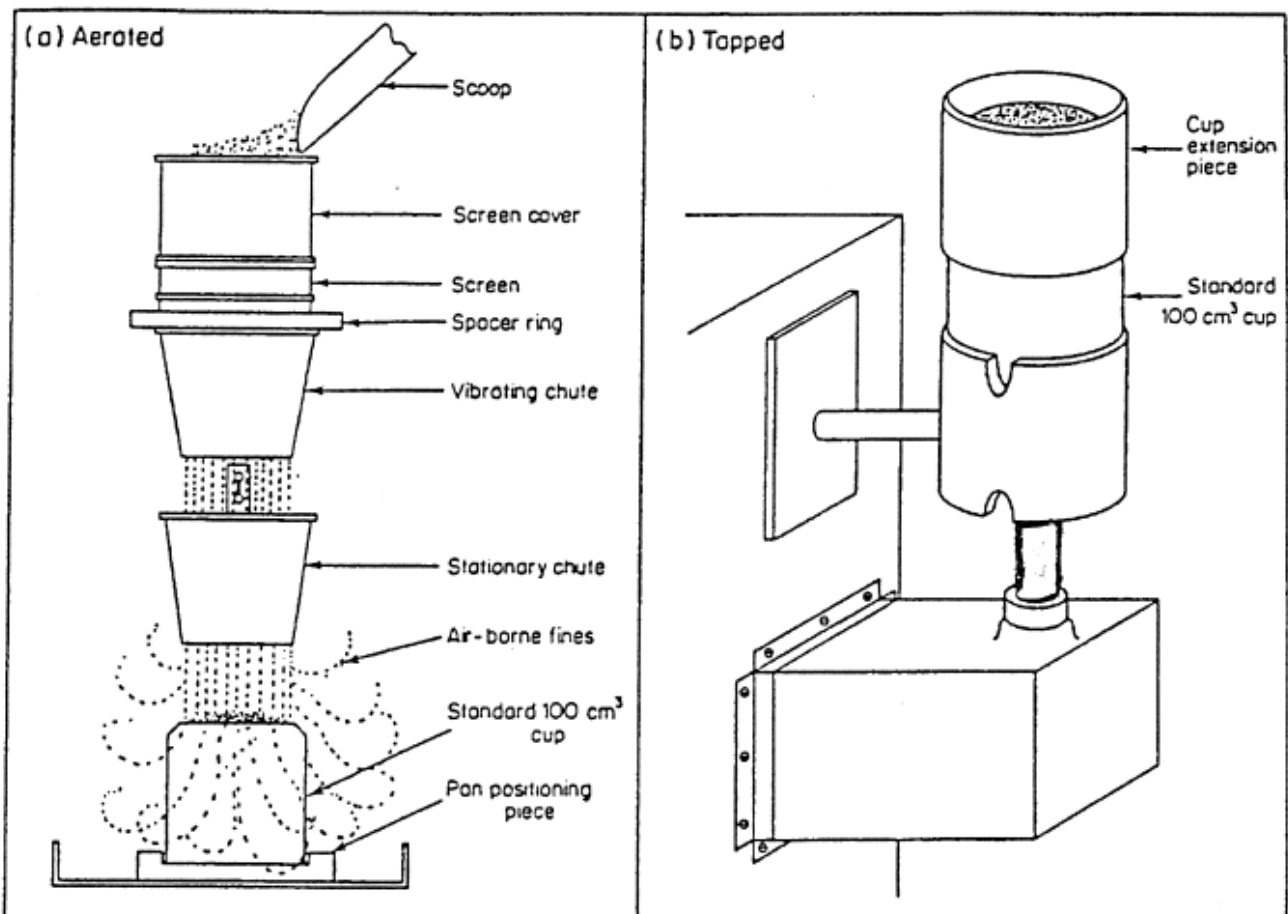


Figure 18: Aerated and tapped densities measurement equipment (Abdullah and Geldart, 1999).

Powders that resist collapse after being poured gently into a vessel have strong structural strength (strong particle cohesiveness) hence have low bulk densities, while those that collapse easily are structurally weaker (free flowing) hence have high bulk densities (Abdullah and Geldart, 1999).

Finally, the respective densities for the two methods discussed earlier, are computed from the values of mass and volume obtained.

- ii. In tapped bulk density measurement, the container having random loose packed powder samples is tapped either by vibrating or hitting over a given period of time until the powder bed stabilises at minimum volume (Canu *et al.*, 2003). The operation principle of tapped density is shown in Figure 18 (b). On tapping, a cohesive powder collapses more than weak or free flowing powder which shows minimal consolidation (Abdullah and Geldart, 1999) since it exists in a consolidated state naturally.

Particle density is measured using a manual or a gas Pycnometer, a vessel with precisely known volume, using Archimedes principle (Katja *et al.*, 2013). A pycnometer is also used to measure specific gravity. There are two types of pycnometers namely manual and gas. In the former a quantity of dry sample whose weight has been determined is poured into a pycnometer (density bottle) followed by filling the remaining part with a liquid of known density usually water (Webb, 2011). This method is mainly used in soil characterization. On the other hand gas pycnometer is used to measure true density of both solid and some liquids. It comprises two chambers as shown in Figure 19. The volume of the lower chamber is calibrated and then filled with known weight of the sample. The upper chamber is filled with inert gas such as helium. The gas is allowed to move to the lower chamber until the pressure stabilises in the two chambers. The volume of sample obtained is then used to calculate the density.

Bulk density is determined using highly volatile xylol and a precision balance equipped with density determination kit (Essen *et al.*, 2009). However, shear testing equipment such as RT4 powder rheometer, Schulze and Jenike shear tester are used to determine powder bulk density (Liu *et al.*, 2008). Bulk density shows the product quality and it is a very important control parameter for volumetric packing machines and during the calibration of moisture content machines (Davies *et al.*, 2005). Bulk density is also used to measure powder flowability.

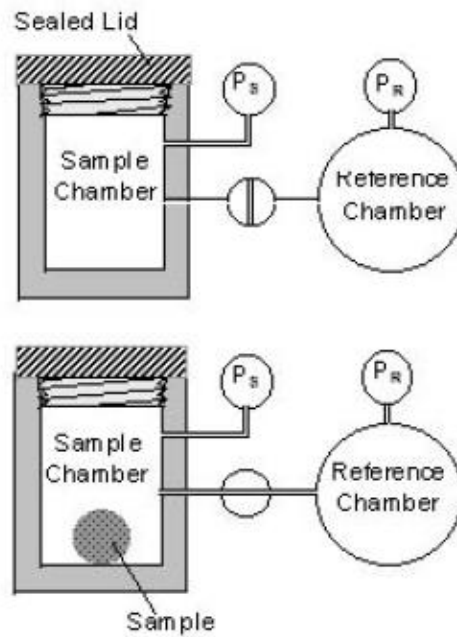


Figure 19: Gas pycnometers (Webb, 2011).

2.6.5 Soundness

Soundness or stability is the ability of the powder to resist disintegration when the powder is stored, transported or while in use as it comes into contact with the environment, through the absorption of moisture and environmental gases such oxygen, nitrogen and hydrogen. This phenomenon may lead to either reduction or increase in the particle sizes which affects the powder flow.

Powder particles are usually surrounded by fluids mostly air between the particles such that both the particle and the fluid are used in the computation of the bulk property. When the powder is stored or packed for a long period, the entrained fluid escapes causing strong chemical bonds to form between particles resulting in agglomeration ([http:// www.freemantech.co.uk](http://www.freemantech.co.uk)). This causes the formation of unwanted build ups, cakes, bridges and lumps that leads to poor flow properties ([http:// www.freemantech.co.uk](http://www.freemantech.co.uk)).

In cement powder, soundness has been determined, using weight ratios. The procedure involves passing the powder through a sequence of sieves of decreasing mesh under vibration (Pohlman *et*

al., 2012). The quantity of material P_M in each sieve tray is measured using high precision weighing balance machine. After the exposure to the environment, the same process is repeated and new weight measurements P_N are obtained for each sieve. The powder soundness is then determined by the percentage change in weight as shown below (California test 214, 2008):

$$\text{Degree of soundness (\%)} = \frac{P_M - P_N}{P_M} \times 100 \quad (6)$$

This soundness measurement method can also be used for titanium powder considering that titanium absorbs environmental gases such as oxygen to form oxides. RT4 powder rheometer equipment has also been used to determine powder soundness ([http:// www.freemantech.co.uk](http://www.freemantech.co.uk)). However, there is no approved universal standard for titanium powder.

2.6.6 Flowability

In the design and operation of powder handling processes such as storage, discharge, transport and packing, powder flowability is one of the important factors to be considered. Powders should possess good flow properties. For example, when being transported from a silo or a hopper, powders should be able to flow easily to avoid the formation of large holes evolving from significant bridging effect that leads to inconsistent flow rates and segregation (Krantz *et al.*, 2009). During pneumatic transportation the powder should be able to expand uniformly to avoid powder agglomeration and clumping when fluidized by a gas (Krantz *et al.*, 2009). In addition, a good flow characteristic is essential during mixing of powders to ensure uniform blending and homogenous mixture (Krantz *et al.*, 2009).

Powder flowability depends on particles properties such as particle size, shape (uniformity and roundness), density, attrition, surface coating, adhesion and agglomeration properties, compressibility, hardness, stiffness, strength, fracture toughness (Matsusaka *et al.*, 2012) and other external factors such as vibration, temperature, humidity, electrostatic charge, aeration, transportation, gravity forces, surface forces (static and dynamic friction) and storage time (Matsusaka *et al.*, 2012; Liu *et al.*, 2008), hence the complexity of flowability models. The incipient flow model conditions are shown here under:

For spherical-shaped particles (Liu *et al.*, 2008):

$$\rho_{\text{Particle}} d^3 g \varepsilon \geq (1 + k) F_{\text{HO}} + k F_{\text{N}} \quad (7)$$

where

ρ_{particle} – Particle density.

d Particle diameter (usually the smallest diameter D10 in laser diffraction method).

ε – porosity of the material.

g – gravitational force.

k – materials contact consolidation constant.

F_{HO} – Adhesion force between particles with no external normal force.

F_{N} – Normal force applied to the powder.

While for non-spherical shaped particles (Liu *et al.*, 2008):

$$\rho_{\text{Particle}} d^3 g \varepsilon \emptyset^2 \geq c \pi (1 + k) F_{\text{HO}} + k F_{\text{N}} \quad (8)$$

where

$\emptyset$ – Particle sphericity

c – Proportionality constant

Powder particles start to flow when the accelerating force (product of the parameters in left hand side) is equal or greater than the resistance force (sum of the parameters in right hand side). The accelerating force parameters in two flow model equations are easily measurable and significantly affect the powder flow rate. In this regard, any increase in particle density, size and material porosity will have a directly proportional effect on the powder flowability for spherical powders (Liu *et al.*, 2008). However, if particle density is taken as a constant (not easily variable for the same material), particle flowability will depend on the particle size and the porosity of material (Liu *et al.*, 2008).

The difference between the accelerating force of the two models is $\emptyset^2$ (the square of sphericity factor), but the sphericity factor is a ratio less than unit, thus equation (7) model confirms the

free flowing nature of spherical shaped particles when compared to non-spherical particles equation (8) (Liu *et al.*, 2008).

These flowability models were developed under the assumption of ideal conditions, where there is constant inter-particle distance between particles of the same powder. However, in practice, different production batches have different material properties, thus it is recommended that each batch should be tested separately (Liu *et al.*, 2008) to determine its flowability.

In general, fine particles <100 µm are more cohesive and, therefore, less free-flowing than larger, denser particles (Abdullah and Geldart, 1999) which are non-cohesive. Nevertheless, the flow properties of fine powders are improved by blending them with dry nano size material that acts as a flow additive (Krantz *et al.*, 2009) thus reducing the van der waals forces. When more fine particles <10 µm are aerated and forced to flow, they behave like fluids and are able to flow through holes and round corners unlike the coarse particles that interlock upon each other hence resisting the flow ([http// www.freemantech.co.uk](http://www.freemantech.co.uk)).

Therefore, prediction of powder flow properties depends on the material flow properties, equipment processing characteristics, handling and processing conditions such as static and dynamic head, consolidation, aeration level, absorbed moisture and the electrostatic charge present. Some of the common problems encountered in powder processing industry are ([http// www.freemantech.co.uk](http://www.freemantech.co.uk)):

- i. Blockages on the hopper or bin discharge.
- ii. Changes of powder density due to aeration.
- iii. Weight variation caused by irregular powder dosing operation due to the entrained fluid.
- iv. Agglomeration caused by particle coalescence.
- v. Particle attrition due to the wear and tear of the moving particles in a conveyor.
- vi. Segregation caused by non cohesive powders having different bulk densities and particle size.
- vii. Consolidation caused by high level of compaction in the silo or hopper during storage or transportation.
- viii. Effects of moisture in the powder causing poor flow properties.
- ix. Controlling of the fluidized powder which behaves as a fluid.

- x. Poor plant design that makes the powder to flow in an irregular pattern (first in, last out).

The powder flowability affects the quality of the final product. For instance, in high speed drug tableting, uneven flow causes capping and lamination defects (Liu *et al.*, 2008) while in powder metallurgy products are produced with sections having imperfections and voids or porosity (Pohlman *et al.*, 2012).

2.6.6.1 Flow measurement methods

Several experimental methods for powder flowability measurement are available, and the choice of method depends on the specific property to be measured (Krantz *et al.*, 2009). Some techniques determine the flow rate when the powder is in a static state (stored) while others determine flowability in a dynamic state (transported) (Matsusaka *et al.*, 2012). Traditionally, methods such as angle of repose, compressibility index (Hausner ratio, Carr's index) and funnels have been used to measure powder flowability, however, with the advancement of technology, avalanche angle and shear testers were developed although the latter is used in silo and hopper design (Freeman, 2006). Currently, the most common methods in use are angle of repose, avalanche angle, Hausner ratio, Carr's index, flowmeters, bed expansion ratio, capillary tube and shear cell tests. The experimental results obtained from these flowability methods are usually modelled using computer software programs such as Matlab and student t test (Emery *et al.*, 2009).

2.6.6.1.1 Angle of repose and avalanche angle method

There are at least eight methods of measuring angle of repose and each method gives a different result (Geldart *et al.*, 2006), and there is no general agreement to the best design of equipment to be used or on the amount of powder required to carry out the test (Geldart *et al.*, 2006). Some of the methods that are commonly used are shown in Figure 20.

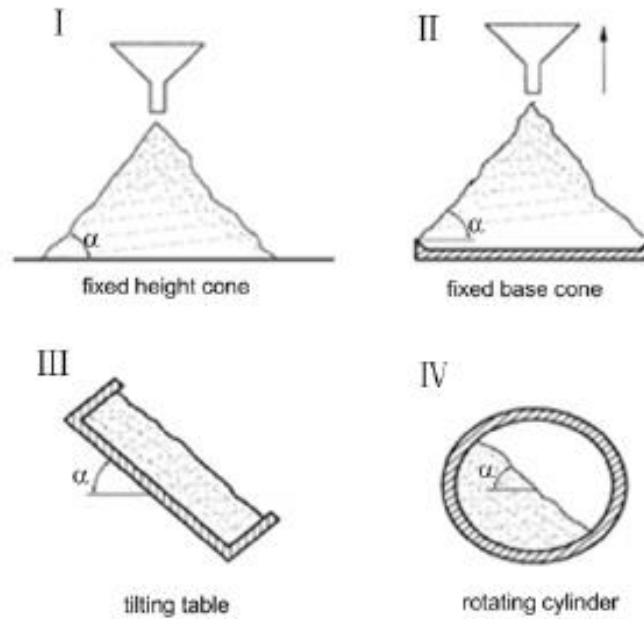


Figure 20: Static and dynamic repose (Geldart *et al.*, 2006).

The angle of repose is defined as the angle at which a conical pile of powder maintains its stability. Table 8 shows how the angle of repose relates to flowability. Low angles of repose signifies less inter particle bonding forces between particles, therefore, the powder flows easily (Krantz *et al.*, 2009). Materials with a high angle of repose may still flow uniformly, but require a greater amount of energy input to maintain steady motion. Decreasing the particle sizes of powders results in poor flow properties (Krantz *et al.*, 2009), suggesting that finer powders have higher angles of repose and hence are less flowable.

Table 8: Flow property (Lumay *et al.*, 2012).

Flow property	Angle of repose (°)	Hausner ratio	Carr's Index
Excellent	25-30	1.00-1.11	5-15
Good	31-35	1.12-1.18	12-16
Fair	36-40	1.19-1.25	18-21
Passable	41-45	1.26-1.34	
Poor	46-55	1.35-1.45	>23
Very poor	56-65	1.46-1.59	
Very very poor	> 66	> 1.6	

Known methods of determining the angles of repose both in static and dynamic states are described briefly. In static angle of repose, powder is poured into a fixed height funnel on top of a flat base or alternatively the funnel is filled with powder then raised gradually to allow the powder to fall out (Geldart *et al.*, 2006). Pictures of the pile are taken using a digital camera when the powder heap has built up to a point where further addition of powder just slides down the slope (Emery *et al.*, 2009) and they are analysed by a image analysis program. The angles measured on the right and left hand sides of the pile are averaged to get a single static angle of repose (Emery *et al.*, 2009).

Alternatively the powder heap is formed on a circular support of diameter b and the heap height h is measured. As shown in Figure 21, the angle of repose α is then calculated using equation 9.

$$\tan \alpha = \frac{2h}{b} \quad (\text{Lumay } et al., 2012). \quad (9)$$

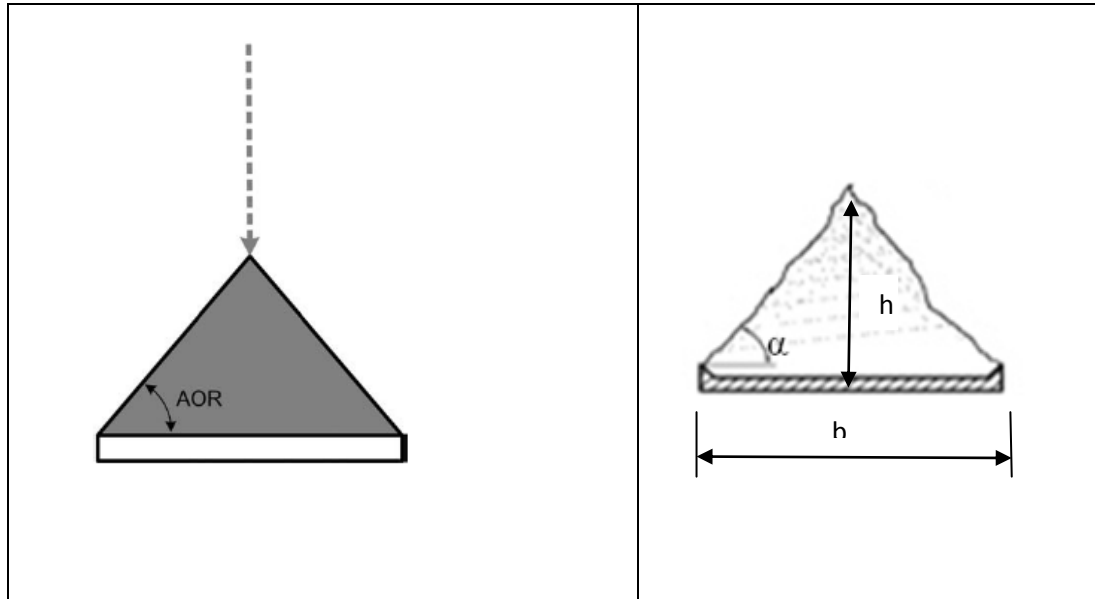


Figure 21: Static angle of repose (Lumay, 2012).

Various methods are used to measure dynamic angle of repose when the powder is in motion; these include rotating drum tumbler, mark 4 tester and electrical capacitance tomography (ECT) (Geldart *et al.*, 2006; Emery *et al.*, 2009);

- i. In the rotating drum tumbler method, the revolving cylinder is mounted on a shaft supported by low friction bearings (Geldart *et al.*, 2006). As the cylinder rotates, the powder forms a

fixed bed that rotates together with the supporting edges of the cylinder until it reaches a point when it can no longer support its weight making it to collapse (Pohlman *et al.*, 2012). This maximum angle attained before collapse is known as avalanche angle (Krantz *et al.*, 2009) and is shown in Figure 22.

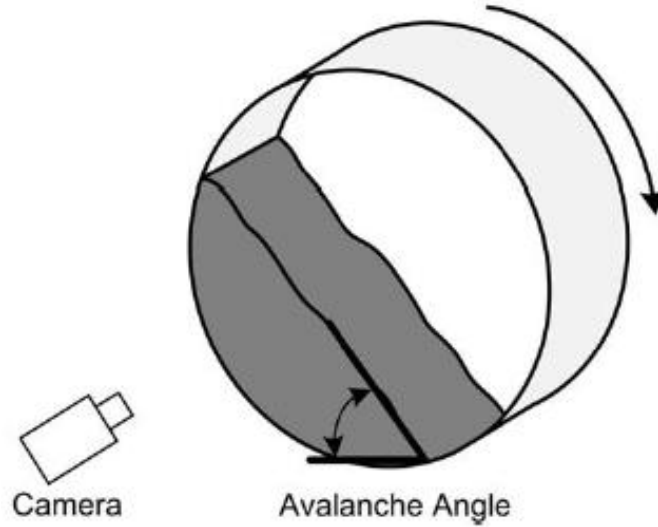


Figure 22: Avalanche angle (Krantz *et al.*, 2009).

On the other hand, the dynamic angle of repose is developed when the fixed bed rises inducing a thin rapidly flowing layer of material where particles decelerate and return to the fixed bed (Pohlman *et al.*, 2012). The prediction of dynamic angle of repose value is done using Froude's number, a dimensionless equation shown here under (Pohlman *et al.*, 2012):

$$F_r = \frac{R\omega^2}{g} \quad (10)$$

where

F_r is Froude's number

R is the radius of the tumbler

ω is the rotational speed

g is the acceleration due to gravity

For titanium powder the value of Froude's number should be between 5×10^{-4} and 5×10^{-3} (Pohlman *et al.*, 2012), in order to generate a continuous thin flow layer of powder in the rotating drum. However, this method is cumbersome since the assembly has to be dismantled to facilitate cleaning of both the bearing and the shaft between tests (Geldart *et al.*, 2006).

- ii. In the mark 4 tester method, the powder flows into a semi cone shape as shown in Figure 23 whose diameter and average radius are easily measurable (Geldart *et al.*, 2006) and the results computed using equation (9). However, it is difficult to obtain a sharp semi cone apex shape of a powder, and thus the height of the cone is usually approximated resulting in inaccurate results (Geldart *et al.*, 2006).
- iii. In the electrical capacitance tomography (ECT) method, the behaviour of powder is observed at the centre of the cylinder using ECT gadget at different cylinder speed (Emery *et al.*, 2009). The results obtained are more accurate than the methods discussed earlier, with a 5% error reduction (Emery *et al.*, 2009).

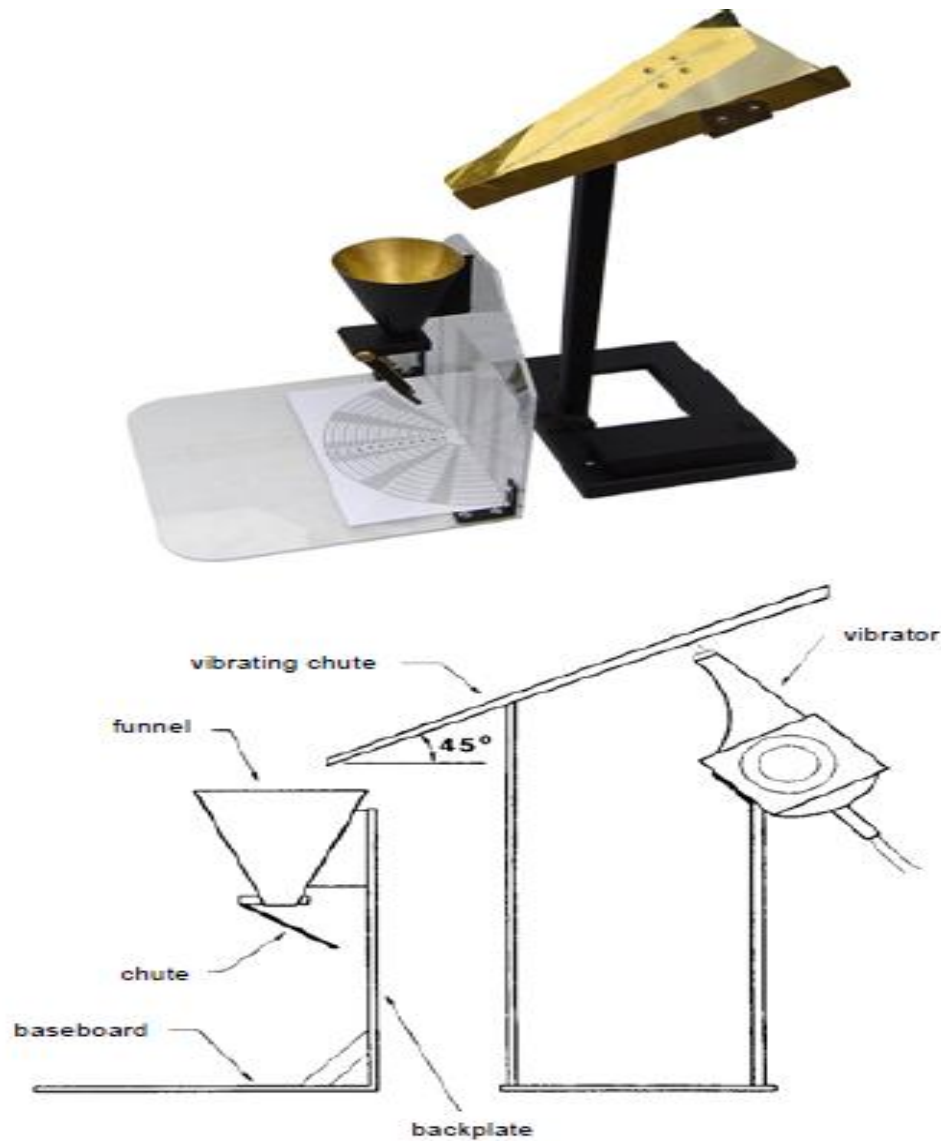


Figure 23: Mark 4 tester (Geldart *et al.*, 2006).

In this regard, the results obtained by static and dynamic angle of repose methods are inaccurate (Geldart *et al.*, 2006) with big error margin.

2.6.6.1.2 Compressibility index method

The Hausner Ratio (HR) and Carr Index (CI) are determined using pour bulk density (untapped) and tapped density. The powder is gently loaded into a cylinder through a funnel and weighed to calculate bulk density (BD). To determine powder tapped density (TD) the cylinder is tapped or mechanically raised and lowered at a set distance until a consistent volume is reached that

corresponds to the maximum packing density of the material. The two ratios are determined as shown by the following expressions (Liu *et al.*, 2008):

$$HR = \frac{TD}{BD} \quad \text{and} \quad CI = \frac{TD - BD}{TD} \times 100\% \quad (11)$$

Table 8 also shows HR and CI flow property values. The accuracy of the results depends on both the equipment sensitivity (Emery *et al.*, 2009) and the operator's precision while taking the reading (Lumay *et al.*, 2012).

2.6.6.1.3 Flowmeters method

Powder flow through an orifice or a fixed funnel is determined by using either Hall flowmeter or Carney funnel equipment as shown in Figure 24. These instruments are usually affected by the presence of moisture, oils, stearic acid, waxes, stearates and temperature in the powder, according to ASTM B212. As per ASTM B213, Hall flowmeter has a funnel diameter of 0.1 inches and is used to measure flow rate and density of freely flowing metal powders which flows unaided through the funnel (Lumay *et al.*, 2012). Carney funnel has funnel diameter of 0.2 inches and measures non free flowing metals (Marcu *et al.*, 2012). The funnels used in both processes under discussion are similar and thus interchangeable. Therefore, to carry out the test only a density cup and one complete stand are required.

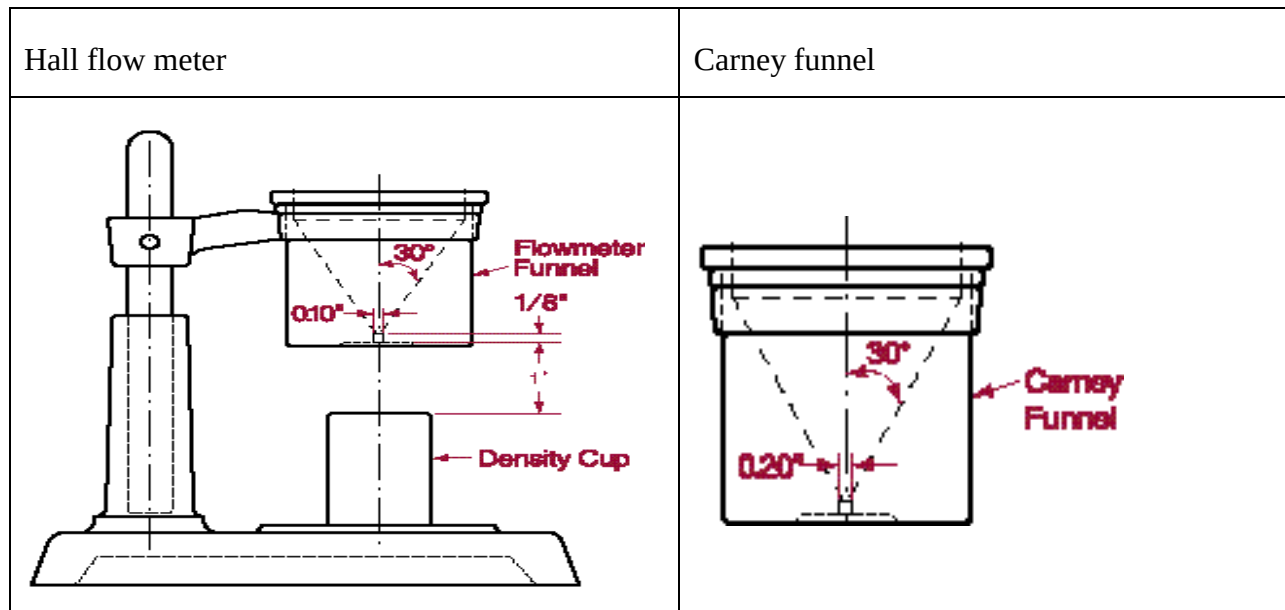


Figure 24: Hall flow meter (ASTM B212) and Carney funnel (ASTM B417).

2.6.6.1.4 Bed Expansion Ratio (BER) method

Powder is loaded into a clear acrylic vertical pipe to a certain depth then using a dry compressed air at superficial velocity the powder is fluidized from the bottom of the pipe resulting into a vigorously bubbling bed thus homogenising the powder (Krantz *et al.*,2009) as shown in Figure 25. The superficial gas velocity is reduced to a constant value allowing the bed to settle down, at which point the first reading is taken. Then the gas flow is cut off and the second reading is done. The ratios of the two readings are computed. For particle sizes below 30 μm the BER should be between 1.4 to 1.5 in order to achieve sufficient fluidization while for larger particles the tolerance of the BER is reduced to compensate for the reduced specific surface area of the particles (Krantz *et al.*, 2009). This process shows the behaviour of powder in a dynamic state where particles are in a continual motion such as pneumatic transportation, however, fluidized powder behaves as a fluid and is therefore difficult to control (Krantz *et al.*,2009).

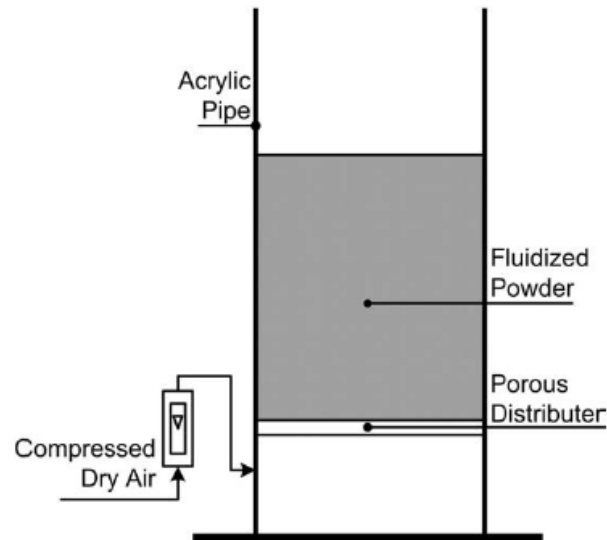


Figure 25: Bed expansion ratio (Krantz *et al.*, 2009).

2.6.6.1.5 Capillary tube method

This is a simple method where the powder is discharged through a capillary tube. Its sensitivity is higher than other methods. However, if the powder has higher inter-particle adhesion forces, bridging occurs inside the capillary making it difficult to take any measurements even with the help of vibration (Matsusaka *et al.*, 2012).

Recently, a vibrator shear tube to measure flowability (Matsusaka *et al.*, 2012) has been developed. It has a piezoelectric vibrator, glass tube and a metallic bottom. The vibration is transferred directly to the particles in the narrow gap between the vibrating tube edge and the flat bottom surface (Matsusaka *et al.*, 2012). The particles experience high shear forces that overcome friction and adhesion forces hence they are able to be discharged through the gap as both static and dynamic measurements are taken (Matsusaka *et al.*, 2012), although errors due to interference occur.

2.6.6.1.6 Shear test method

Shear test on the powder is carried out using either direct or indirect methods. The operation principle used in the direct method equipment is either linear, ring or rotational while the indirect method uses axial cells. Powder rheometer shear testers are classified as either linear, rotational or ring. For instance, FT4 powder rheometer is rotational, Schulze shear tester is a ring type while Jenike shear tester is linear. These types of shear testers are currently being used to determine flow properties in the industry (Marcu *et al.*, 2012). These shear test methods use the same operation principle to obtain flow function which is used in predicting flowability of bulk material (Krantz *et al.*, 2009). However, the Jenike shear tester is commonly used in the industry (Marcu *et al.*, 2012) because of its simple design construction. It has a circular cross section shear (Cagli *et al.*, 2007) fitted with load applications points for both normal and shear loads on the machine frame as shown in Figure 26. Normal stress is induced by hanging vertical standard loads to the system shear cell while shearing stress is provided by an electromechanically driven loading system that moves horizontally (Cagli *et al.*, 2007) at an average speed of 2.5 mm/min.

The shear test involves two stages namely pre-shear stage and steady state flow stage also referred to as shear step. In the pre-shear stage, the powder sample is consolidated by shearing using a constant normal stress until a critical state is reached (Cagli *et al.*, 2007), ensuring that all the shear cell cavities are fully packed at pre-consolidated stress (Freeman *et al.*, 2009), hence constant and consistent shear stress values are obtained between the tests. On the other hand, in the shear step, the sample is sheared using a normal stress that is less than the initial pre shear normal stress (Krantz *et al.*, 2009). The ASTM D6128-00 standard recommends the use of pre shear standard loads of 1.5kPa, 3kPa and 6kPa (Emery *et al.*, 2009). In addition, half of the top

cover weight is added to the above pre shear loads to obtain the total applied load (Emery *et al.*, 2009).

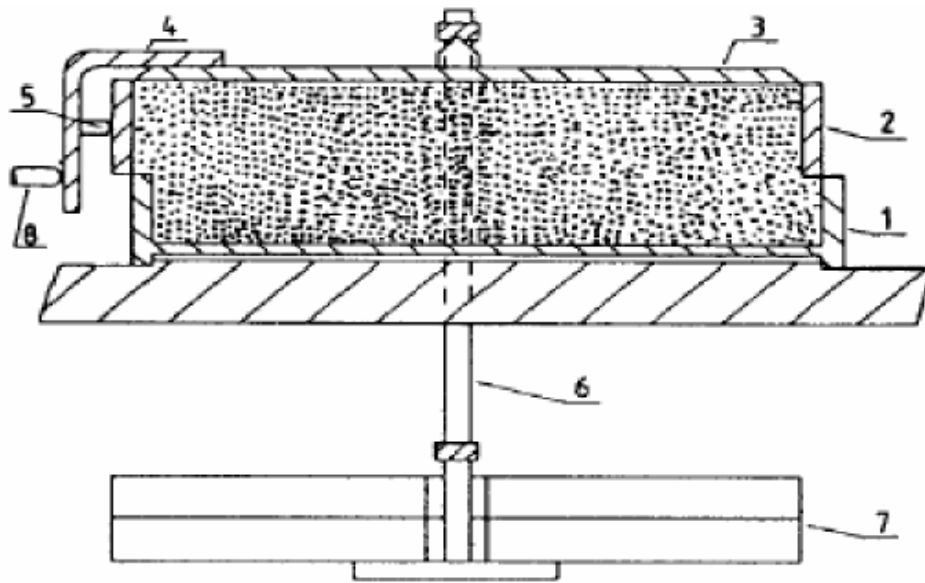


Figure 26: Jenike shear tester (Cagli *et al.*, 2007).

where

- | | |
|--------------------|---------------------|
| 1. Base | 5. Pin |
| 2. Shearing ring | 6. Weight hanger |
| 3. Shearing lid | 7. Standards weight |
| 4. Loading bracket | |

A Mohr circle is constructed graphically from different values of shear stress τ and normal stress σ obtained during the pre-shear and shear step stages. The yield locus is obtained by drawing a straight line touching all the semicircles as shown in Figure 27.

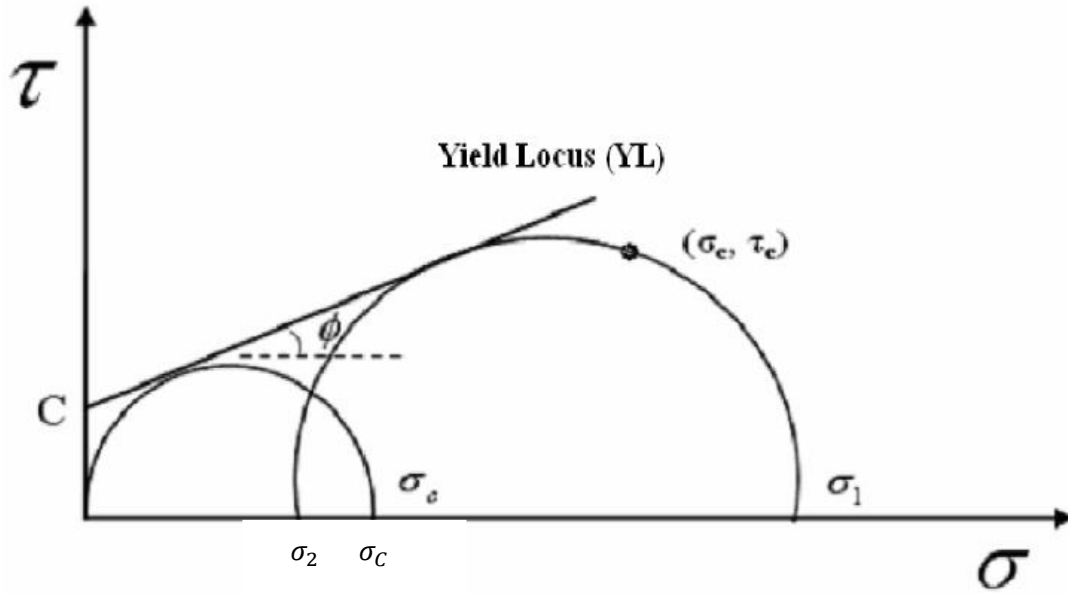


Figure 27: Yield locus (Cagli et al., 2007).

where C is the cohesion value, ϕ is the angle of internal friction, σ_c is the unconfined yield stress (the maximum normal stress value beyond which flow occurs), σ_2 is the minor consolidation stress and σ_1 is the major consolidation stress. The ratio of σ_2/σ_1 is referred to as stress ratio K and ranges between 0.3 to 0.6 for bulk solids (Schwedes and Schulze, 1990).

The computation of yield locus expression in equation (12) gives various flow properties parameters such as angle of internal friction (ϕ), cohesion value (C), kinematic angle of friction and flow function (Cagli et al., 2007) which are also used in silo and hopper design (Guo et al., 2012). Flowability or flow function (FF) is calculated by dividing the major consolidation yield stress σ_1 with unconfined yield stress σ_c .

$$\tau = \tan\phi\sigma + C \quad (12)$$

Flow index (FI) is a straight line plotted on a σ_c against σ_1 graph (Cagli et al., 2007) as shown in Figure 28. FI shows consolidated powder strength to be surmounted before flow occurs (Emery et al., 2012). In addition, the slope of the curve classifies the ability of powder to flow as either cohesive or free flowing (Cagli et al., 2007). The classification of powder flowability is shown in Table 9.

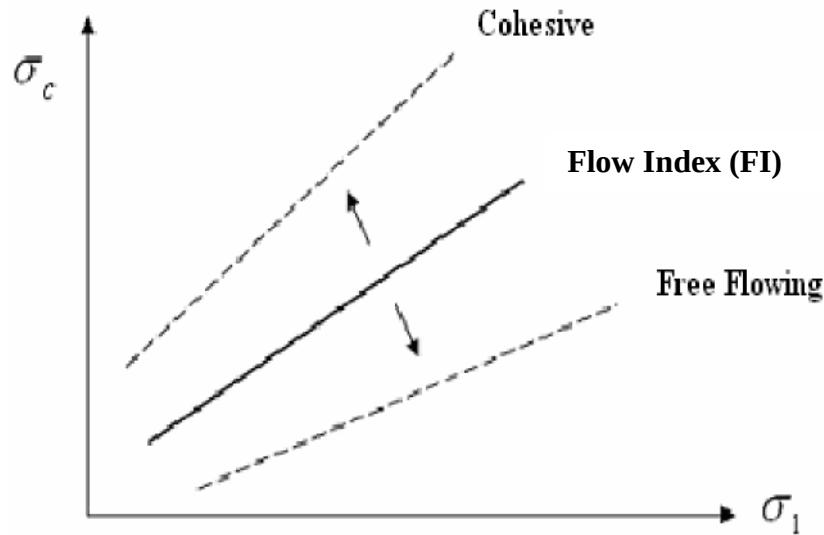


Figure 28: Flow function (Cagli *et al.*, 2007).

Table 9: Flow Index (Cagli *et al.*, 2007).

Flowability	Hardened	Very cohesive	Cohesive	Easy flowing	Free flowing
Flow function	< 1	>1 to ≤ 2	>2 to ≤ 4	> 4 to ≤ 10	> 10

According to Liu *et al.* (2009) a higher angle of internal friction signifies free flowing properties of the material. Yield locus with steep slope and high cohesion values show that the flow of the material is poor (hardest), while higher values of flow index show that the flow is easier (Emery *et al.*, 2012). The yield locus of a coarse powder is a straight line passing through point zero signifying both minimum cohesion and unconfined yield strength values (Freeman *et al.*, 2009), whilst fine powders have non linear yield locus curve with convex shape exhibiting much greater cohesion values and shear strength (Freeman *et al.*, 2009). However, maximum basic flow energy (BFE) is required by non cohesive powders to start flowing due to their low particle shear strength and compressive index which leads to high forces transmission from particle to particle (Freeman *et al.*, 2007). Alternatively, since flow is a chain reaction, cohesive powders contain entrained air between particles, making them more compressible, thus aiding the flow (Freeman *et al.*, 2007).

The major drawback of Jenike shear test is that it requires a certain level of expertise since the movement of shear stress is limited (Matsusaka *et al.*, 2012) and time consuming (Emery *et al.*, 2009). In this regard, shear test methods give more comprehensive flow information having greater sensitivity and reproducibility, however, large amount of quantities of sample material is required to perform the test (Liu *et al.*, 2008).

2.7 Evaluation of powder flow measurement methods

Flow measurements methods such as static and dynamic angle of repose, avalanche angle, Hausner ratio, Carr index, flowmeters, bed expansion ratio, cohesion, flow index and internal friction are plotted graphically against powder characteristics such as particle size, mass and moisture content (Figure 29) to show their correlation (Geldart *et al.*, 2006; Krantz *et al.*, 2009) over a given range of values.

Powder in static and dynamic state

Figure 29 shows a graph of Hausner ratio and angle of repose values (static flow measurements methods) plotted against varying particle size to determine whether the powder is free flowing or cohesive (Krantz *et al.*, 2009). Similarly, Figure 30 shows avalanche angle and bed expansion ratio (dynamic flow measurements methods) are also plotted against varying particle size (Krantz *et al.*, 2009). The results from the two figures discussed earlier show that as the particle size increase the flow becomes free flowing and vice versa. This signifies that there is a consistent relationship between the two flow measurement methods (Krantz *et al.*, 2009).

Comparison of powder characterization methods

Figure 31 shows the comparison of angle of repose against Hausner ratio (Static vs static) and angle of repose against bed expansion ratio (static vs dynamic) (Krantz *et al.*, 2009). In the former the two methods are converging by giving the same results, therefore the use of one method will predict the other (Geldart *et al.*, 2006) while in the latter the data points of two methods are scattered therefore it is not possible to use one method to predict the other (Krantz *et al.*, 2009). It is, therefore, inappropriate to extend results obtained from static evaluation process to dynamic process and vice-versa. Since static technique determines powder

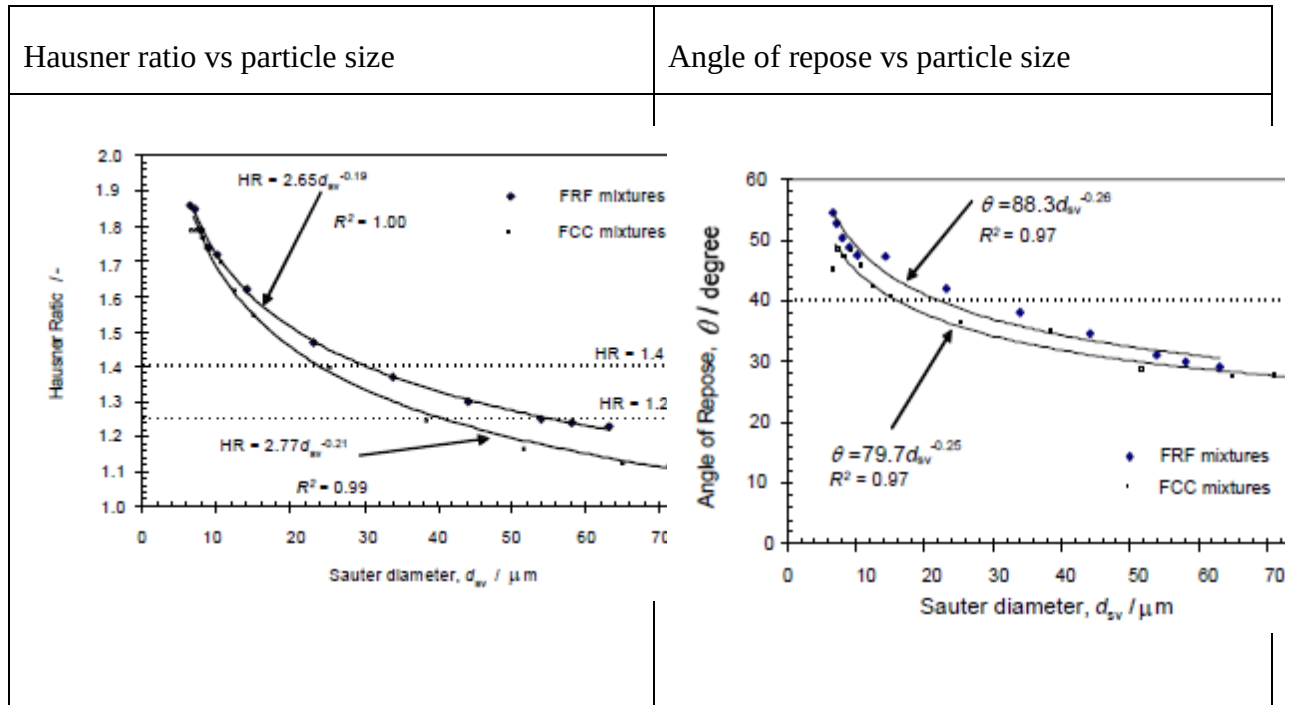


Figure 29: Static methods vs particle size (Geldart et al., 2006).

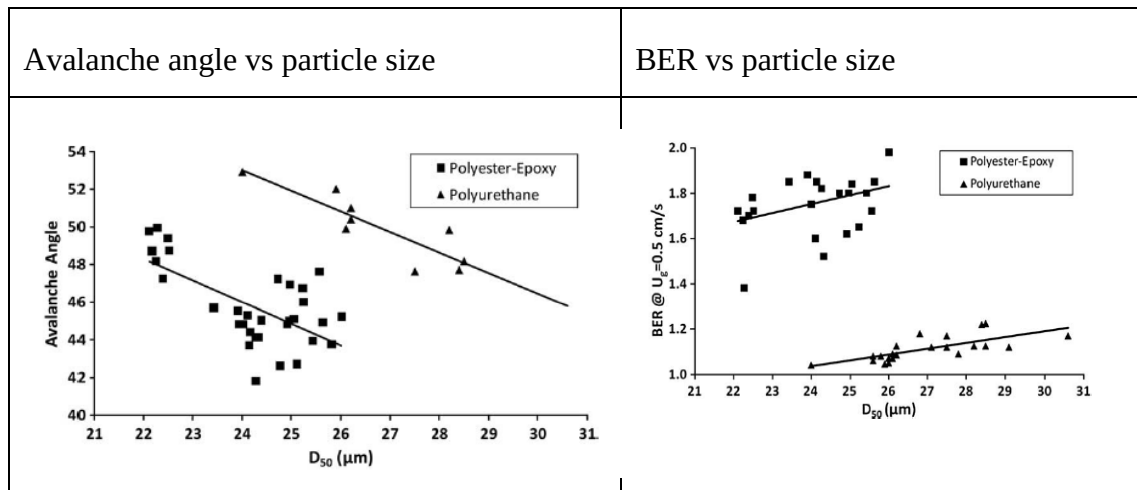


Figure 30: Dynamic methods vs particle size (Krantz et al., 2009).

stability properties (storage) whereas dynamic technique determines dynamic properties (transportation), therefore both static and dynamic processes should be carried out independently (Matsusaka et al., 2012).

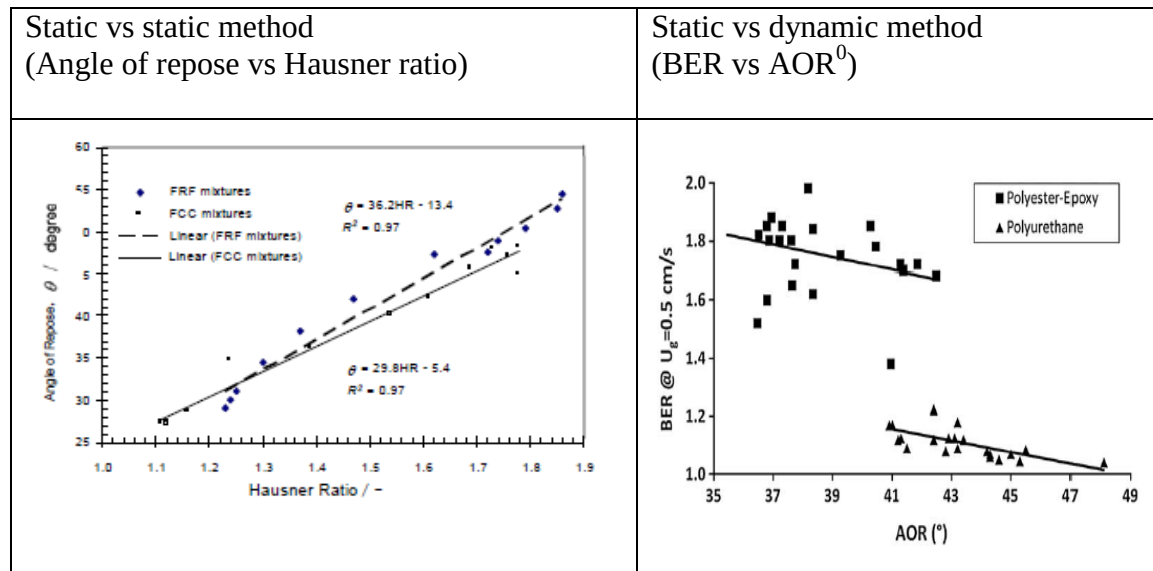


Figure 31: Comparison of static and dynamic methods (Geldart et al., 2006; Krantz et al., 2009)

2.8 Current study

This study dealt with the effects of various physical parameters such particle size, shape, chemical analysis, density and soundness on flowability of titanium grade 5 alloys powder in additive manufacturing. In addition worldwide market survey of titanium powder manufacturers and suppliers was conducted.

From reviewed literature there are various methods used to accomplishing the above tasks. However, the choice of a particular method of testing depended on the equipment accuracy, availability and application. The obtained results were compared with their respective ASTM standards to establish the level of deviations.

Chapter Three: Methodology

3.1 Introduction

This chapter describes both the qualitative and experimental techniques adopted in this study. In the qualitative technique, questionnaires were used to conduct a market survey of Companies trading in titanium powder. While experimental methods were used to characterize titanium alloy powder that was supplied in twelve different particle size ranges. The powder characterization involved particle size, shape, chemical composition, density, soundness and flowability.

3.2 Potential supplier base

Research on potential suppliers was conducted using two different questionnaires shown in Appendixes I and II. The questionnaires were delivered via email to a total of 105 manufacturers and suppliers listed in Appendix III during the month of January and March 2013, respectively.

3.3 Materials

Twelve powder samples of titanium alloy grade 5 (Ti6Al4V) were supplied by Central University of Technology (CUT) and Aerosud Company. Both organizations have research collaboration with the Council of Scientific and Industrial Research (CSIR). On receiving the samples, numerical identification tags were assigned and the supplier specifications recorded as shown in Table 10.

Table 10: Titanium powder supplier specifications of delivered samples

Sample No.	Company	Size μm	Powder name	Batch/Lot No.	Amount received (grams)	Remarks
1	TLS	150-200	Ti6Al4V	0937/3	699.3	Aerosud.
2	TLS	10-60	TiGd5	1441/3	668.3	Aerosud.
3	TLS	≤ 25	TiGd5	1441/3	686	Aerosud.
4	TLS	45-75	Ti64	0735/3	181.6	Aerosud.
5	TLS	20-60	Ti6Al4V	1354/3	721.5	Aerosud.
6	TLS	45- 90	Ti Gdi	1503/03	681.6	Aerosud.
7	TLS	20 -45	Ti6Al4V	1441/3	708.21	Aerosud.
8	TLS	10-45	Ti6Al4V	1441/3	686	Aerosud.
9	EOS	Not Specified (N/S)	Ti64	0576/3	1000	CUT. Old.
10	EOS	N/S	Ti64	0839/3-M	1000	CUT. Very old.
11	EOS	N/S	Ti64	N/S	1000	CUT. Obtained from MZ80 equipment.
12	EOS	N/S	Ti64	N/S	1000	CUT. Brand new

3.4 Characterization of raw titanium grade 5 alloy powder

The equipment used for powder characterization are shown in Table 11.

Table 11: Equipment used for characterization of titanium grade 5 alloy powder

S/No.	Characterization	Equipment used
1.	Particle size	Laser diffraction
2.	Particle shape/morphology	Scanning Electron Microscope
3.	Chemical composition	XRD, XRF, Combustion method
4.	Particle density	Manual pcynometer (Density bottle)
5.	Bulk density	RT4 Rheometer
6.	Soundness or stability	RT4 Rheometer
7.	Flowability	RT4 Rheometer

The quantity of powder supplied for sample No. 4 was insufficient, therefore only particle size, shape, chemical composition and true density tests were conducted. Two or three sets of experiments were performed on each powder characteristics. The results obtained from these tests were then averaged. The experimental procedure adopted is briefly described as follows:

3.4.1 Particle size

The particle size test was performed in wet conditions using Laser Diffraction equipment (Make: Microtrac). Water was used as the carrier fluid at 55% flow rate. The range of particle size was measured from the smallest size of D10 to the largest size of D95, with D50 being the average particle size. The equipment was calibrated to this measuring range.

3.4.2 Particle shape

The particle morphology analysis was done using Scanning Electron Microscope (Make: Joel 733 fitted with 4 Spectrometers). Powders were added to a conductive adhesive tape and coated with a thin layer of carbon and attached to the sample holder. The test was conducted using a 20kV accelerating voltage and 20nA probing current. The particle morphology was then viewed under secondary electron image at suitable selected position in both low and high magnifications. The images/photos were then taken and recorded.

3.4.3 Chemical composition analysis

The chemical composition analysis of the powder samples was carried out in two stages, namely, crystallographic and elemental analyses.

3.4.3.1 Crystallographic analysis

The crystallographic analysis was performed using two different models of X-Ray Diffraction (XRD) equipment to identify the pattern of alpha and beta phases in the powder samples. The results obtained from the XRD equipment were then compared with each other to validate the results. Further verification of XRD results was carried out separately at Council of Geoscience laboratory.

The operation principle of XRD is such that X-rays of known wavelength enter a crystal of unknown spaces between planes referred to as d-spacing. The X-rays are then diffracted at certain angles forming diffraction peaks with different intensities. The intensities of diffraction peaks are then plotted against the diffraction angles to obtain a diffraction pattern. Using Braggs' equation, in which the d-spacing of the material was calculated by:

$$n\lambda = 2d\sin\theta \quad (13)$$

where

n – an integer (usually 1)

λ - the wavelength of the x-rays

θ - the angle of diffraction peak

d – the d-spacing of the material

Every known crystalline material has its own unique diffraction pattern in terms of diffraction angles and intensity peaks. The XRD equipment contains a selection of the standards of diffraction pattern of known materials which is then compared to the diffraction pattern obtained to identify the material.

The first XRD equipment (Make: Shimadzu XRD 700) used Copper $K\alpha$ radiation as its X-ray source. As per the equipment virtual standards, the goniometer and spectrometer slits were set at 0.3 and 0.15 μm , respectively. In addition, the goniometer was also set to run from 10° to 80° at 2° per second. Powder particles < 150 μm size (finely grounded) were added to the sample holder. Subsequently, the XRD test was performed to identify the phases.

The X-rays for the second XRD equipment (Make: Panalytical Emyrean diffractometer) were emitted by Fe filtered Cobalt $K\alpha$ radiation. The equipment was fitted with PIXcel detector and its slits were firmly fixed. The powder samples were prepared using a zero background holder and analysed with X'Pert Highscore plus software to identify the phases.

3.4.3.2 Quantitative elemental analysis

The quantitative analysis of elements heavier than sodium which were present in the sample was done using X-ray fluorescence (XRF) equipment (Make: Rigaku Primini). The samples were first moulded into circular pellets or discs using mounting press (Make: Struers Labopol). The pellets were made by mixing the powder sample with white boric acid powder in arbitrary ratio of 1:1. This ratio was found to produce firm pellets in comparison to other alternative ratio after several tests. The mixture was then poured gently into the mounting press circular bore and pressed at 30 kN at 150° for 5 minutes, followed by 1 minute cooling as per the equipment testing procedure to form pellets. The pellets were then scanned by the XRF equipment under vacuum to produce semi-quantitative data using virtual standards.

The verification of XRF results were performed externally at Sci-ba laboratories using a PANalytical Epsilon 3 XL ED-XRF spectrometer, equipped with a 50kV Ag-anode X-ray tube, 6 filters, a helium purge facility and a high resolution silicon drift detector. Further verification of XRF results was carried out at the Council of Geoscience laboratory.

Finally, the quantitative analysis of the amount of oxygen, nitrogen and hydrogen present was done by a combustion analyzer instrument (Make: Eltra ONH 2000) at NECSA laboratory. The samples were added to a tin capsule using a nibbled nickel flux and tested in accordance with equipment testing procedure.

3.4.4 Particle density

The density bottle also referred to as manual pycnometer is a small transparent glass bottle with a stopper. The density bottle was cleaned with acetone to remove any grease traces and dried at 40⁰ C in the oven. In addition the powder samples were also dried in the oven to remove any moisture. The experimental masses were determined as follows;

$$M_1 = \text{Dry, clean bottle} + \text{stopper.}$$

$$M_2 = \text{Bottle} + \text{stopper} + 5\text{-}10\text{g of sample added.}$$

Further, the entrained air in the sample was removed using a desiccator. The procedure involved pouring titanium powder sample in the density bottle followed by distilled water until it was half full. The density bottle containing the mixture was then placed in the desiccators for two minutes, after which it was removed and filled up with distilled water. The corresponding experimental masses were also determined as shown here under;

$$M_3 = \text{Bottle} + \text{stopper} + \text{sample} + \text{distilled water filled up to the stopper}$$

$$M_4 = \text{Bottle} + \text{stopper} + \text{only distilled water filled up to the stopper.}$$

Particle density ρ_{particle} was then computed using equation 14 as follows;

$$\rho_{\text{particle}} = \frac{M_2 - M_1}{(M_4 - M_1) - (M_3 - M_2)} \times \rho_w \quad (14)$$

Where

ρ_w - Density of water

3.4.5 Bulk density, flowability and soundness

The experimental procedure adopted in this section was similar to the one recommended by Freeman (2007), Freeman *et al.* (2009) and Krantz *et al.* (2009). The work was carried out at CSIR powder characterization laboratory.

A powder Rheometer, (Make: FT4 Powder Rheometer) was used to determine powder bulk density, flowability, stability, flow and specific energy. The Rheometer had a 25 mm diameter sample feeding vessel made of borosilicate glass. It was also fitted with 24 mm high precision stainless steel blade, vented piston and shear cell head accessories. These accessories can be simultaneously rotated and moved axially into the powder sample to measure rotational and axial forces. In addition, the rheometer operation was fully automated, thus limiting human operation to sample preparation and feeding into the testing vessel. The automatic operation was controlled by 3 control modes namely torque, velocity and normal force which automatically generated output for a particular test.

The powder testing process commenced with feeding the sample gently into the rheometer cylindrical vessel. Thereafter the sample was pre-conditioned by upward and downward transversing of the blade to remove any excess air or pre-consolidation thus creating a uniform, lightly packed sample that is reproducible. This was followed by splitting the powder sample into two volumes, of 10 ml used for shear cell test while 25 ml was used for dynamic testing. At this point, conditioned bulk density was measured automatically by RT4 equipment.

3.4.5.1 Shear cell test

The shear cell test was carried out by placing the whole powder section under an arbitrary specified normal stress of 9 kPa using a vented piston. The vented piston was then exchanged with a shear head and the sample was sheared under the above specified normal stress until a constant shear stress was attained. To maintain this constant normal stress throughout the process, the shear head was adjusted either upwards or downwards whenever the sample enlarges or compresses, respectively. This provided a critical steady flow state also known as pre-shearing and it is used to increase repeatability of the results obtained between tests.

At this critical steady flow state, the powder was placed under lower normal load than the one used for pre-shearing and sheared again. The shear stress found in this shear step (just before the powder deformed/flowed) was used to locate the first point of the yield locus for every powder sample. Additional points for drawing the yield locus were obtained by repeating the pre-shearing process and shearing the sample under progressively lower normal stress. After carrying out arbitrary six repeated tests, the yield locus line was drawn and extrapolated up to zero normal stress (y axis). Using Mohr circle analysis equation (12), the parameters such as unconfined yield strength, maximum principal stress, cohesion and flowability values were obtained.

3.4.5.2 Dynamic testing

Dynamic test was conducted using a 20 ml powder sample. The powder was forced to flow by a rotating twisted blade moving axially downwards and in the opposite direction (used previously in powder consolidation stage), to impose compaction at 100 mm/s (-100 mm/s) to the sample. The axial and rotation forces on the blade were measured continuously to determine the energy used to displace the powder. This energy also known as the basic flow energy (BFE) is obtained by running 7 consecutive tests at a constant tip speed (100 mm/s) on the powder sample, referred to as repeatability test (Rep). The 7th test was taken as the BFE value of the powder.

The other parameters such as powder stability index, variable flow rate and specific energy were determined as follows;

- i. Powder Stability Index (SI) was calculated by dividing BFE values obtained from the 7th test and the 1st test to identify any changes during repeated testing or processing. According to RT4 powder rheometer operation manual, a powder is regarded to have a stable rheology when its stability index lies between $0.9 < SI < 1.1$, and unstable when it falls outside this range.
- ii. Variable flow rate test was done by reducing the blade speed from 100 mm/s on the 8th test to 10 mm/s on 11th test. Flow rate index (FRI), was then calculated by dividing the flow energy obtained from the 11th test with 8th test.

- iii. Specific energy (SE) test was performed by moving the rotating blade axially upwards thus producing shear on the powder sample with no compaction or consolidation to determine the powder resistance to flow in unconfined environment. As per RT4 rheometer equipment specification, SE was also used to determine powder cohesiveness under the classification shown in Table 12.

Table 12 : Classification of specific energy

Non cohesion	Medium cohesion	Strong cohesion
SE < 5	5 < SE < 10	SE > 10

The results obtained from this study are presented and discussed in Chapter Four.

Chapter Four: Results and Discussion

4.1 Introduction

The results obtained from the methods used in the previous Chapter are presented in the form of figures and tables in this chapter. These results and implications thereof are also discussed in relation to the literature.

4.2 Potential supplier base

The companies that confirmed trading in titanium powder are presented in Table 13.

Table 13 : List of Companies selling titanium powder

S/No.	Company name	Email address	Remarks
1	Raymor Industries	bbeauchamp@raymor.com	Quoted (see Appendix IV)
2	Timet Powder metals	Chris.Hinshaw@timet.com	Quoted (see Appendix V)
3	Ma Teck GmbH	info@mateck.de	Quoted (see Appendix VI)
4	Sumitomo Corporation light metal products	akihiko.shono@sumitocorp.co.jp	They trade in titanium powder (Tilop64-45 type) for £ 250- 300 per 50 kg bag.
5	Wellmet international	info@wellmetusa.com	They trade in spherical shaped titanium powder exceeding quantities of 2000 pounds.
6	ADMA products	moxson@admaproducts.com	They trade both in commercially pure and blended elemental titanium powder with spongy morphologies and irregular shape particles. The price range is between £10.00 to 30.00 per pound.
7	International Titanium	itp@itponline.com	They trade in titanium powder

	Powder (ITP)		with coral shape.
8	AccushapeInc	accushapeinc@msn.com	They trade in titanium sponge granules produced from sodium sponge reduction process
9	CSIRO titanium technologies	John.Barnes@csiro.au	They trade in titanium powder with flake and coral shapes only.

Out of 105 companies contacted (in Appendix III), that deal with Titanium, only 9 of them (shown in Table 13) reaffirmed their trading in titanium powder, which translates to 9% of the total questionnaires sent. Serial number (S/No.) 1-3 sent complete quotations (See Appendix IV, V and VI). These companies trade in spheroidal shape titanium powder particles produced by Plasma Atomization (PA) and Plasma Electrode Process (PREP) techniques. In addition, they advised that the price varies inversely with an increase in quantity purchased and vice versa. This trend conformed to the normal law of demand and supply in the market as cited by Froes (2000).

Responses from S/No. 4-9 indicated that the concerned companies do not sell spheroidal shaped titanium powder, however, they sell other shapes such as flakey, coral, and spongy. According to Froes (2000), these are the commonly sold type of shapes in the market. It was also noted that some companies had a minimum quantity limit that they could sell, for example 50 kg and 907.2 kg (2000 pounds) for S/No. 4 and 5, respectively. This shows that these Companies only do business with clients who order large quantities of the titanium powder.

According to International Air Transport Association (IATA) regulations, titanium is a highly flammable material and therefore cannot be transported by air. During transportation, its normally packed in special material which leads to increase in overall costs. The feedback from the questionnaires indicated that, Fed Ex Priority Company is currently preferred for transporting titanium powder worldwide.

In general, it was established that only a small number of companies were willing to disclose their business ventures. This was attributed to stiff competition and existing marketing strategy. From the questionnaires, one respondent claimed that when they secure a purchase order for a

product they do not have, they purchase it from their competitor in the market at a lower price, and re-sale in the same form without any value addition at a higher price hence making profit. This business strategy led to unwillingness by the firms to disclose their business interests and transactions. This strategy is also associated with the prevailing higher prices of titanium powder in the market.

4.3 Characterization of titanium grade 5 alloy powder

4.3.1 Particle size

The cumulative particle size curves for the twelve samples are shown in Figure 32. The data used for graph construction are found in Appendix VII.

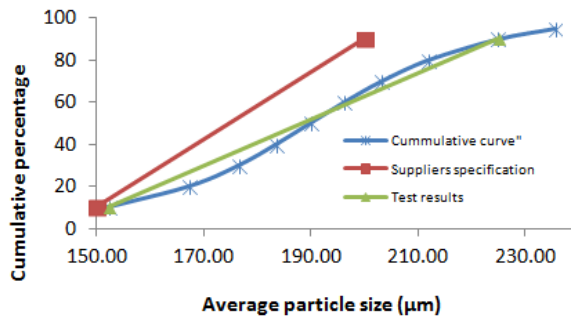


Figure 32 (a) Sample 1

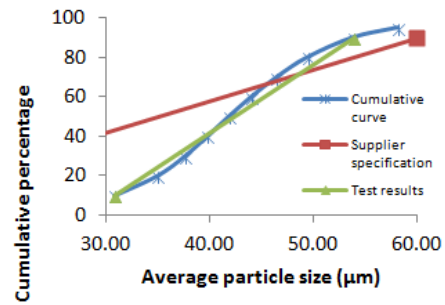


Figure 32 (b) Sample 2

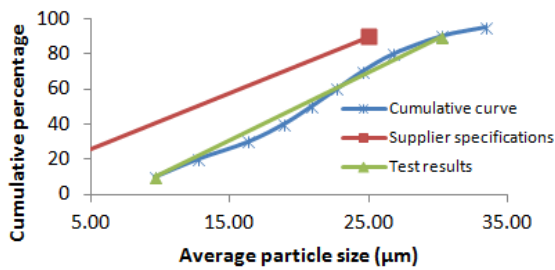


Figure 32 (c) Sample 3

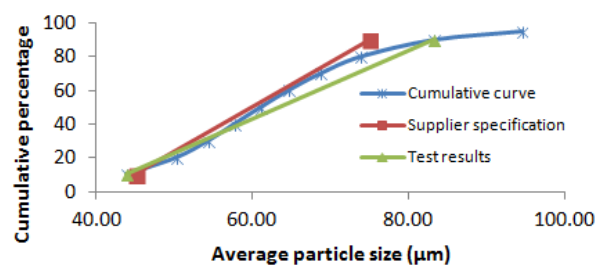


Figure 32 (d) Sample 4

Figure 32: Graph of cumulative particle size distributions for each sample of Ti6Al4V powder. Also shown are the supplier specifications regarding grain sizes of their products, where available. The legend “Test results” shows the overall size range measured by laser diffraction.

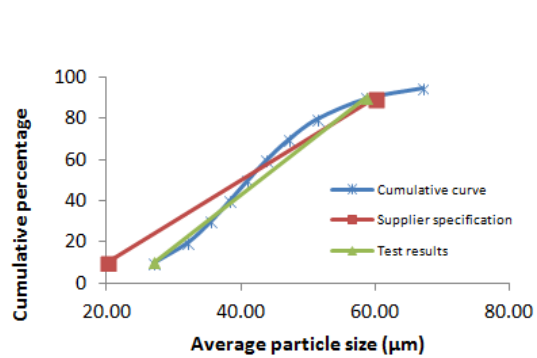


Figure 32 (e) Sample 5

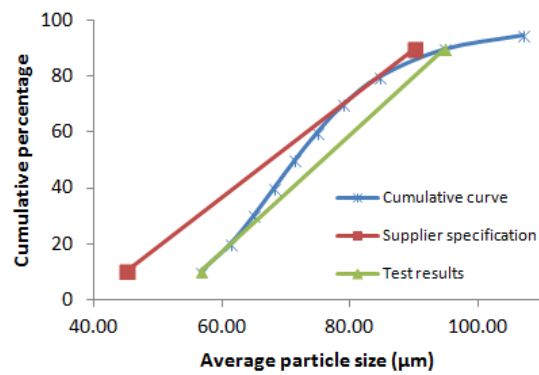


Figure 32 (f) Sample 6

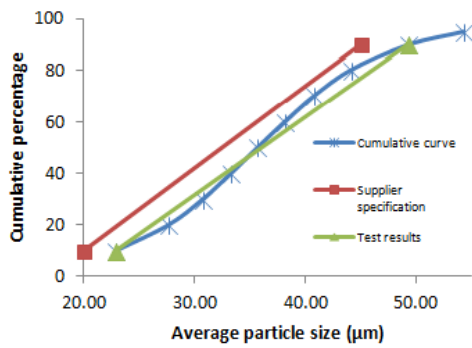


Figure 32 (g) Sample 7

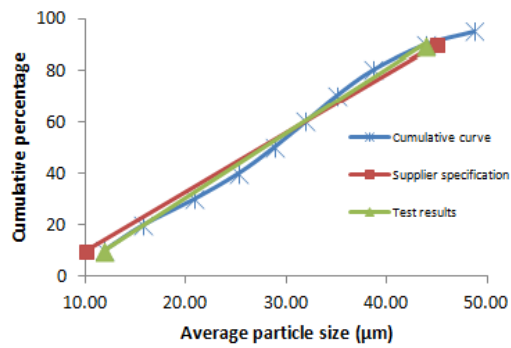


Figure 32 (h) Sample 8

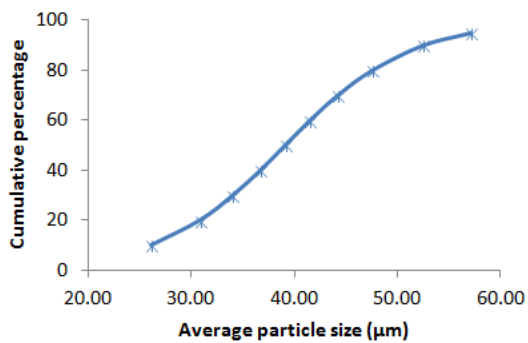


Figure 32 (i) Sample 9

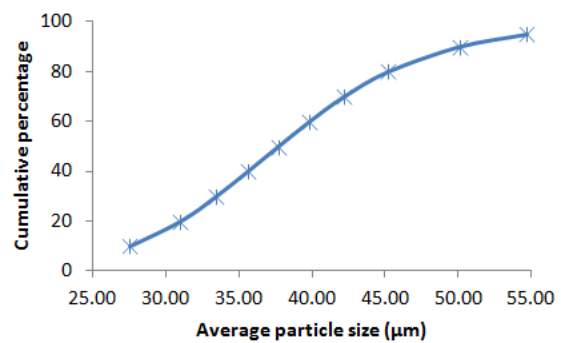


Figure 32 (j) Sample 10

Figure 32: Continued

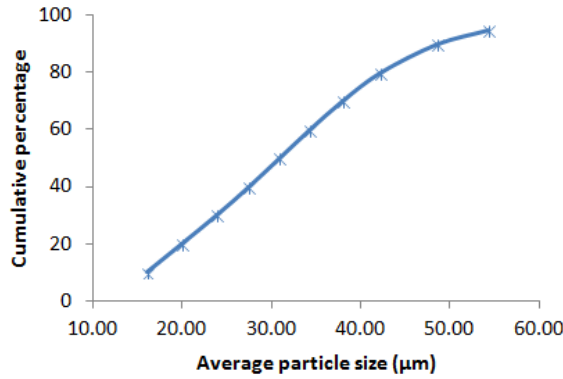


Figure 32 (k) Sample 11

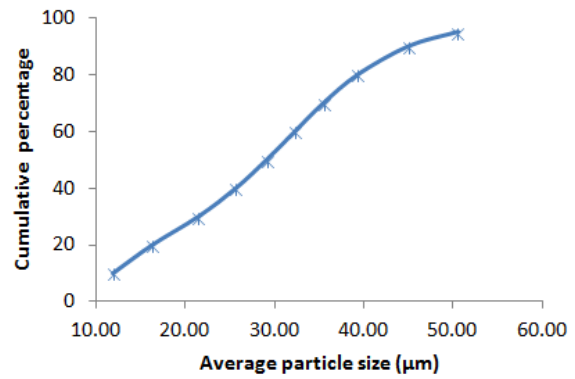


Figure 32 (l) Sample 12

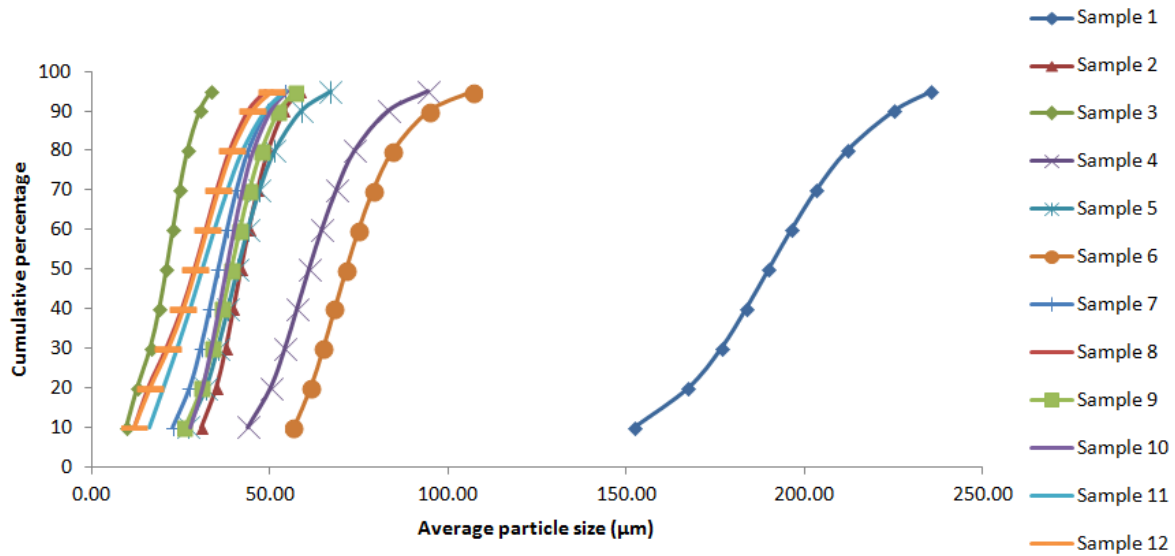


Figure 32(m) Comparison of cumulative particle size curves

The particle cumulative curves shown in Figure 32 were drawn by averaging the three sets of tests performed. The results from the laser diffraction method were in undersize cumulative percentage by volume against the varying average particle size. For example, in sample No.1 D50 indicates that 50% of the particles sizes contained in the sample are less than 189.97 μ m. It was also noted that cumulative curves for all the samples were S-shaped signifying congestion of plots at the extremities of the curves. The overall standard deviation of the cumulative curves ranged from 7.5 to 25.8 for sample Nos. 3 and 1 respectively. The standard deviations for the other samples are shown in Appendix VII.

From Figure 32 (m), except for sample No. 1, all other samples had their particle diameters $<110\ \mu\text{m}$. This particle size range signified the presence of high cohesion forces between particles which leads to particle agglomeration. According to Schwedes and Schulze (1990), particle agglomeration occurs naturally especially in small particles sizes. It is usually caused by physical, chemical or biological factors. Such factors include particle crystallization, chemical processing, enlargement of contact areas due to plastic deformation, capillary condensation and biological fungal growth. Resulting in uncontrolled build up, caking, bridging or lumping as noted by Krantz *et al.* (2009). Moreover, as cited by Emery *et al.* (2009), particle agglomeration causes poor powder flow properties.

Straight line method was used for the purpose of comparing the laser diffraction results to the supplier's specification of samples Nos. 1 to 8 listed in Table 10. Size D90 was adopted as the upper particle size range in line with previous studies conducted by Marcu *et al.* (2012), Krantz *et al.* (2009) and Liu *et al.* (2008), despite not having been specified in the suppliers' specification. The respective cumulative curves in Figures 32 (a) to (h) showed a noticeable difference between measured data and suppliers' specification in particle size range. In all the samples, except for sample No. 2, the laser measured data indicated a significant fraction of the particles as having a greater particle size than that specified by the suppliers. This was attributed to the failure of the laser diffraction equipment to break the particle agglomeration, thus giving erroneous results. Similar observations were made by Otsuki *et al.*, (2010). Particles agglomeration may be reduced by vibrating the powder using a mechanical shaker. This observation explains why many powder samples undergo vibratory sieving before use as confirmed by similar study done by Pohlman *et al.* (2012). However, since this study focused on the behavior of particle agglomeration with time, it was not recommended to subject the powder to vibration before testing. Samples Nos. 2 and 5 show higher proportions of coarse particle sizes than that suggested by the supplier specifications. Only the results of sample No. 8 were close to those of the supplier specification.

As seen in Figure 32 (m), the overall particle size range of powders tested lay between 0-230 μm , which was within the range of powder production sizes discussed earlier in section 2.6.1, besides producing spheroidal shaped particles. The methods of manufacture include Plasma Electrode Process (PREP), Titanium Gas Atomization (GA) and Plasma Atomization (PA),

which produce spherical powder particles having size range of 100-300 μm , 50-350 μm and 0-250 μm respectively (Oh *et al.*, 2003; Oliveira *et al.*, 2006). In this regard, sample Nos. 2, 3, 7-12 may have been produced by PA process, sample No. 4 and 6 by either PA or GA process, while sample No. 1 by PREP.

4.3.2 Particle shape (Morphology)

The low and high magnification images obtained from SEM equipment are shown in Figure 33. The magnification value for each sample is indicated below the image. The images show the particle shape, surface texture, agglomeration and packing density.

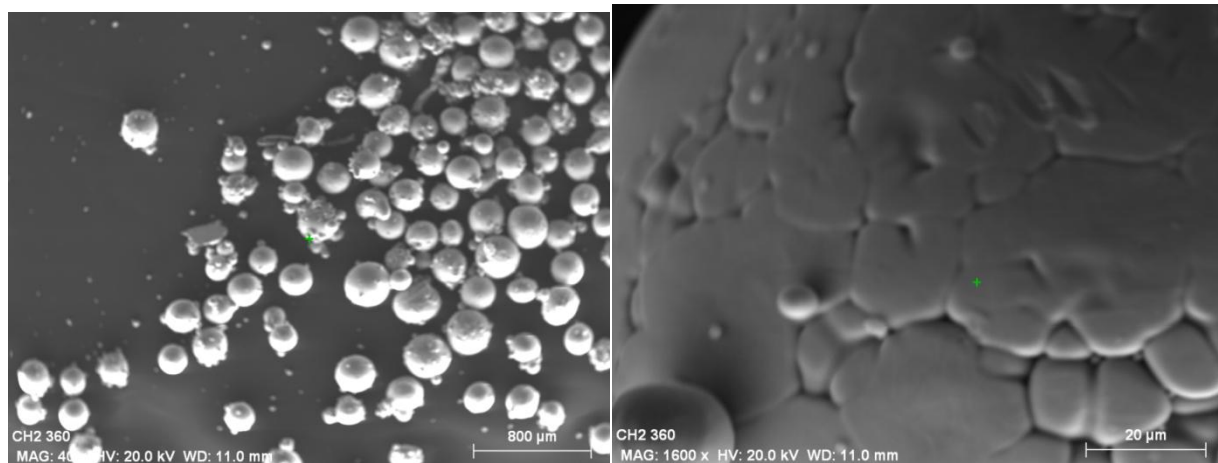


Figure 33 (a) Sample 1.

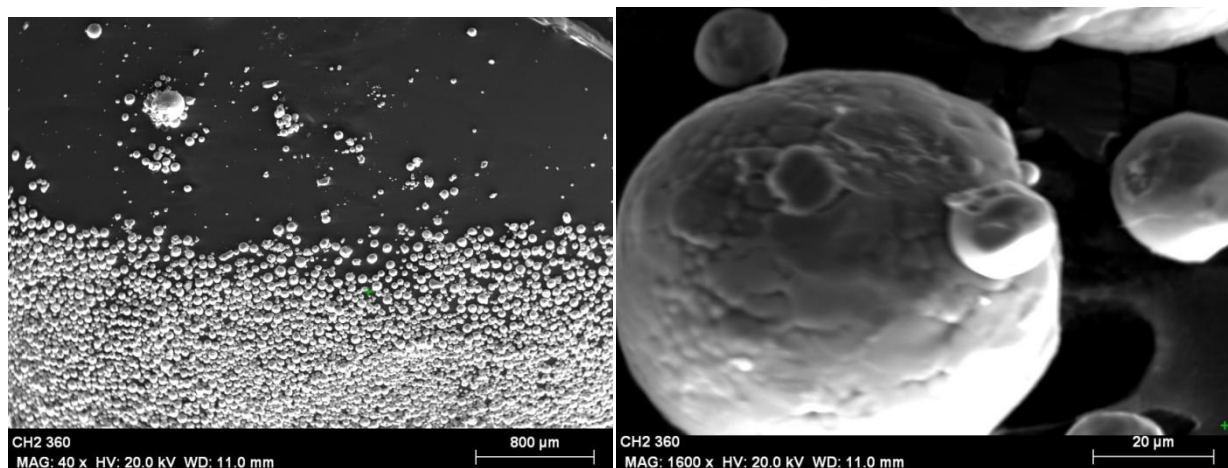


Figure 33 (b) Sample 2

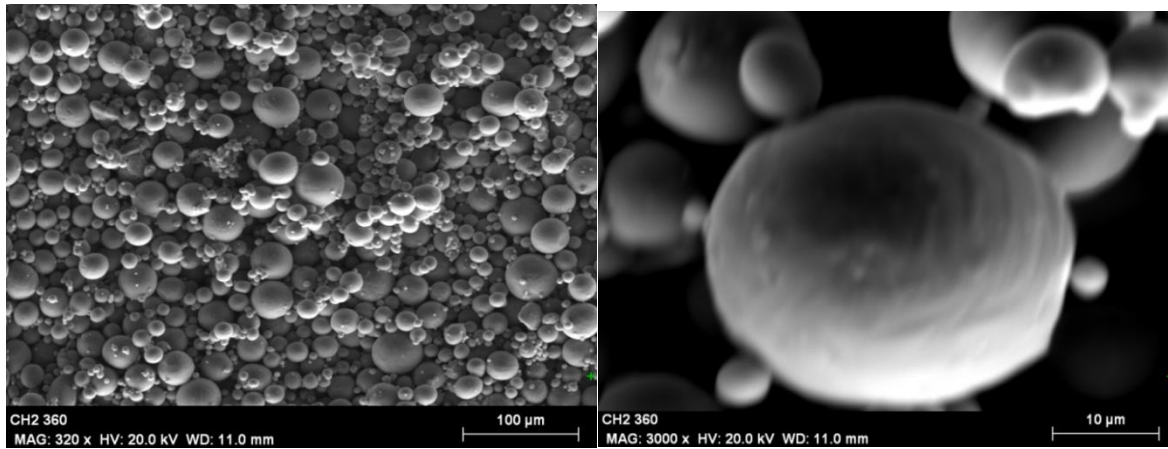


Figure 33 (c) Sample 3

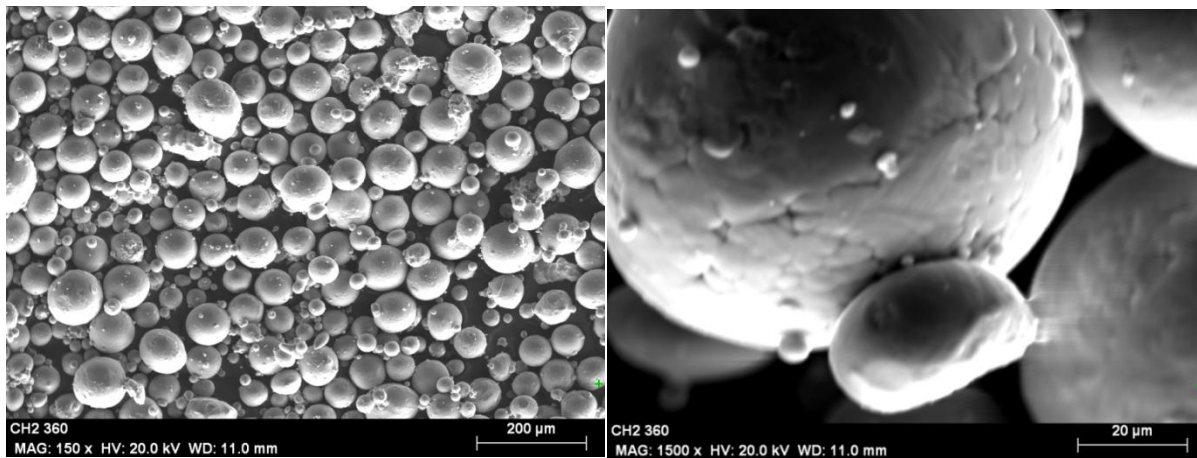


Figure 33 (d) Sample 4

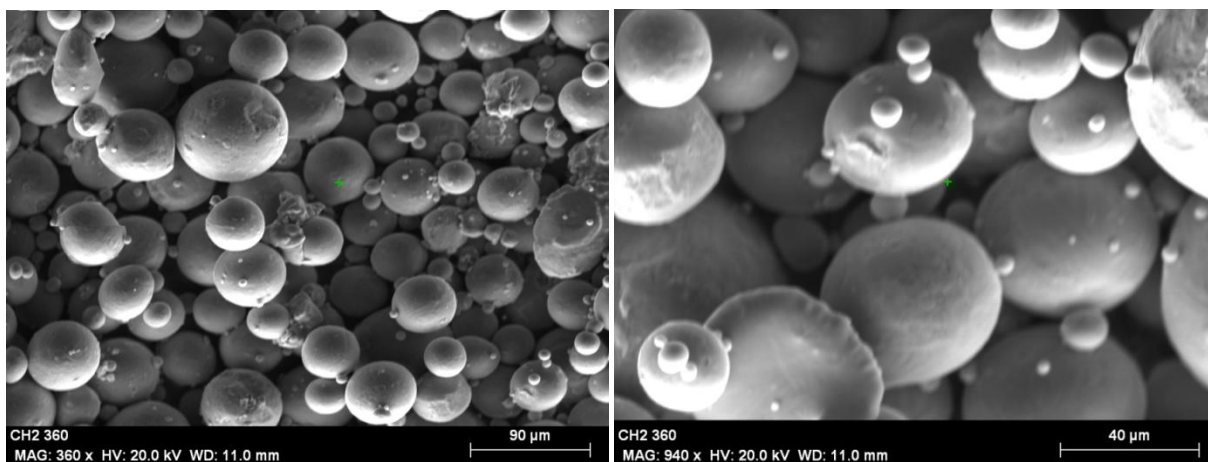


Figure 33 (e) Sample 5

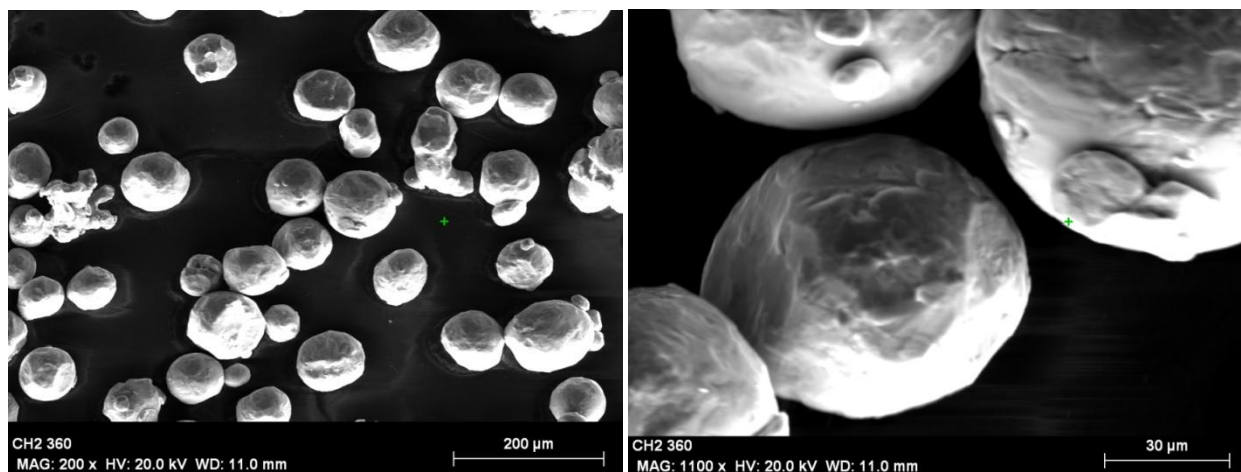


Figure 33 (f) Sample 6

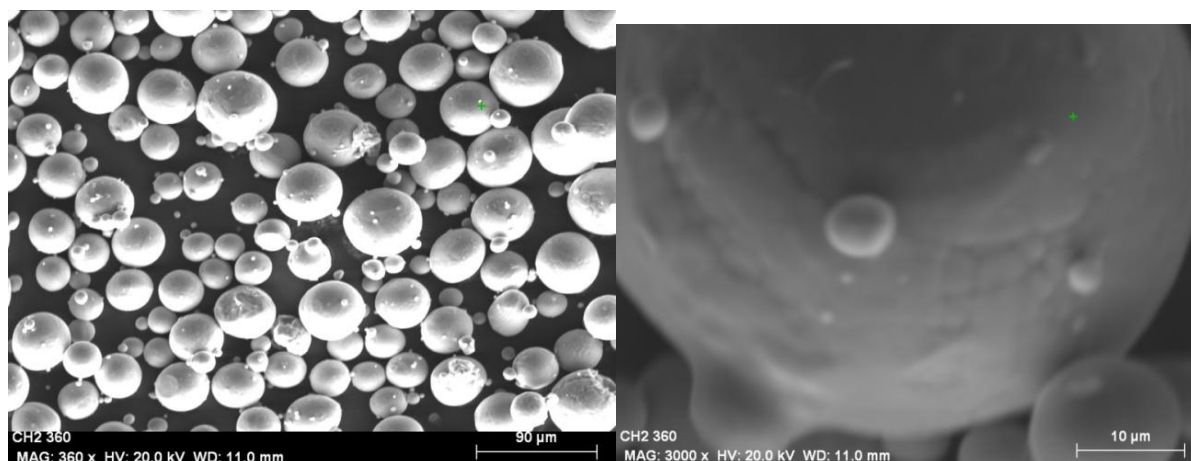


Figure 33 (g) Sample 7

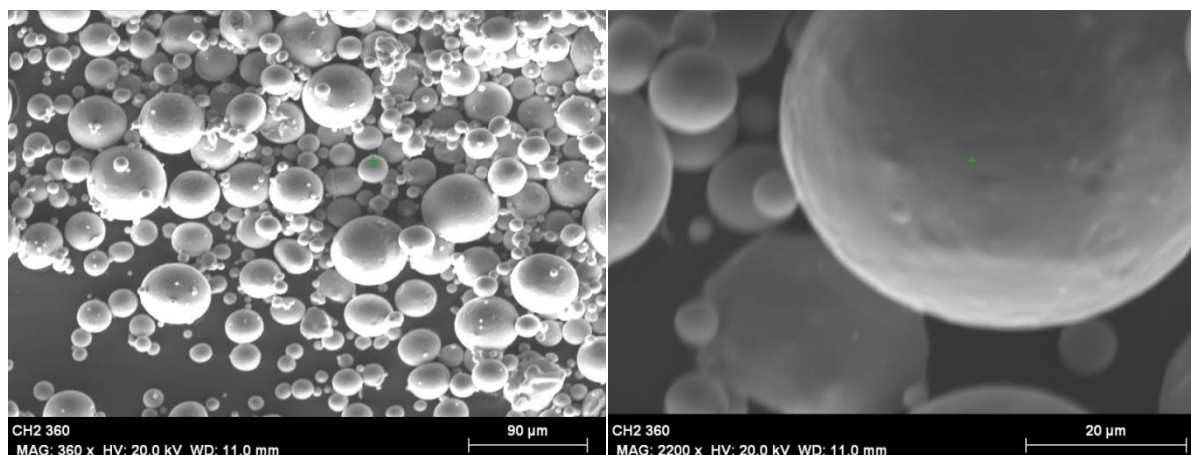


Figure 33 (h) Sample 8

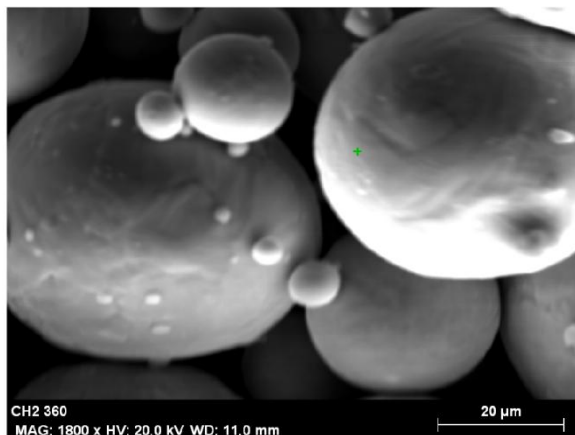
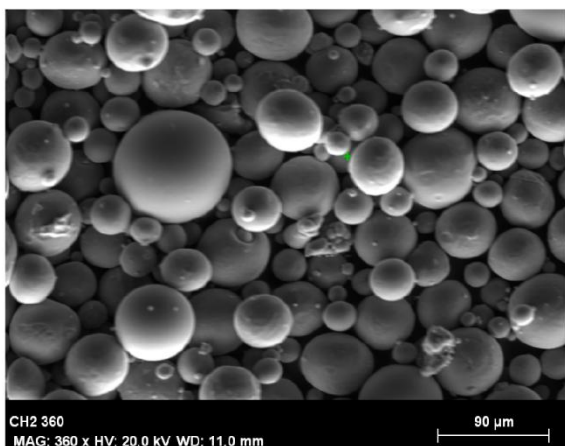


Figure 33 (i) Sample 9

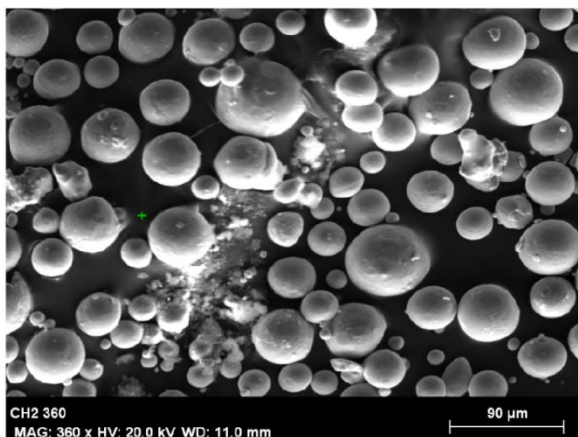


Figure 33 (j) Sample 10

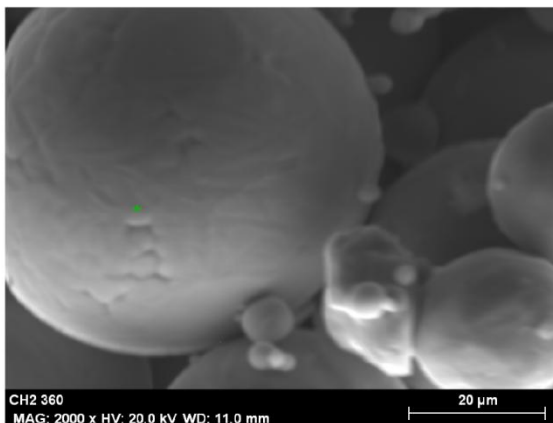
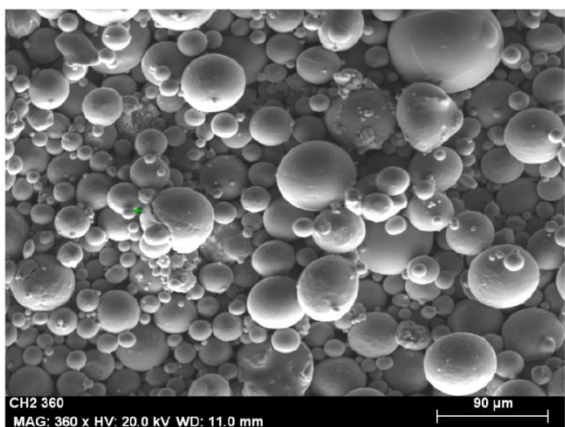


Figure 33 (k) Sample 11

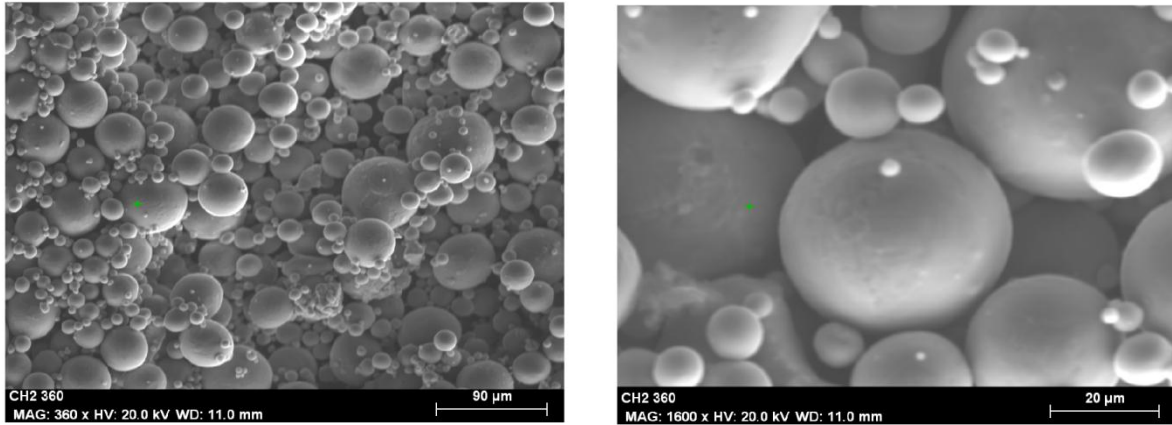


Figure 33 (l) Sample 12

Figure 33: Particle morphology of the twelve samples as seen under the SEM

The scanning electron microscope images in Figure 33, showed that all the powders were spheroidal in shape. However, the particle shape of sample No. 6 was found to be more angular than the other samples, a condition attributed to the method of powder production used. These shapes justified the use of laser diffraction method, since it is more appropriate for spherical particles as observed by Takeshi (2011). Besides, spherical shaped powders are also used as feedstock materials in additive manufacturing processes because they have good flow properties and packing density among others. This assertion is also reported by other studies (Mostafa *et al.* (2009), Gai *et al.* (2008)).

The ability of the spherical shaped powder particles to have good packing properties was confirmed by the SEM images. The SEM images showed smaller particles sticking to larger particles to form satellite particles, hence particle agglomeration. Powder samples with smaller mean particle sizes $\leq 31\mu\text{m}$ such as those observed in samples 3, 12, 8 and 11, had higher percentage of agglomerated particles compared to the rest of the samples with particle sizes $\geq 36\mu\text{m}$. This occurred due to the presence of higher van der Waals forces between smaller particles, which decreased with an increase in particles size, an observation also made by Emery *et al.*, (2009).

The SEM images in Figure 33 showed particles with rough and bumpy surface textures with entrenched cavities, especially sample nos. 1, 2, 4, 6 and 7. This was attributed to the method of

powder production used. The rest of the samples had smoother particle surfaces compared to the former. This may have been caused by the method of powder transportation which made adjacent particles to tear and wear thus obtaining smoother surfaces as reported by Tafesse *et al.*, (2012) and Krantz *et al.*, (2009).

4.3.3 Quantitative analysis

Table 14 shows the quantitative analysis of all the elements present in the samples as obtained from both XRF and combustion analyser methods. These elements were then compared to the maximum ASTM grade 5 standard in Table 6. Column 2-13 show the quantitative analysis of sample 1 -12 while the last column shows the ASTM requirements.

Table 14: Chemical composition for the twelve titanium powder samples

	SAMPLE												
Elements	1	2	3	4	5	6	7	8	9	10	11	12	ASTM
AL	1.67	3.60	3.65	3.45	3.43	0.00	3.57	3.53	3.55	3.05	3.74	4.08	5.50
V	0.00	4.14	4.71	4.21	4.53	0.00	3.13	3.59	3.17	4.24	4.00	4.19	3.40
Fe	0.00	0.27	0.24	0.00	0.25	0.00	0.00	0.18	0.00	0.00	0.00	0.21	0.19
Si	1.46	1.31	1.21	1.32	1.18	1.61	1.25	1.18	1.42	1.40	1.27	1.20	0.00
O	0.35	0.28	0.34	0.36	0.26	0.17	0.23	0.25	0.23	0.20	0.17	0.10	0.12
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
N	0.15	0.21	0.18	0.32	0.23	0.12	0.06	0.10	0.16	0.27	0.11	0.13	0.01
H	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.02	0.03	0.02	0.01	0.00
Cl	0.00	0.00	0.00	0.03	0.01	0.00	0.00	0.02	0.00	0.00	0.01	0.00	0.00
K	0.10	0.07	0.06	0.07	0.08	0.06	0.07	0.07	0.08	0.09	0.06	0.06	0.00
S	0.00	0.00	0.01	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Ti	96.28	90.11	89.58	90.23	90.02	98.03	91.67	91.08	91.36	90.72	90.61	90.02	90.77

The hydrogen, oxygen and nitrogen were analysed by combustion methods by an external service provider. The other elements were analysed by a Rigaku Primini XRF spectrometer using virtual standards that come with the instruments software.

The twelve samples were split into three different sets for XRF analysis. One set was analyzed at the VUT laboratory while the other two were sent to two external service providers namely; Sci-ba and Council for Geoscience laboratories for further analysis. The XRF analysis results obtained from the external laboratories are presented in Appendices VIII, IX and X. Results from

Sci-ba and Council for Geoscience laboratories were denoted as external provider (1) and (2), respectively. In the case of the Council for Geoscience results, some of the samples were not analyzed due to lack of sufficient material. While the data provided by Sci-ba laboratories for all the samples did not add up to 100%. The Council for Geoscience used fused beads for analysis of major elements (such as SiO_2 , Al_2O_3 , FeO , MgO , CaO , TiO_2 , MnO , Na_2O , K_2O , P_2O_5) and pressed pellets for trace elements (including vanadium). These fused bead procedures are typical for the analysis of geological samples. The results from these two laboratories indicate that, it is difficult to obtain accurate quantitative XRF data commercially, due to lack of proper standards and procedures for the analyses. Therefore, the results were found to be inaccurate and hence were not considered in this study

At the VUT laboratory, the XRF analyses were done using Rigaku Primini WDS instrument, and the analyses were standard-less and semi quantitative in nature. The instrument virtual standards and built in programme were used. These data were consistent and reasonably precise, but the accuracy is unknown. An important observation made during the analytical work was that the titanium $K\alpha$ peak overlapped with vanadium $K\alpha$ peak. Therefore, vanadium measurement was done using the $K\beta$ peak.

From Table 14, it was observed that none of the samples met the ASTM standard. The quantities of the alloying were either above or below the specified standard limit, besides the presence of impurities.

Traces of impurities such as chlorine, potassium and sulphur elements were noted in the compositions with potassium being present in all the samples. However, these impurities are some of the compounds which exist in titanium ore which are difficult to separate completely from titanium. A similar observation was made by Cheng *et al.* (2011).

The minimum amount of vanadium of 3.4 % as stipulated in the ASTM standard was met by all the samples except for sample Nos. 1 and 6 (Sample 6 may be pure titanium not an alloy). In contrast, the minimum quantity of aluminium element (5.5%) was not met by any of the samples, despite being one of the major alloying elements. According to ASTM standards in Table 6, there should be no silicon element present in the titanium. In spite of this, all the samples contained significant amount of silicon element which is a beta stabilizer, ranging from 1.2 to

1.6%. In this regard, only sample No. 1 was classified as dual phase alloy (alpha and beta alloy) since it contained significant amount of both alpha and beta alloying elements. The rest of the samples were classified as beta alloys because they had higher amounts of beta stabilizing elements and small amounts of alpha elements compared to ASTM standard. Similar observations were also made by Ezugwu and Wang (1997).

The hydrogen quantity in samples Nos. 10 and 11 exceeded the specified limits in the ASTM standard by almost 200%, despite its ability to form hydrides that cause embrittlement and subsequent cracking of titanium products when the maximum limit is exceeded. As for the rest of the samples, the quantity was within the ASTM specification range.

With exception of sample No.12, the amount of oxygen contained in the other samples was 1.5 to 3 times above the specified standard limit as shown in Table 14. In addition, the quantity of nitrogen present in all other samples was high, ranging from 0.06 to 0.32 %, contrary to 0.05% limit specified in the standard. This was attributed to the highly reactive nature of titanium which readily reacts with nitrogen and oxygen in the atmosphere and dissolves completely in titanium thus making it difficult to be removed. Moreover, neither the presence of carbon nor neutral alloying elements such as zirconium, hafnium or tin were detected in any of the samples, with carbon being one of the alloying element in the ASTM standard.

Figures 34 to 37 show the comparison between the major alloying elements present in the sample to the ASTM standard.

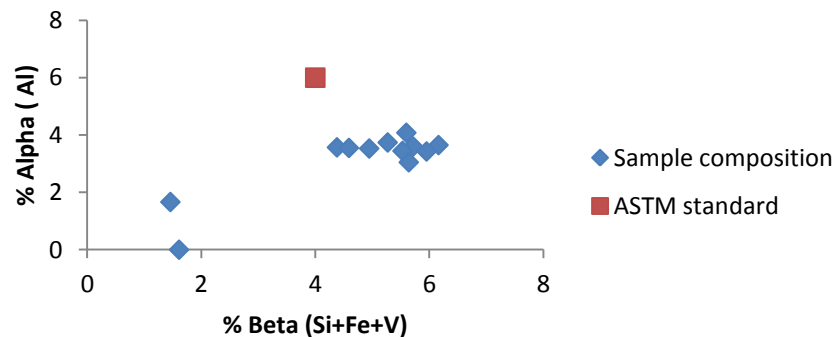


Figure 34: Composition of Alpha and Beta alloy in the powder samples

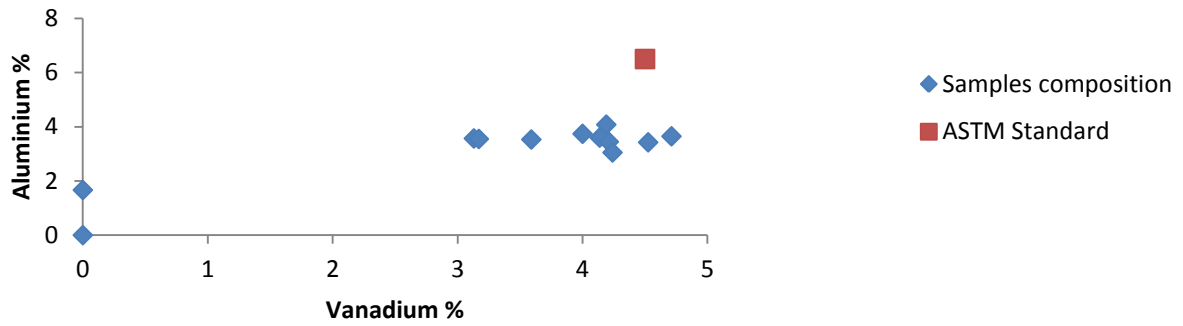


Figure 35: Composition of the major alloying elements in the titanium powder (Aluminium and vanadium)

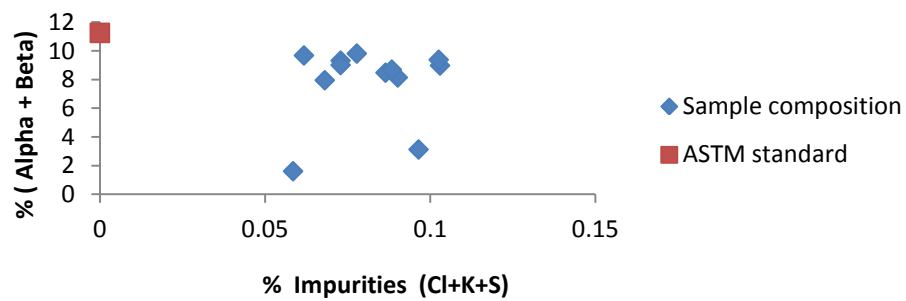


Figure 36: Compositions of major alloying elements (Alpha+Beta) and impurities.

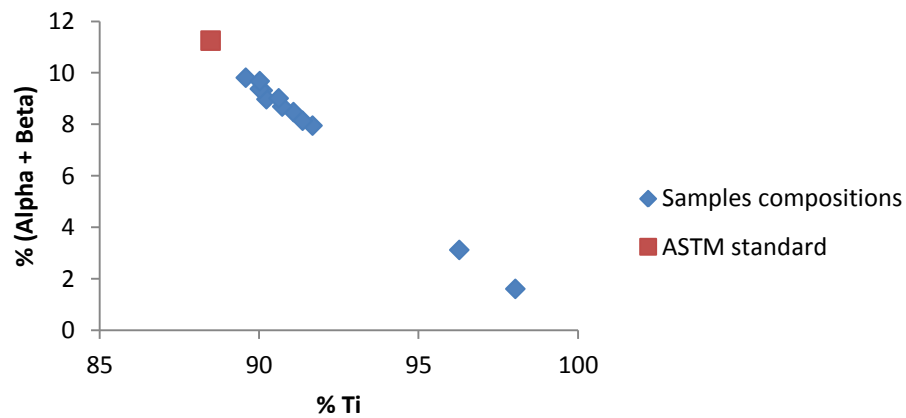


Figure 37: Compositions of major alloying elements and titanium element

In general, from the Figures 34 to 37 the quantities of the alloying elements were either above or below the specified ASTM standard of titanium grade 5 alloy. The remedy for the samples with lower amount of alloying elements as indicated by Bolzoni *et al.* (2012a) is to introduce the desired ratio into the sample and mix thoroughly in a rotating tumbler. However, samples with excess alloying element are removed.

4.3.4 Crystallographic analysis

Figures 38 (a) and (b) show the diffraction pattern of the twelve samples obtained from Copper $K\alpha$ and Cobalt $K\alpha$ XRD equipment, respectively. The magnitude and positions of alpha and beta peaks are summarized in Table 15.

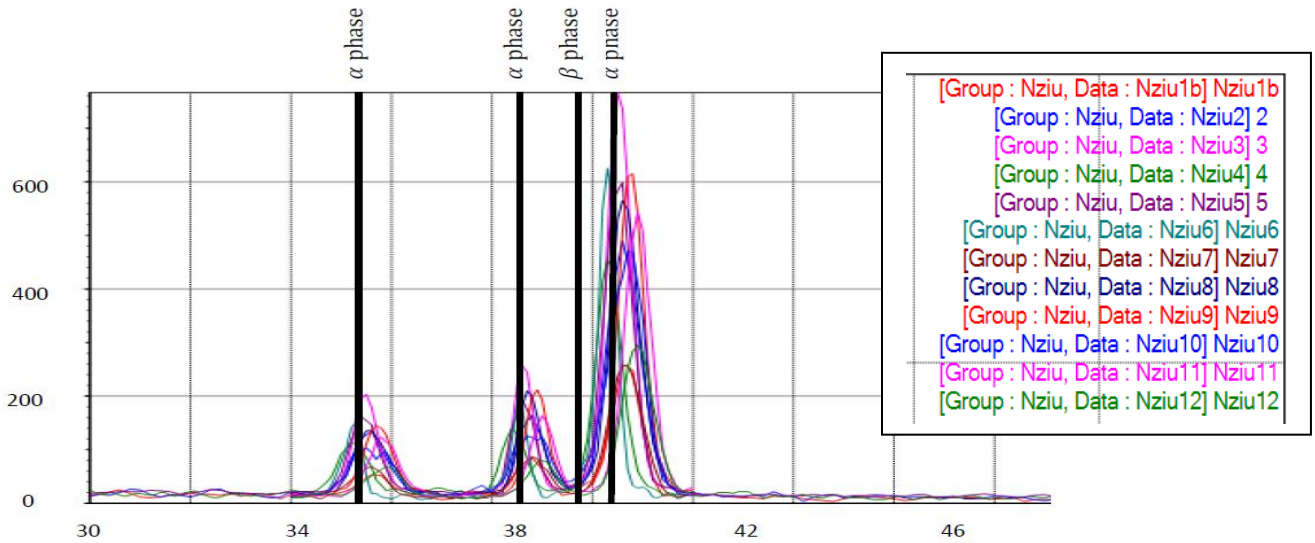


Figure 38 (a) Copper $K\alpha$ radiation diffraction pattern

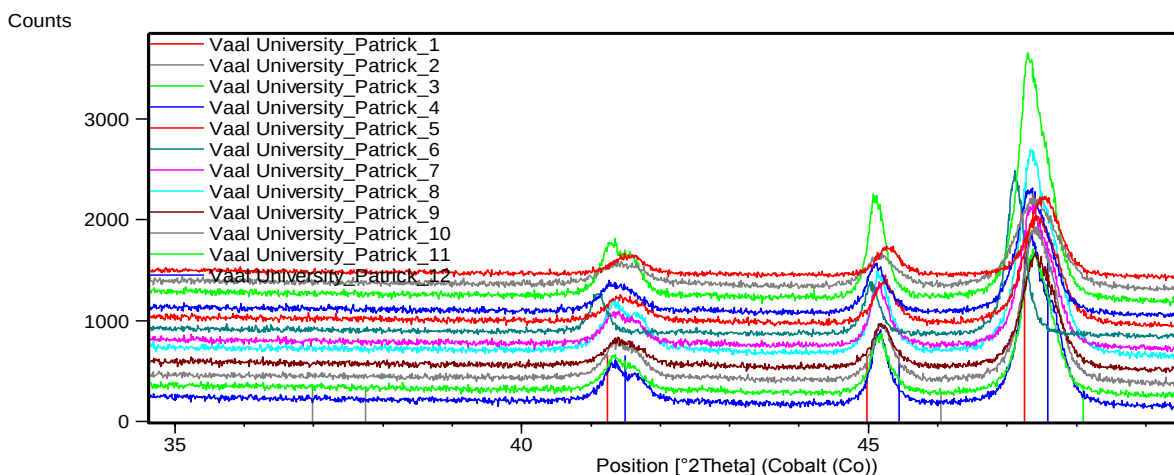


Figure 38 (b) Cobalt –K α radiation diffraction pattern

Figure 38: Titanium powder diffraction pattern for all the samples.

Table 15 : Crystallographic analysis

Phase	Copper K α			Cobalt K α		
	Peak intensity (%)	Position (2 θ)	d-spacing (Å)	Peak intensity (%)	Position (2 θ)	d-spacing (Å)
Alpha	100	40.17	2.24	100	47.25	2.23
	30	38.42	2.34	26	44.98	2.34
	25	35.09	2.55	25.8	41.24	2.54
Beta	100	38.48	2.34	100	48.10	2.19
	12	55.54	1.65	12.6	70.38	1.55
	17	69.64	1.34	20	89.80	1.26

The crystallographic analysis results showed that the values of d-spacing obtained for both alpha and beta phases were very close to each other, thus validating both the method used as well as the calibration condition of the equipment. The diffraction pattern indicates the presence of only alpha phase in the samples. Although the alloy contains both α and β phase stabilizing elements, the actual presence of a specific phase is dependent on the thermal treatment of the material. The

β phase is stable at high temperatures and converts to α phase upon cooling, unless the sample is quenched.

In comparison to titanium alloy diffraction pattern shown in Figure 17, the positions of alpha phase peaks obtained from the copper K α equipment (Figure 38 (a)) occurred at the same points i.e. 40.17° , 38.42° and 35.09° . The peaks were broad, signifying continuous variation in the powder composition. Figure 38 (a) reaffirmed that all the samples had well developed α phase peak. The β phase peak was absent from the data of all samples, indicating the conversion of β phase to α phase.

For verification of the XRD results presented in Figure 38, similar samples were sent to the Council of Geoscience laboratory for analysis and they were found to agree. These results are shown in Appendix XIII. The Rietveld analysis done at the Council of Geosciences confirmed the insignificance of β phase in the samples (See appendix XIII).

4.3.5 The effect of density on flowability

The density results are summarized in Table 16

Table 16 : Density results

Sample No	Particle size (μm)	Theoretical density (g/cm^3)	Particle density (g/cm^3)	Bulk density (g/cm^3)	Porosity ratio (n)	Cohesion (KPa)	Flow function (FF)
1	190	4.35	4.09	3.24	0.19	0.337	Free flowing (13)
2	42	4.40	4.05	2.48	0.39	0.3095	Free flowing (14)
3	21	4.41	4.03	2.33	0.4	0.792	Easy flowing(6)
4	61	4.39	4.05	-	-	-	-
5	41	4.41	4.08	2.62	0.36	0.24	Free flowing (20)
6	71	4.39	4.04	2.63	0.37	0.264	Free flowing (17)
7	36	4.38	4.12	2.51	0.39	0.354	Free flowing (15)
8	29	4.40	4.08	2.4	0.41	0.761	Easy flowing (6)
9	40	4.38	4.05	2.69	0.34	0.321	Free flowing (13)
10	38	4.40	4.03	2.8	0.31	0.218	Free flowing (19)

11	31	4.40	4.1	2.76	0.33	0.309	Free flowing (14)
12	29	4.40	4.11	2.38	0.42	0.682	Easy flowing (7)

From Table 16, the particle density was obtained empirically using a pycnometer and the raw data are presented in the Appendix XI. The theoretical density was obtained by multiplying the elemental percentage of the sample with their respective particle density as shown in Appendix XII.

Figure 39 shows the relationship between theoretical and particle densities. It was observed that the values of theoretical and particle densities were close to each other. The variation between the two densities ranged from 0.29 to 0.38. This variation may be attributed to entrained air in the distilled water used in the experiments despite using the desiccators to remove the moisture.

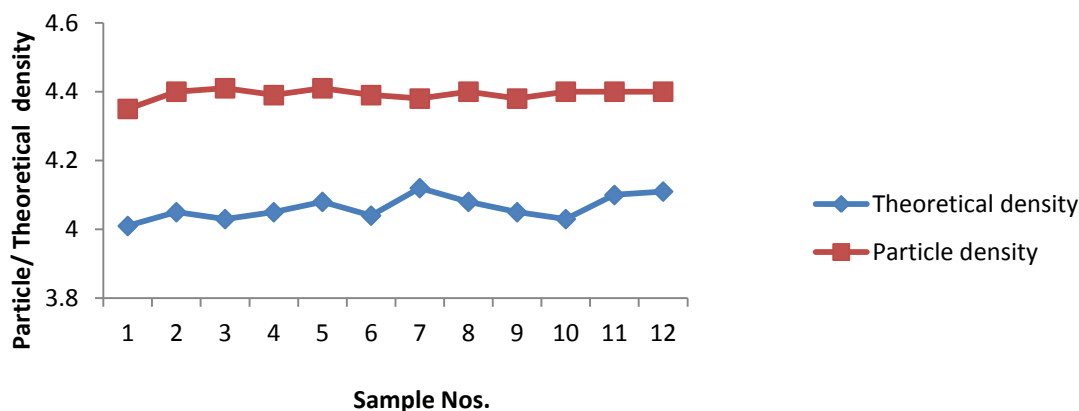


Figure 39: relationship between theoretical and particle densities

From Table 16, the sample Nos. 3 and 5 had the highest values of theoretical density of 4.41 g/cm³. This was attributed to the higher quantities of vanadium element in the samples as shown in Table 14. Moreover, vanadium element is a beta stabilizer and has higher particle density (6.11 g/cm³) in comparison to other alloying elements as shown in Table 6. In contrast, Sample 1 had the lowest theoretical density and had no vanadium element. This relationship was further

reaffirmed by Figure 40 that showed an increase of theoretical density with an increase in percentage quantity of vanadium element.

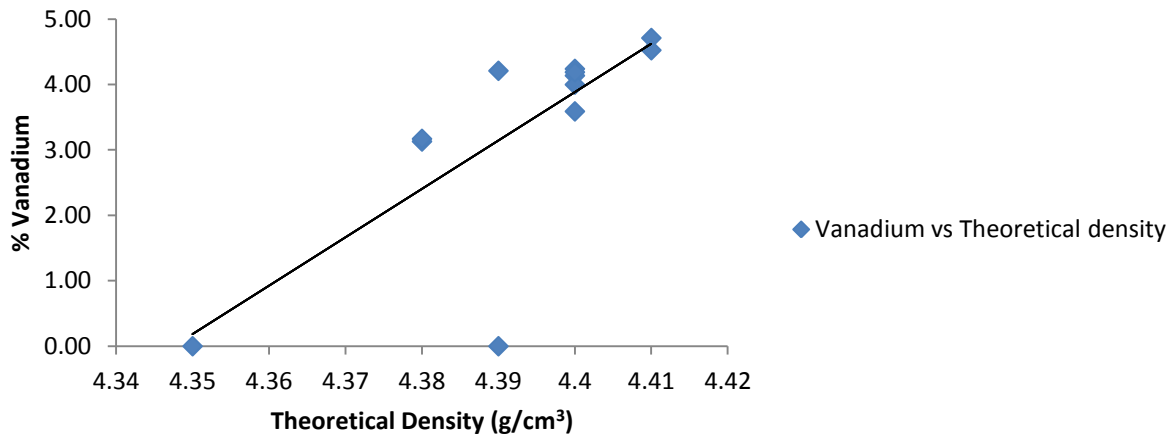


Figure 40 Relationship between percentage amount of vanadium present in the samples and theoretical density

Figure 41 shows the linear trend line relationship between increasing particle size with porosity ratio, bulk density and cohesion for all the samples.

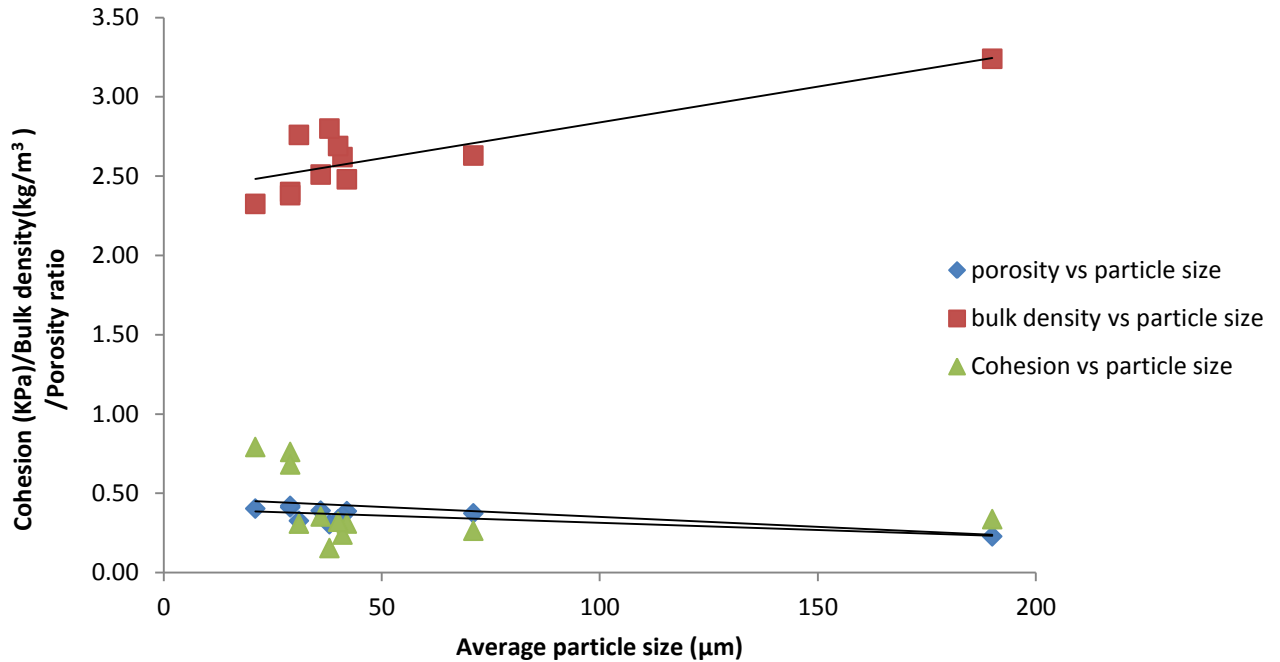


Figure 41: Relationship between average particle size and cohesion, bulk density and porosity ratio

It was noted that as the particle size increased, the powder porosity increased while the cohesion and bulk density decreased (Figure 41). It can also be seen that as the particle size increased, the corresponding sample porosity reduced significantly from 0.4 to 0.19. This relationship indicated that powders with larger particles sizes contained less amount of entrained air or moisture than powders with smaller particles. This phenomenon led to higher bulk density of the samples with larger particle size. This observation was in agreement with similar studies carried out elsewhere (Liu *et al.*, 2008).

From Table 16, sample Nos. 3, 8 and 12 had the lowest mean diameters of 21, 29 and 29 μm respectively, despite having the highest cohesion values of 0.792, 0.761 and 0.683 Kpa respectively. These results signified the presence of high adhesion forces between smaller particles as noted by previous studies by Emery *et al.* (2009). Noticeably, the same samples also had the lowest values of bulk density at 2.33, 2.4 and 2.38 g/cm³, respectively. This was attributed to the presence of strong inter-particle forces which was confirmed by the flow

function values presented in Table 16 that categorized the powders under easy flowing ($> 4 \text{ FF} \leq 10$) signifying the ability to resist collapse hence low bulk densities.

The rest of the samples had a mean diameter size of $\geq 31\mu\text{m}$. From Table 16, these samples had higher bulk densities ranging from 2.76 to 3.24 g/cm^3 , which increased with an increase in particle size, but with low cohesion values ranging from 0.218 to 0.354 kPa. This was attributed to weak forces between particles that enabled particles to collapse easily resulting in high bulk densities. These weak forces led to the free flowing nature of the powder as confirmed by the flowability results ($\text{FF} > 10$). These findings concurred with previous studies done by Abdullah and Geldart (1999). Figures 42 and 43 show relationship between bulk density with cohesion and flowability respectively.

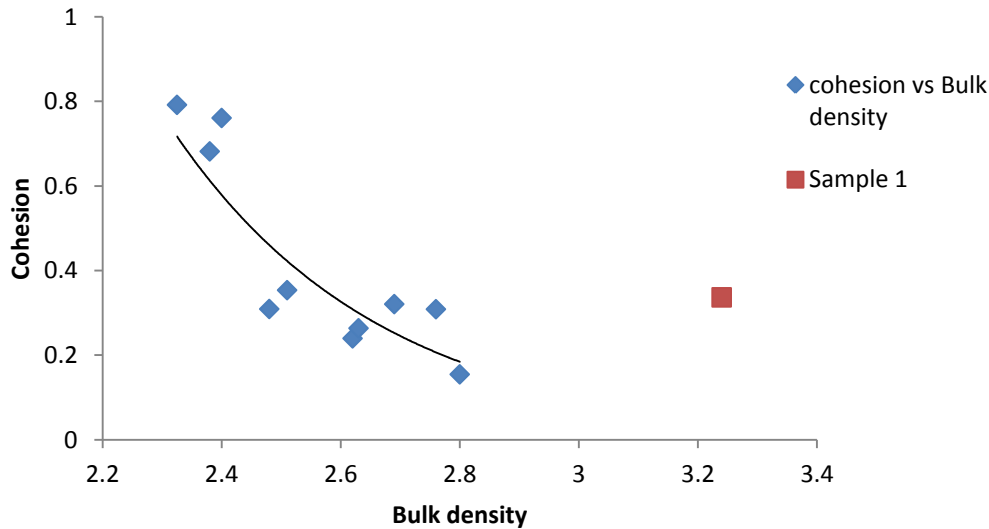


Figure 42 : Relationship between cohesion and bulk density

Figure 42 shows an exponential relationship between bulk density and cohesion. As the bulk density increased the cohesion reduced exponentially. However, the position of sample No. 1 which had the highest grain size was outside the exponential curve range, therefore, it was left out.

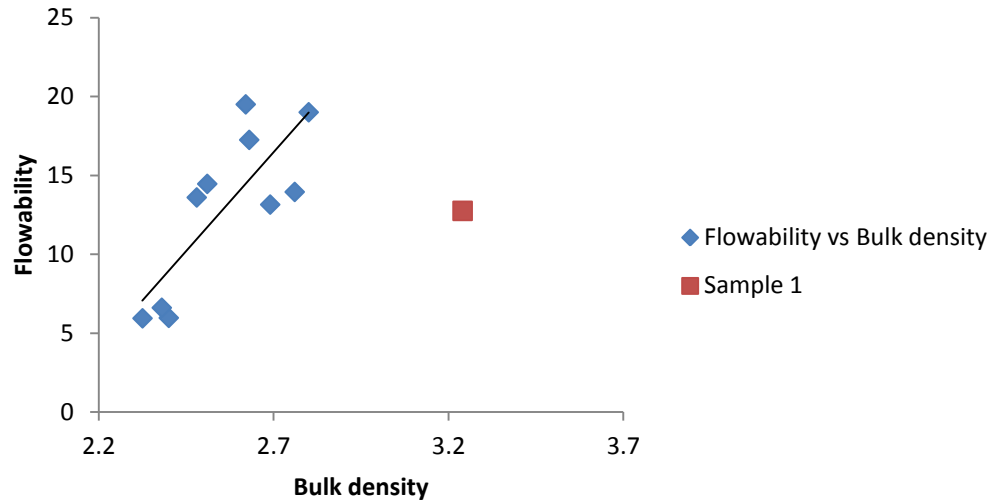


Figure 43: Relationship between bulk density and flowability

Figure 43 shows that flowability increased with bulk density. Similarly, position of sample No. 1 was left out since it fell outside the curve range. The data distributions in Figure 42 and Figure 43 reaffirm that bulk density is a function of grain size.

Figure 44 shows an exponential relationship between cohesion and flowability. As cohesion reduced, flowability increased. However, the position of sample No. 1 was within the exponential curve range. This indicates that the relationship between cohesion and flowability is not dependent on particle size range.

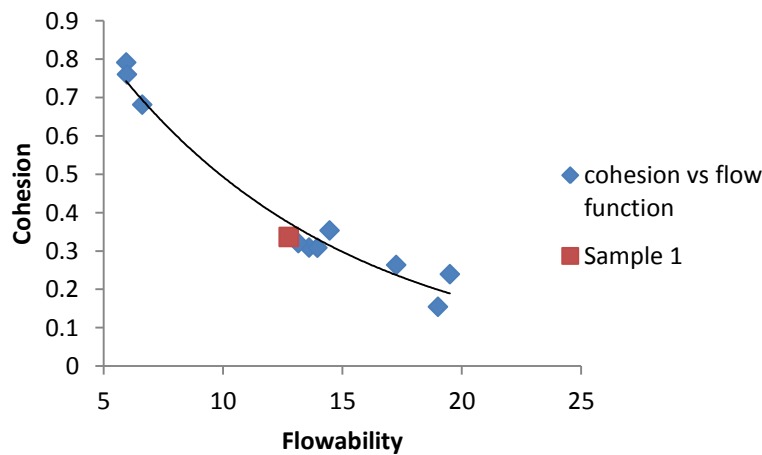


Figure 44: Relationship between cohesion and flowability

Particle size range also plays a role in bulk density and flowability. This may be shown by plotting the standard deviation of the particle size against bulk density, porosity and flowability as shown in Figures 45, 46 and 47. However, the correlations between these parameters and particle size distribution are poorer than that with particle sizes. The position of sample No.1 was isolated from other points.

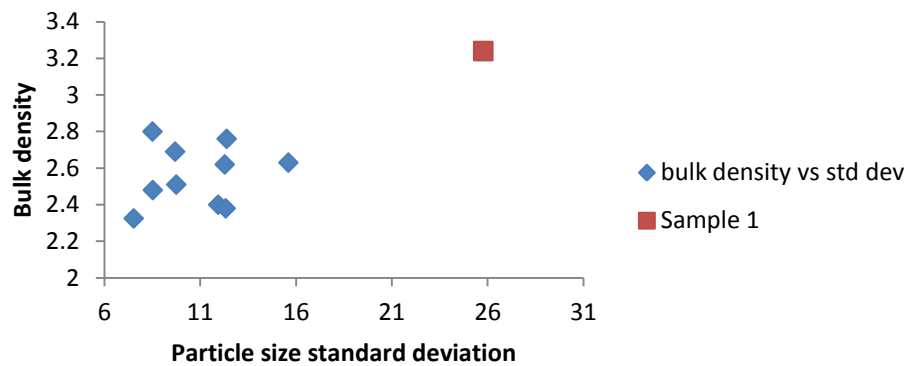


Figure 45 : Relationship between bulk density and particle size standard deviation

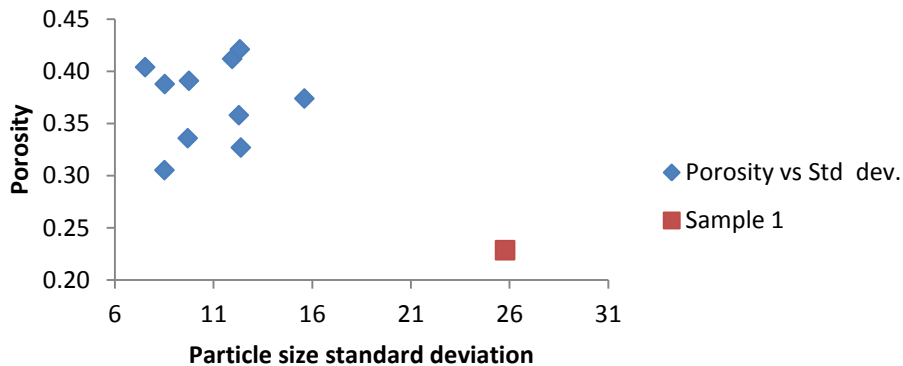


Figure 46: Relationship between porosity and particle size standard deviation

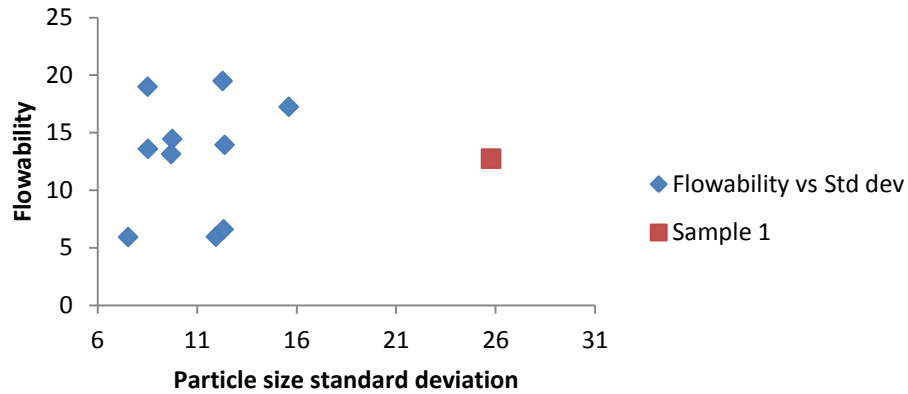


Figure 47: Relationship between flowability and particle size standard deviation

4.3.6 Effect of alloying elements on flowability

Figure 48 shows the effects of selected alloying elements on flowability. The linear trend line was used to analyze the plotted data. The quantity of nitrogen and hydrogen had an increasing effect on flowability while that of oxygen was found to have a reducing effect. However, potassium element in the powder had no significant effect on flowability.

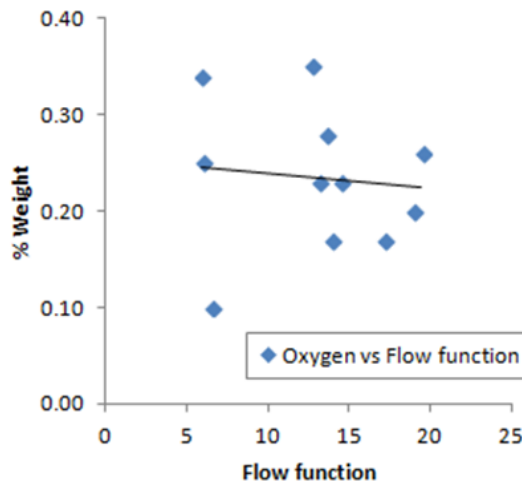


Figure 48 (a) Oxygen element vs Flowability

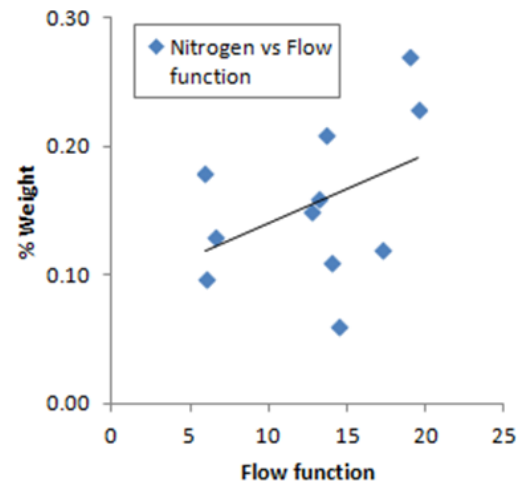


Figure 48 (b) Nitrogen element vs Flowability

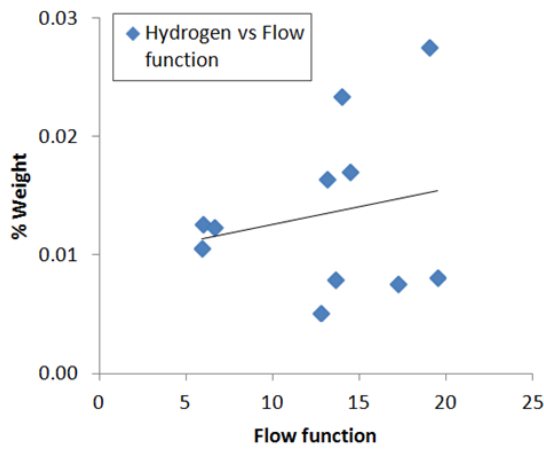


Figure 48 (c) Hydrogen element vs Flowability

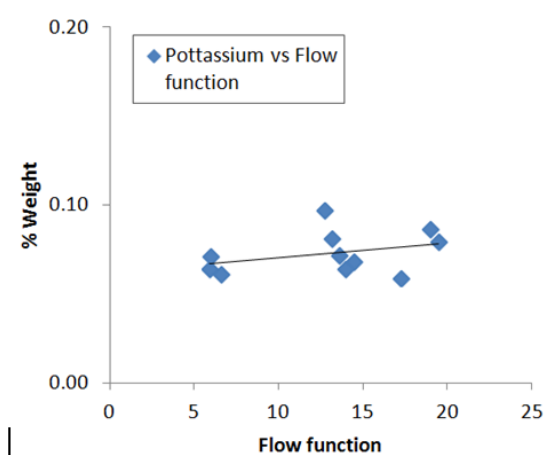


Figure 48 (d) Potassium element vs Flowability

Figure 48: Relationship between percentage weight and flowability of selected alloying elements

4.3.7 Effect of shear on flowability

4.3.7.1 Shear cell test

The shear cell results are presented in Table 17. Mohr circles for all the samples were drawn from values computed from equation 12 (the yield loci equation). Figure 49 show Mohr circles for the entire powder samples.

Table 17: Shear cell test results

Sample No.	Average size (μm)	Major stress σ_1 (kPa)	Minor stress σ_2 (kPa)	Stress ratio	Unconfined stress σ_c (kPa)	Flow function FF	Flowability	Particle accelerating Force (N) (Computed from the flow model equation below $(\rho_{\text{Particle}} d^3 g \epsilon) \times 10^{10}$)	Angle of internal friction (θ°)
1	190	15	4.50	0.30	1.19	12.75	Free flowing	274.9	30.65
2	42	13.3	4.91	0.37	0.98	13.6	Free flowing	4.1836	25.55
3	21	13.8	5.23	0.38	2.35	5.94	Easy flowing	0.1346	21.95
5	41	12.6	5.13	0.41	0.72	19.5	Free flowing	0.28172	23.3
6	71	12.8	5.08	0.40	0.81	17.25	Free flowing	27.729	23.85
7	36	13.0	5.4	0.42	1.04	14.46	Free flowing	1.878	21.99
8	29	13.5	5.08	0.38	2.26	5.97	Easy flowing	2.723	26.95
9	40	12.3	5.32	0.43	0.94	13.15	Free flowing	2.388	21.2
10	38	12	5.39	0.45	0.45	19	Free flowing	2.55	21.35
11	31	12.5	5.21	0.42	0.92	13.95	Free flowing	0.557	22.25
12	29	13.5	5.11	0.38	2.05	6.61	Easy flowing	0.286	22.55

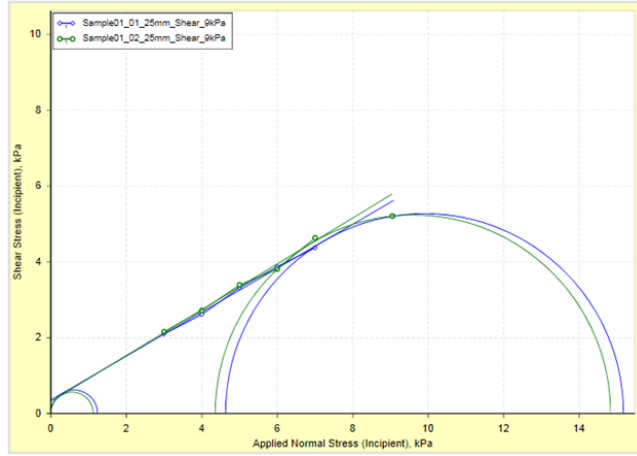


Figure 49 (a) Sample 1

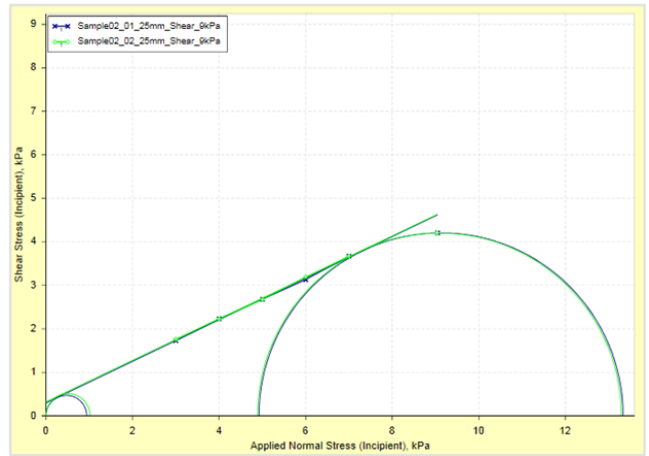


Figure 49 (b) Sample 2

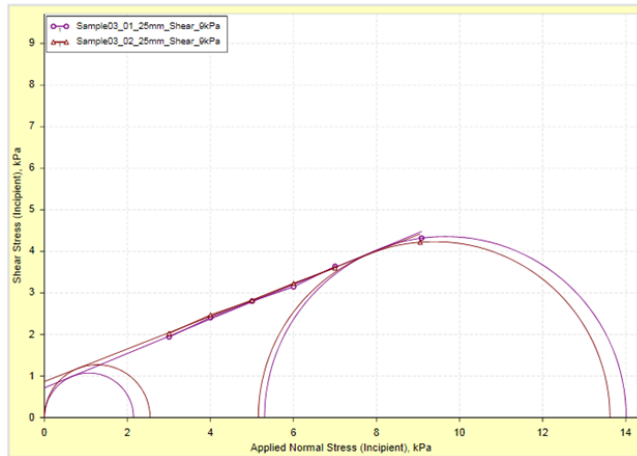


Figure 49 (c) Sample 3

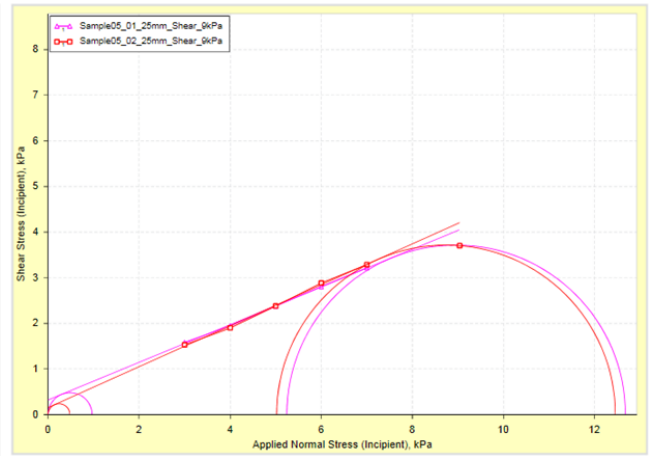


Figure 49 (d) Sample 5

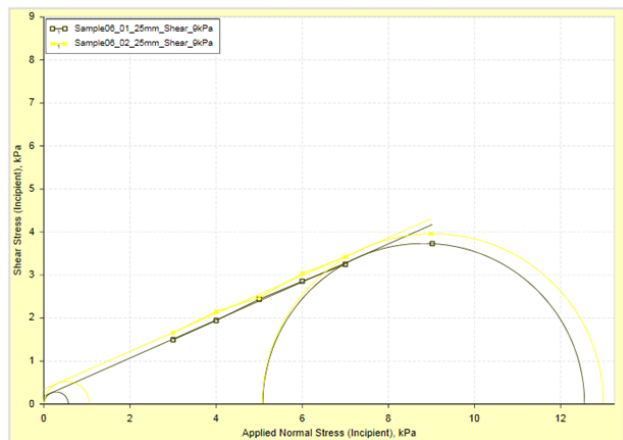


Figure (e) Sample 6

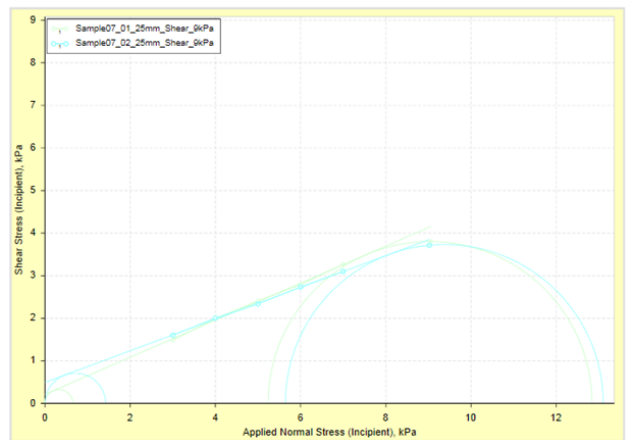


Figure (f) Sample 7

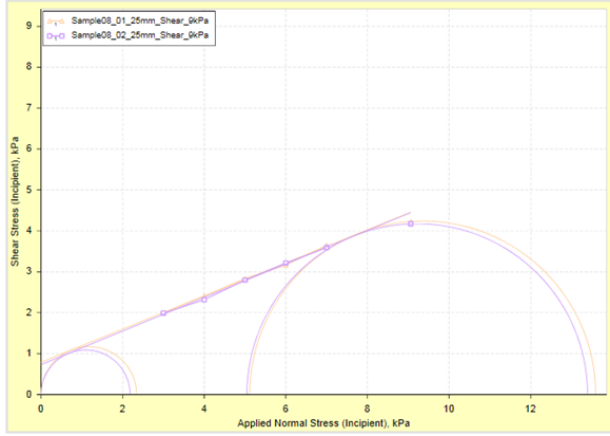


Figure 47 (g) Sample 8

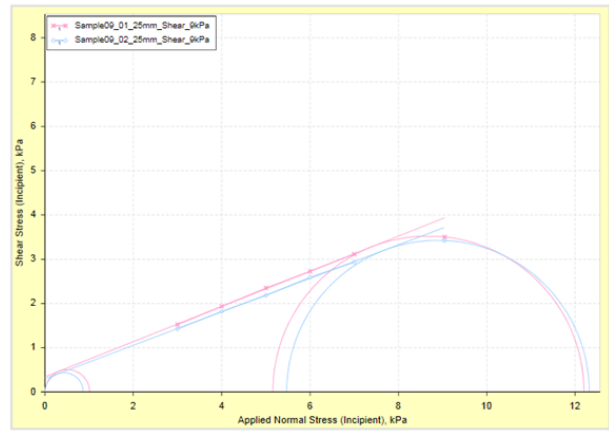


Figure 47 (h) Sample 9

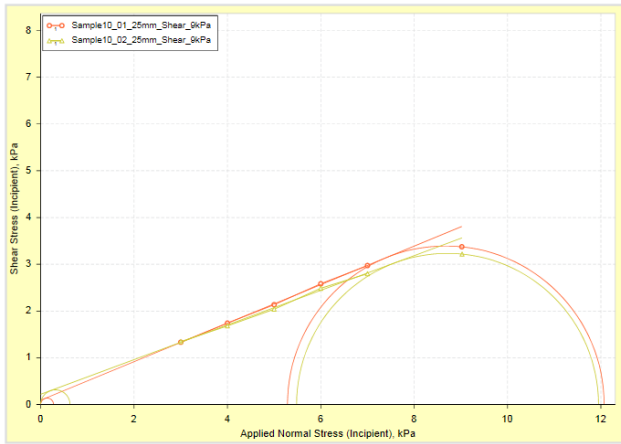


Figure 47(i) Sample 10

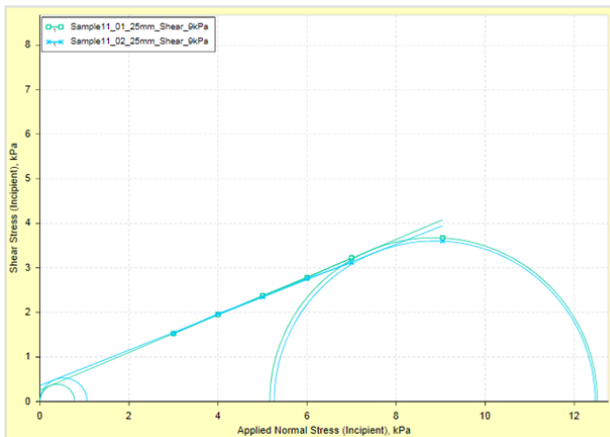


Figure 47 (j) Sample 11

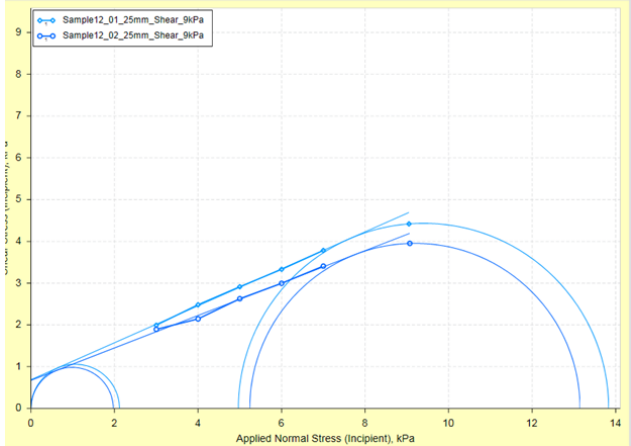


Figure 47 (k) Sample 12

Figure 49: Mohr circle for all the titanium alloy powder samples

Samples Nos. 3 and 10 had the highest and lowest values of unconfined yield stress respectively. However, it was noted that both the pre-shear and shear step stress circles for the entire samples were not intersecting as in the case of normal yield locus for bulk solids and powders as shown in Figure 27.

This trend indicated that the powder flow or deformation occurred in the elastic region, below minor principal stress value (the plastic region). This behavior was attributed to the free flowing nature of spherically shaped particles.

4.3.7.2 Effect on particle size on flowability

From Table 17, samples Nos.3, 8 and 12 with the lowest average particle sizes ($\leq 29 \mu\text{m}$), also had the highest values of unconfined yield stress of 2.345, 2.26 and 2.05 kPa, respectively. Consequently, higher major stress was required to initiate flow than the rest of the samples. This behavior was further confirmed by flowability results which categorized the samples under easy flowing.

The rest of the samples with particle sizes $\geq 31 \mu\text{m}$, were categorized as free flowing. In addition, the same samples with particle size $\geq 31 \mu\text{m}$ had lower values of unconfined yield stress ranging from 0.451 to 1.185 kPa, confirming the free flowing nature of particle with larger particle sizes than smaller particles as observed by other workers (Emery *et al.*, 2009).

The stress ratio values for all the powders lie between 0.3 and 0.42 which was within the specified range for bulk solids at 0.3 to 0.6 as reported in previous studies by Schwedes and Schulze (1990). The angles of friction for all the samples were high, ranging from 20.3° to 30.65° , thus indicating good flow properties which were attributed to the spherically shaped particles.

Flow characteristics of the entire powder samples are shown in Figures 50 and 51. Figure 50 shows that unconfined yield stress increases with an increase in the major consolidated stress. The trend line obtained from the data plotted was skewed to the right intercepting the y axis at point -4.4948, with a slope of 0.4377. The flow index (FI) curve is obtained by dividing unconfined yield stress with major consolidated stress. Comparing the trend line of Figure 50

with flow index curve in Figure 28, the powders were classified under free flowing category since the curve gradient was small. These observations were in line with what was reported in the literature by Cagli *et al.* (2007).

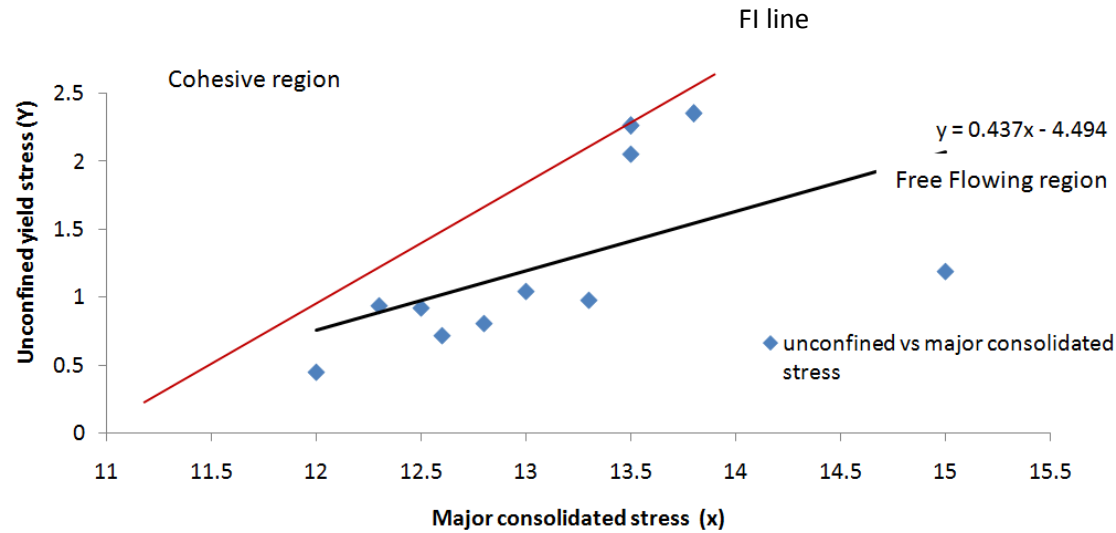


Figure 50: Relationship between major consolidated stress and unconfined yield stress

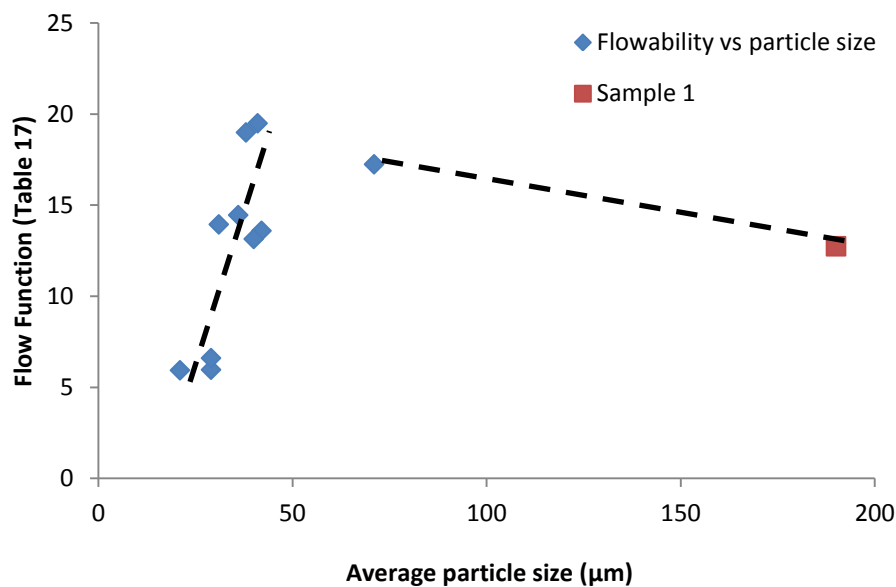


Figure 51: Relationship between average particle size and flow function (Table 17)

The trend line in Figure 51 showed that flowability increases with an increase in particle size. This relationship reaffirmed that larger particles have better flow characteristics than smaller particles.

However, it was also observed that as particle size increased from 5 to 20 μm , flowability also increased until it reached a maximum value. The highest flowability was noted at particle size of 41 μm . After which flowability began reducing with further increase in particle size. This reaffirmed the existence of a particle size range that gives optimum flow conditions.

4.3.7.3 Dynamic testing

Dynamic testing results are summarized in Table 18.

Table 18: Dynamic testing results

Sample No.	Particle size (μm)	Basic flow energy (MJ)	Specific energy	Stability Index (MJ/kg)	Flow rate index	Cohesion (kPa)
1	190	309	1.8	0.958	0.989	0.337
2	42	489	2.95	1.035	1.19	0.3095
3	21	344	4.49	0.966	1.26	0.792
5	41	414	3.01	1.05	1.175	0.24
6	71	419	1.98	0.948	1.01	0.264
7	36	410	3.05	1	1.16	0.354
8	29	353	4.03	0.986	1.21	0.761
9	40	419	2.52	1.02	1.13	0.321
10	38	404	2.15	1.06	1.15	0.218
11	31	398	2.6	1.01	1.26	0.309
12	29	324	3.41	0.96	1.2	0.682

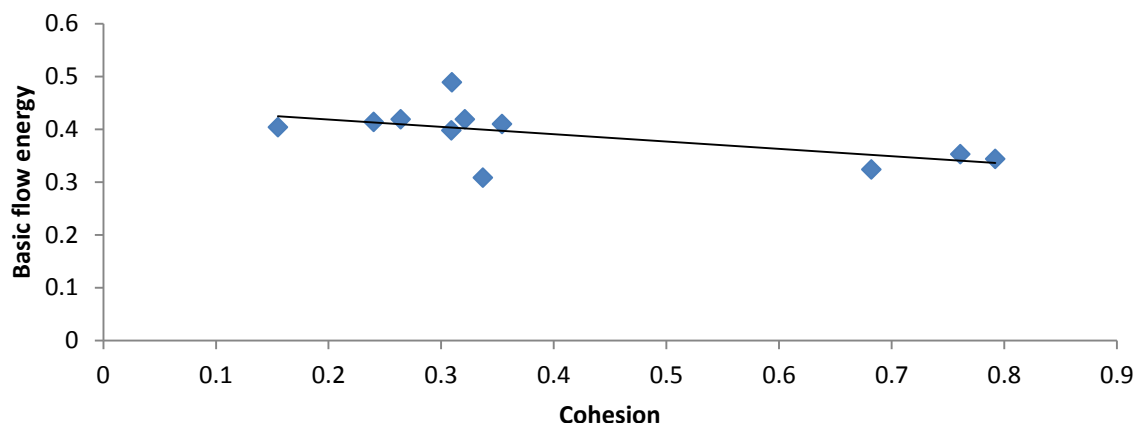


Figure 52: Relationship between cohesion and basic flow energy

The basic flow energy (BFE) is the energy needed to move a conditioned powder. BFE values for all the powders ranged from 0.309 to 0.489 kJ. Figure 52 shows the relationship between basic flow energy and cohesion. It was noted that more cohesive powders (sample Nos. 3, 8 and 12) required slightly less energy to start flowing, 344, 353 and 324 MJ, respectively, than non-cohesive powders (sample No 2, 6 and 9) that consumed more energy i.e 489, 419 and 419 kJ respectively. This tendency confirmed that cohesive powders have more fluid like characteristics which enable high transmission of forces between particles resulting in the formation of chain flow reaction which improves powder flow.

The seven repeatability tests (see appendix XIV), conducted on all the powders to determine the amount of basic flow energy, showed a high degree of reproducible results, signifying a stable rheology. These results were further validated by the stability index ratio shown in Table 18, that ranged from 0.94 to 1.04, therefore falling within the stable region of $0.9 < SI < 1.1$ (see Table 12). This stable nature of the powders was attributed to the spherical shape of the particles.

In this stable region, the powders have no tendency to settle or segregate between tests thus maintaining constant homogeneity. Thus, the results showed that there was no significant variation on particle agglomeration, moisture or air content which are some of the factors that affect powder stability (www.freemantech.co.uk). Powders with unstable rheology have their SI values falling outside $0.9 < SI < 1.1$ range indicating poor reproducible results necessitating extra tests to be done to verify them. (www.freemantech.co.uk).

From Table 18, flow rate index results for all the powders ranged from 0.989 to 1.26. With the exception of Sample No. 1, all other samples had their FRI >1 , these samples therefore be classified under non Newtonian fluid. The behavior of non Newtonian fluids is such that more basic flow energy is needed to move the powder slowly (usually at slow blade speeds). In comparison to Newtonian fluids (sample No. 1) which require less flow energy to move the powder slowly.

The specific energy results for all the powders ranged from 1.8 to 4.9, as shown in Table 18 falling within non-cohesive region $SE < 5$ (see Table 12), thus signifying less resistance to flow. Sample Nos. 3, 8 and 12 with smaller average particle sizes had the highest ratios of specific energy at 4.49, 4.03 and 3.41, respectively, indicating higher resistance to flow. Additionally, sample No. 1 had the largest particle size, but with the lowest value of specific energy at 1.8 indicating lower resistance to flow.

Figure 53 clearly demonstrates the inverse correlation between specific energy and average particle size. It was noted that as the particle size increased, the specific energy decreased.

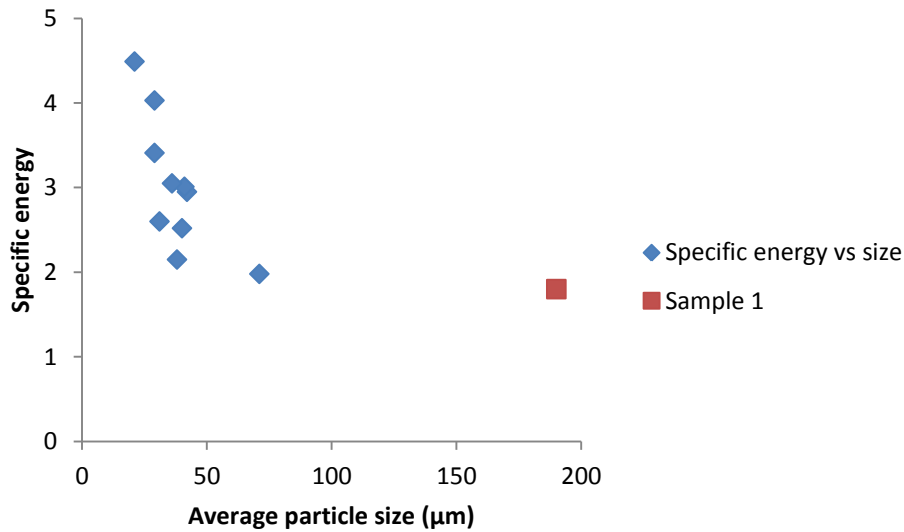


Figure 53: Relationship between average particle size and specific energy

Inverse relationship between powder flow function (ability to flow) and specific energy (resistance to flow) is illustrated in Figure 54 confirming that powder particles with good flowability properties have less resistance to flow and vice versa.

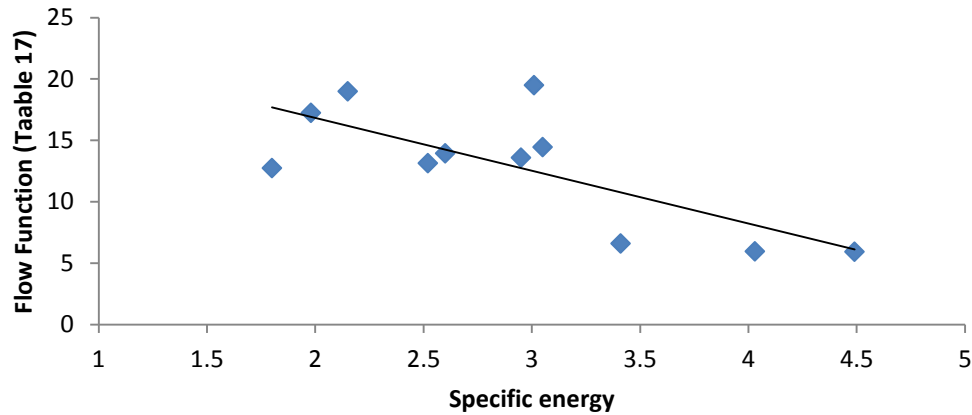


Figure 54: Relationship between specific energy and flow function (Table 17)

4.3.7.4 Flowability model

Flowability model data was calculated using equation (8) and presented in Table 17. From the table, the force required to accelerate the flow ($\rho_{\text{Particle}} d^3 g \epsilon$) increased significantly with an increase in the minimum particle size (D10) in the sample and vice versa. This accelerating force is also dependent on particle density and porosity ratio. However, according to the model equation ($\rho_{\text{Particle}} d^3 g \epsilon$), particle size had more effect on powder flowability than particle density and porosity. This is because the value of particle size was cubed.

Also from Table 17, the data generated from the flowability model was plotted against the flow function data (Table 17) for verification as shown in Figure 55. Interestingly, the generated points on the graph were broadly scattered, therefore this flowability model could not be used to predict flowability of titanium powder.

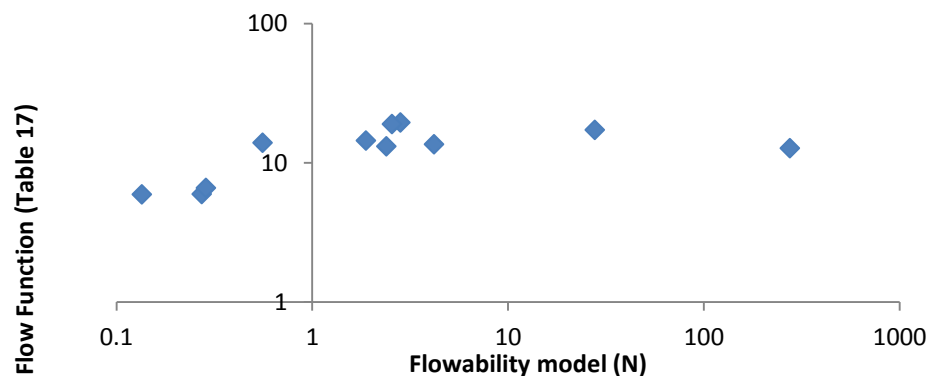


Figure 55: Relationship between flowability model and flow function (Table 17)

Particle density is a function of chemical composition that is the alloying element present in the sample and also a parameter used to determine porosity ratio (see equation (5)). Other parameters such as bulk density, porosity, cohesion and agglomeration are influenced by the particle size.

It was also noted that, for this particular spherical shape, powder soundness was found to be affected by the shape of the particle. Particle shape is a function of sphericity ratio (ϕ).

From the two preceding paragraphs, this study concluded that powder flowability for spherically shaped particles (mono shape) is mainly determined by particle size.

Chapter Five: Conclusions

The following conclusion were drawn from spherical shaped titanium grade 5 alloy powder,

- i. Manufacturers and suppliers are not willing to disclose information about their products.
- ii. Powder agglomeration is higher in particles with smaller mean particle size $\leq 31\mu\text{m}$ in comparison to larger particle sizes $\geq 36\mu\text{m}$.
- iii. None of the 12 samples studied met the chemical composition requirements set by ASTM standards. It was also noted that silicon was used as beta alloying element instead of vanadium that is stipulated by ASTM standards.
- iv. The XRF data acquired commercially were not usable and therefore there is need for future work to be done to establish reliable chemical analysis method of titanium alloy powders.
- v. Theoretically, particle density depends on the quantity and type of alloying elements present in the powder. Samples with higher amounts of beta alloying elements had higher theoretical densities than those containing higher amounts of alpha alloying elements. The empirical density determination in this study were not accurate enough to confirm this.
- vi. Bulk density depends on particle size and cohesion. Particles with smaller mean sizes $\leq 31\mu\text{m}$ had high cohesion values resulting to low bulk density, whilst particles with mean particle size $\geq 36\mu\text{m}$ had low cohesion hence high bulk density. Bulk density varies exponentially with flowability and inversely with porosity ratio.
- vii. Flow of spherically shaped particles occurs in the elastic region thus signifying that low normal stress is required to excite the flow. Smaller particles with mean size $\leq 29\mu\text{m}$ were classified under easy flowing. This is because they required higher normal stress to start flowing in comparison to particle size $\geq 31\mu\text{m}$ that needed less normal stress hence categorized under free flowing. The highest flowability was noted at particle size of $41\mu\text{m}$.
- viii. Particles with mean sizes $\leq 29\mu\text{m}$ were cohesive and required less basic flow energy in comparison to particle sizes $\geq 31\mu\text{m}$ which were less cohesive. This is because cohesive powders had higher transmission of forces between particles resulting in chain flow reaction.
- ix. Specific energy which determines the particles resistance to flow, categorized all powders tested under non cohesion ($SE < 5$). It was observed that specific energy varies inversely with powder flowability.

- x. All the samples apart from sample No.1, had mean particle size $\leq 71\mu\text{m}$ and are therefore, classified as non Newtonian fluids since their flow rate index < 1 indicate that they need more energy to move slowly.
- xi. All particles were spherically shaped and had stable rheology ranging from 0.9 to 1.1. Thus, they did not undergo particle transformation caused by agglomeration or change of moisture content.
- xii. Powder flowability is affected by particle size, shape, chemical composition, density and soundness. Particle density is a function of chemical composition that is the alloying elements and impurities present in the sample. Particle size also influences the bulk density, porosity, cohesion and agglomeration. Sphericity factor determines the shape of the particle which also affects its flowability. Hence, powder flowability is affected predominantly by particle size and shape.

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Appendix

Appendix I First questionnaire sent to titanium companies



Dear Sir,

Mr Patrick K Nziu is my postgraduate student at Vaal University of Technology in South Africa pursuing master of technology degree in mechanical engineering. We are carrying out a research on “characterization and flowability of titanium grade 5 alloy powders”. This research seeks to establish a credible global supplier reference catalogue for titanium powder. The research findings will be published and copies send to you.

We would like to source spherical shaped titanium grade 5 alloy powders (Ti6Al4V) from your firm. We kindly request for information as shown below.

QUESTIONNAIRE		
DATE		
Organization particulars	Name	
	Physical address	
	Telephone	
	Mobile number	
	Fax	
	Email address	
	Contact person	
	Designation	
Titanium alloy Ti6Al4V (Grade 5) powder characteristics		
Particle shape (e.g. angular/spheroidal)		
Particle sizes ranges (μM)		
Production process used		
Prices per Kilogram(USD)		
Density		
Flowability		

Soundness (%)	
Size Distrubution(sieve analysis)	
Size distribution	
Chemical Analysis (%Al,V,C,Fe<O,N,H,Ti)	
Young modulus of elasticity	
Hardness (HV)	

APPENDIX 2



Dear Sir,

Mr Patrick K Nziu is my postgraduate student at Vaal University of Technology in South Africa pursuing master of technology degree in mechanical engineering. We are carrying out a research on “**characterization and flowability of titanium grade 5 alloy powders**”. This research seeks to establish a credible global supplier reference catalogue for titanium powder. The research findings will be published in journals and copies send to you. Below is a titanium alloy powders questionnaire to be filled. Kindly assist.

TITANIUM POWDER QUESTIONNAIRE

Name of your company.....

Postal Address.....

Contact Person.....

Email address.....

1. What type of titanium powder do you produce?

- i. Commercially pure? Which Grade.....
- ii. Alloy? Which Grade.....

2. Which production method do you use to produce your powder?

- i. Gas atomized (GA)
- ii. Hydride Dehydride (HDH)
- iii. Plasma Electrode Process (PREP)
- iv. Plasma atomized (PA)
- v. Armstrong process (Sodium reduced)
- vi. Blended elemental process
- vii. Others
specify.....

3. What is the chemical composition of your powder?

- i. Commercial pure (Ti, Al, V, Fe, Si, O, C, N, H, etc)
a) Grade.....

- b) Grade.....
 - c) Grade.....
 - d) Grade.....
 - ii. Alloy (Ti, Al, V, Fe, Si, O, C, N, H, etc)
 - a) Grade.....
 - b) Grade.....
 - c) Grade.....
 - d) Grade.....
- 4. What is the particle shape of your powder produced?
 - i. Spheroidal
 - ii. Angular
 - iii. Spongy
 - iv. Flake or coral
 - v. Others
 - specify.....
- 5. Which powder particle size ranges or mesh sizes do you produce? e.g Sieve No.25, Mesh size 707 μM .
 - a)
 - b)
 - c)
 - d)
- 6. Which is your minimum quantity of powder available for sale e.g Packaging is done in;
 - i. 4 Kg
 - ii. 50kg
 - iii. Pound
 - iv. Others
 - specify.....
- 7. How much titanium powder do you produce per year (Production capacity in tonnes/year)
 - iii. Commercial pure
 - a) Grade.....
 - b) Grade.....
 - c) Grade.....
 - d) Grade.....
 - iv. Alloy
 - a) Grade.....
 - b) Grade.....
 - c) Grade.....

- d) Grade.....
8. What is the price range of your titanium powder per the minimum quantity sold? e.g US dollars or Euros per Pound or Kilogram.
- i. Commercial pure
- a) Grade.....
- b) Grade.....
- c) Grade.....
- d) Grade.....
- ii. Alloy
- a) Grade.....
- b) Grade.....
- c) Grade.....
- d) Grade.....
9. Which international testing standards do you use; e.g ASTM, BS, etc, specify
- i. During powder production
- a)
- b)
- c)
- ii. Final product testing
- a)
- b)
- c)
10. What shipping method do you prefer?
- a) Sea
- b) Air
- c) Any other (Specify).....
11. When an order is placed, how long would take to deliver to South Africa?
- a)
- b)
12. Attach any relevant additional information or indicate the website
-
-

RSVP

Prof LM Masu
Supervisor
leonard@vut.ac.za

Prof P. Mendonidis
Co-Supervisor
peter@vut.ac.za

Mr PK Nziu
Student
pnziu@yahoo.com

Appendix III List of titanium powder companies contacted

Titanium powder manufacturers and suppliers

S/No.	Company name	Email address
1	3SD Industries	pony@worldwide4seasons.com
2	A.D.MackayInc	admackay@sbcglobal.net
3	AccushapeInc	accushapeinc@msn.com
4	Active metals limited	sales@activemetals.co.uk
5	ADMA products	moxson@admaproducts.com
6	Advanced specialty metals inc	sales@asmpowders.com
7	Affinity international	info@affinityintl.com
8	A-Flame Division of Merlyn Corporation	merlyncorp@gmail.com
9	AG materials inc	sales@agmaterials.com
10	Alfar-Aesar	info@industrialanalytical.co.za nerine@industrialanalytical.co.za specialquotes@alfa.com
11	American elements	customerservice@americanelements.com
12	<u>ATI Wah Chang - Allegheny Technologies</u>	http://www.atimetals.com/products/Pages/powder-metals.aspx
13	Atlantic Equipment Engineers	info@micronmetals.com

14	Atlantic Equipment Engineers (AEE)	info@micronmetals.com
15	Aubert and duval(an eramet group company formerly Tecphy)	Gerard.raisson@aubertduval.fr
16	Australian metal powders	sweir@metalpowders.com.au
17	Bango Alloy Technologies Co. Ltd	maya@chtungsten.com
18	Baoji Orchid Titanium Industry Company Limited	sales@titanchina.cn
19	Barkiv Limited	akivilis@barkiv.com
20	Bayville Chemicals Supply Co.Inc	info@bayvillechemical.com
21	Bongen Titanium Company Limited	sales@china-titanium.com
22	CDM Titanium Industry	info@cdmti.us
23	Chaoyangjinda titanium co ltd	cyjdtitanium@163.com
24	Chinatungsten Online Corp	hanns@chinatungsten.com
25	Comps ServiciousGlo SLU	sales@alloy-valves.com
26	Continental steel & tube company	Don@continentalsteel.com
27	Crucible materials	sales@crucible.com
28	CSIRO titanium technologies	John.Barnes@csiro.au
29	Dr Fritsch F & Co Kg	info@dr-fritsch.de
30	Dynamet technology incorporated	info@dynamettechnology.com
31	Dynametal Technologies	mlclark@dynametal.com

32	EOS	India@eospower.com
33	Fox metal	sales@foxmet.com
34	Foxmet SA	sales@foxmet.com
35	GFE Gesellschaft fur ElektrometallurgiembH	contact@gfe.com
36	GFE Metalle und Materialien GmbH	contact@gfe.de
37	Global titanium Inc	jstout@globaltitanium.com
38	Good fellow	info@goodfellow.com info@goodfellowusa.com
39	Goodfellow Cambridge Ltd	info@goodfellow.com
40	Grandis titanium	titanium@grandis.com
41	Hangzhou King Titanium Company Ltd	sales@king-titanium.com
42	Huizhou Tian Yi Care Mat C Ltd	mayiuqiu@hotmail.com
43	IAP Research Inc	bhanu@iap.com
44	Indo-US MIM Tec(P) Ltd	sachin@mimindia.net
45	Inframat Corporation	info@inframat.com
46	Intermetal SAS	infosas@intermetal.it
47	International Titanium Powder (ITP)	itp@itponline.com
48	JRD Bipel limited	sales@jrdipel.com

49	K-mat GmbH	info@k-mat.de
50	LobaChemie Pvt. Limited	vic@lobachemie.com
51	M G Industries	Info_request@mgind.com
52	Ma Teck GmbH	info@mateck.de
53	Malvern Instruments	Alison.vines@malvern.co.uk
54	Materials & Electromechanical Research (MER) Corporation	mercorp@mercorp.com
55	Metallisation Limited	spray@metallisation.com
56	Micron metal inc(A subsidiary of RTI international metal inc)	dwinnegge@aol.com
57	Mint Chemical Group	jercey@tatichem.com
58	Monico alloys incorporated	info@monicoalloys.com jzenk@monicoalloys.com
59	NanoE	contact@nanoe.fr
60	Nanomaterials Inc	nanomaterials@nanomet.com
61	Nanoval	info@nanoval.de
62	Nanoval GmbH and Company	Info @nanoval.de
63	Noah Technologies Corporation	dmilner@noahtech.com
64	Noble Tech Global Sourcing	vpgs@nobletechglobal.com
65	Northwest Institute for Non ferrous	ybzhu@xanet.edu.cn

	metal research	
66	Nova Tech Inc	sales@novatechinc.com
67	Phelly materials	sales@phelly.com
68	Phoenix Scientific Industries Ltd	info@psiltd.co.uk
69	PSI Limited	info@psiltd.co.uk
70	PyrogenesisInc	plasma@pyrogenesis.com
71	Rajasthan Electricals and Powders	Kankaria_jaipur@hotmail.com
72	Raymor (Advanced powders & coatings)	apcinfo@raymor.com
73	Reade	quotations@reade.com
74	Reade Advanced materials	info@reade.com
75	Reade advanced materials	Info.panama@reade.com
76	Red Earth Steel & Alloy Pvt Ltd	redearthforge@in.com
77	RTI International Metal Inc	http://rtiintl.com/en-us/about/Pages/ContactUs.aspx
78	Sandvik materials technology	Gary.grade@sandvik.com
79	SE Jong materials	Contact page
80	Shaanxi Hillan Int'l Company Limited	peter@hititanium.com
81	ShanghaiHuaxia Industry Company Ltd	Helen@nonferrous-metal.com

82	Shanghai Jiangxi Metals Company Limited	shjxmetals@hotmail.com
83	Shenzhen TMN Metals Ltd	tmnroger@hotmail.com
84	Shieldalloy Metallurgical Corp	map@shieldalloy.com
85	Sigma-Aldrich	cheorders@sial.com
86	Starmet	sales@starmet.com
87	Strategic Metal Investments Ltd.	info@strategic-metal.com
88	Sumitomo Corporation light metal products	akihiko.shono@sumitocorp.co.jp
89	Synertech P/M Inc	Charlie@synertechpm.com
90	The metal powder company ltd	pradeep@mepco.co.in
91	The powder metallurgy association of south africa	info@pmasa.co.za
92	ThyssenKrupp Commerce Japan Limited	material@thyssen.co.jp
93	Tico titanium inc	intlsales@snappymaterials.com
94	Timet powder metals	Chris.Hinshaw@timet.com
95	Titanium Industries Inc	corp@titanium.com
96	TLS Technik (TLS) (SMEP,Germany)	ulric.ljungblad@arcam.com
97	Toho titanium Co Ltd	chigasaki_szn_tec@tohotec.co.jp

98	Trans-global Resources Inc	ardelleperi@sbcglobal.net
99	Virambe Scientific	bvcholkar@gmail.com
100	Wellmet international	info@wellmetusa.com
101	West penn testing group	jcdechellis@westpenntesting.com afletcher@westpenntesting.com
102	William Rowland ltd	email@william-rowland.co.uk
103	Wogen Resource Ltd	wogen@wogen.co.uk
104	Xi'an metals & minerals import & export company limited	info@tiwmo.com
105	Zirconium Research Corporation	sales@Zirconiumresearch.com

Appendix IV Titanium powder quotation 1

Appendix 4



Dear Sir,

Mr Patrick K Nziu is my postgraduate student at Vaal University of Technology in South Africa pursuing master of technology degree in mechanical engineering. We are carrying out a research on “characterization and flowability of titanium grade 5 alloy powders”. This research seeks to establish a credible global supplier reference catalogue for titanium powder. The research findings will be published and copies send to you.

We would like to source spherical shaped titanium grade 5 alloy powders (Ti6Al4V) from your firm. We kindly request for information as shown below.

QUESTIONNAIRE		
DATE	15-01-2013	
Organization particulars	Name	Raymor Industries
	Physical address	3765 la Vérendrye, Boisbriand, QC, Canada J7H 1R8
	Telephone	+1.450.434.1004
	Mobile number	
	Fax	+1.450.434.1200
	Email address	bbeauchamp@raymor.com
	Contact person	Bruno Beauchamp
	Designation	Sales Director
Titanium alloy Ti6Al4V (Grade 5) powder characteristics		
Particle shape (e.g. angular/spheroidal)	Spheroidal	
Particle sizes ranges (µm)	0-25, 15-45, 0-45, 45-106, 45-250, 0-250	
Production process used	Plasma Atomization	

*

Appendix 4

Prices per Kilogram(USD)	100-300 \$/ kg depending size distribution and quantity
Density	Apparent density : 54-60%, Tap density: 75-83% depending size distribution
Flowability	20-120 s depending size distribution (Per ASTM B964)
Soundness (%)	NA (depends of processing of the powder)
Size Distrubution(sieve analysis)	Conform ASTM B214 or better according customer needs
Size distribution	Conform ASTM B822 or better according customer needs
Chemical Analysis (%Al,V,C,Fe<O,N,H,Ti)	Conform to ASTM B348, ASTM F1580 and ASTM B863, O possible from 0.07-0.20%
Young modulus of elasticity	NA (depends of processing of the powder)
Hardness (HV)	NA (depends of processing of the powder)

Appendix V Titanium powder quotation 2

January 18, 2013

Quotation 5000074

Prepared for:

Patrick Nziu

Vaal University of Technology in South Africa

+2774 824 8094

pnziu@yahoo.com



221 Mountain View Road
Morgantown, PA 19543

Inside Sales Contact:

Stephanie Williams

636-887-9062 Phone

636-887-9098 Fax

stephanie.williams@timet.com

Technical Sales Contacts:

Chris Hinshaw

408-887-8881 Mobile

Chris.Hinshaw@timet.com

Bill MacDonald

610-968-1247 Phone

William.MacDonald@timet.com

Timet Powder Metals is pleased to quote your requirements as follows:

Item	Description	Quantity	UOM	Unit Price	Total Price
1	4 KG -230/+325 Ti 6AL 4V PREP ® Powder (Lot No. 250047-A)	1	Lot	\$ 1,200.00	\$ 1,200.00
	44 KG -120/+325 Ti CP 02 PREP ® Powder (Lot No. 251190-1) Powder Sold "as is" Lead-time: Can Ship 1-2 weeks ARO				
Total					\$ 1,200.00

NOTES:

* EXW: Morgantown, PA

*TIMET Powder Metals, LLC (TPM) standard terms and conditions of sale apply

* A purchase order is accepted only upon issuance by TPM of a written acknowledgement of acceptance on TPM's standard form of order acknowledgment. Confirmations of purchase order receipt are not acknowledgments of order acceptance.

*Quote valid 15 days

*Freight Terms: Collect or prepay and add (must state on P.O.)

*Prices subject to change depending on quantity purchased

*Materials are subject to prior sale

*Pricing valid for deliveries through 2013 only

*Quoted lead time subject to change at time of order acknowledgement

*Terms: Subject to credit approval

This quotation is neither an offer to sell nor an acceptance of an offer to buy the goods covered hereby; and all goods covered here by are subject to prior sale.

Sale of the goods covered by the quotation will be subject to the terms and conditions set forth on the reverse side of the seller's acknowledgement.

Appendix VI

Titanium powder quotation 3



MATERIAL-TECHNOLOGIE & KRISTALLE GMBH

MaTeck GmbH, Im Langenbroich 20, 52428 Jülich

Vaal University of Technology in South Africa
SOUTH AFRICA

Date 17.01.2013
Customer No. 12561
Page 1 / 1
Customer name Mr. Nziu

Your sign: your inquiry dated 12th of January 2013
Our offer No. 13011709 - 10154

Thank you for your inquiry. We are pleased to offer as follows:

Description	Amount	ME	Price	VAT	Total EUR
1 chemicals, Ti, powder, Ti/Al/V-90/6/4-Powder spherical 45-75 micron #902493 Item Code: CH.Ti.100002 Price: ex works without packing and transport. Delttime: about 4 - 5 weeks Payment: direct after receiving the goods Without engagment	40,00	100g	59,80	0,00	2.392,00

Please note that the material is hazardous (UN3089, II) therefore the freight charges will be higher than usual!

Subtotal	2.392,00
Net Amount	2.392,00
Total EUR	2.392,00

We hope this offer is of interest to you. If you have any questions please do not hesitate to contact us.

Kind Regards

MaTeck Material Technologie & Kristalle GmbH
Im Langenbroich 20
D-52428 Jülich
Germany

Tel.: +49-(0)-24 61 - 93 52-0
Fax: +49-(0)-24 61 - 93 52-11
e-mail: info@mateck.de
<http://www.mateck.de>

Amtsgericht Düren HRB 3801 - Gf.: Dr. Hugo Schlich
Ust.-Id Nr.: DE 811770042
Sparkasse Düren BLZ 395 501 10 Kto.-Nr. 65 433
Postbank Köln BLZ 370 100 50 Kto.-Nr. 528 888 506

Appendix VII Particle size raw data for all the samples

Cumulative	Sample 1		Supplier specifications 150-200 μM		
	1 test	2 test	3 test	Average	
10	151.2	156.1	149.7	152.33	
20	164	173.4	165	167.47	
30	173.3	181.1	175.7	176.70	
40	180.5	187.1	183.3	183.63	
50	186.8	192.8	190.3	189.97	
60	193	198.5	197.5	196.33	
70	199.6	205	205.4	203.33	
80	207.6	213	215.3	211.97	
90	220.5	225.4	229.3	225.07	
95	232	235	240	235.67	

Cumulative	sample 2		Supplier specification 10-60 μM		
	1 test	2 test	3 test	Average	
10	31.93	29.81	30.73	30.82	
20	35.48	34.82	34.57	34.96	
30	37.93	37.72	37.27	37.64	
40	40	39.94	39.44	39.79	
50	42.03	42.04	41.54	41.87	
60	44.19	44.22	43.75	44.05	
70	46.67	46.6	46.29	46.52	
80	49.66	49.38	49.4	49.48	
90	54.2	53.37	54.07	53.88	
95	58.79	57.14	58.79	58.24	

Cumulative	Sample 3		Supplier specification $\leq 25 \mu\text{M}$		
	1 test	2 test	3 test	Average	
10	9.85	9.41	9.48	9.58	
20	13	12.39	12.54	12.64	
30	16.89	15.8	16.21	16.30	
40	19.41	18.33	18.81	18.85	
50	21.34	20.35	20.83	20.84	
60	23.08	22.26	22.68	22.67	
70	24.84	24.2	24.55	24.53	
80	26.99	26.53	26.8	26.77	
90	30.24	30.1	30.27	30.20	
95	33.21	33.38	33.5	33.36	

		Sample 4		Supplier specifications 45-75 μ M	
Cum	1 test	2 test	3 test	Average	
10	44.73	43.58	43.34	43.88	
20	50.26	49.87	50.73	50.29	
30	54.19	53.99	54.82	54.33	
40	57.6	57.45	58.12	57.72	
50	61.03	60.86	61.36	61.08	
60	64.75	64.49	64.72	64.65	
70	69.11	68.64	68.47	68.74	
80	74.75	73.85	73.1	73.90	
90	85.12	83.38	81.36	83.29	
95	97.87	94.45	91.25	94.52	

		Sample 5		Supplier specification 20-60 μ M	
Cum	1 test	2 test	3 test	Average	
10	26.83	25.28	28.7	26.94	
20	31.81	31.08	33.23	32.04	
30	35.1	34.56	36.44	35.37	
40	37.93	37.52	39.15	38.20	
50	40.6	40.25	41.76	40.87	
60	43.46	43.14	44.56	43.72	
70	46.82	46.51	47.75	47.03	
80	51.18	50.89	51.81	51.29	
90	58.87	58.53	58.61	58.67	
95	67.91	67.46	65.55	66.97	

		Sample 6		suppliers specifications 45- 90 μ M	
Cum	1 test	2 test	3 test	Average	
10	54.01	56.27	59.69	56.66	
20	58.14	61.14	64.67	61.32	
30	61.51	64.72	68.43	64.89	
40	64.44	67.88	72	68.11	
50	67.26	71.05	75.7	71.34	
60	70.21	74.6	79.67	74.83	
70	73.6	78.99	84.19	78.93	
80	78.42	84.61	90.54	84.52	
90	86.33	94.87	102.9	94.70	
95	95.03	108.3	117.7	107.01	

		Sample 7		Supplier specifications 20 -45 μ M	
Cum	1 test	2 test	3 test	Average	
10	24.22	22.03	22.27	22.84	
20	28.29	26.79	27.73	27.60	
30	31.18	29.91	31.04	30.71	
40	33.72	32.47	33.56	33.25	
50	36.22	34.85	35.88	35.65	
60	38.85	37.3	38.15	38.10	
70	41.83	40	40.51	40.78	
80	45.65	43.3	43.32	44.09	
90	51.82	48.5	47.55	49.29	
95	58.06	53.47	51.27	54.27	

		Sample 8		Supplier specifications 10-45 μ M	
Cum	1 test	2 test	3 test	Average	
10	12.34	11.61	11.57	11.84	
20	16.47	15.28	15.41	15.72	
30	21.85	20.05	20.44	20.78	
40	26.19	24.55	24.9	25.21	
50	29.62	28.14	28.42	28.73	
60	32.67	31.36	31.59	31.87	
70	35.7	34.52	34.71	34.98	
80	39.25	38.17	38.35	38.59	
90	44.24	43.44	43.63	43.77	
95	48.96	48.34	48.63	48.64	

Sample 9				
Cum	1 test	2 test	3 test	Average
10	26.67	26.3	25.17	26.05
20	31.16	30.71	30.51	30.79
30	34.23	33.76	33.98	33.99
40	36.9	36.39	36.74	36.68
50	39.33	38.83	39.1	39.09
60	41.81	41.31	41.41	41.51
70	44.63	44.05	43.91	44.20
80	48.11	47.56	47.01	47.56
90	53.37	52.72	51.31	52.47

Sample 10				
Cum	1 test	2 test	3 test	Average
10	29.35	26.04	27.23	27.54
20	32.15	30.24	30.59	30.99
30	34.27	33	33.02	33.43
40	36.25	35.33	35.17	35.58
50	38.23	37.48	37.32	37.68
60	40.3	39.55	39.56	39.80
70	42.7	41.76	42.05	42.17
80	45.8	44.45	45.32	45.19
90	51.05	48.53	50.61	50.06
95	56.26	51.89	55.89	54.68

Sample 12				
Cum	1 test	2 test	3 test	Average
10	11.65	12.12	11.97	11.91
20	15.71	16.72	16.52	16.32
30	20.57	21.99	21.9	21.49
40	24.84	26.09	26.11	25.68
50	28.38	29.45	29.52	29.12
60	31.66	32.54	32.64	32.28
70	34.98	35.68	35.8	35.49
80	38.91	39.46	39.57	39.31
90	44.79	45.08	45.12	45.00
95	50.54	50.59	50.42	50.52

STANDARD DEVIATION FOR THE CUMULATIVE CURVES												
Sample No.	1	2	3	4	5	6	7	8	9	10	11	12
Standard deviation	25.8	8.53	7.5	15.4	12.2	15.6	9.8	11.9	9.7	8.5	12.4	12.4

Appendix VIII XRF results (major elements) acquired from an external provider (1)

Major Element Analysis														
Sample	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	Cr	S	Va	Total
Unit	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
6	0.14	53.19	<0.01	0.01	<0.01	0.11	0.01	0.04	0.04	0.02	0.12	<0.01	<0.01	53.68
5	0.82	55.82	5.75	0.09	0.08	0.14	<0.01	0.16	0.03	0.03	<0.01	<0.01	1.58	64.5
4	0.8	51.24	5.55	0.05	0.06	0.1	<0.01	0.22	0.03	0.03	<0.01	<0.01	1.4	59.48
2	0.82	55.21	5.79	0.08	0.08	0.12	<0.01	0.06	0.03	0.03	<0.01	<0.01	1.57	63.79
1	0.77	56.04	5.38	0.04	0.09	0.1	<0.01	0.34	0.02	0.03	<0.01	<0.01	1.57	64.38
8	0.78	53.63	5.46	0.08	0.08	0.01	<0.01	0.63	0.02	0.03	<0.01	<0.01	1.52	62.24
9	0.74	41.04	4.86	0.03	0.06	0.18	<0.01	0.44	0.03	0.04	<0.01	<0.01	1.17	48.59
3	0.73	53.2	5.02	0.08	0.08	0.08	<0.01	0.23	0.04	0.03	<0.01	<0.01	1.45	60.94
12	0.81	54.84	5.74	0.09	0.08	0.09	<0.01	0.02	0.03	0.03	<0.01	<0.01	1.6	63.33
10	0.79	54.2	5.65	0.05	0.07	0.07	<0.01	0.17	0.03	0.03	<0.01	<0.01	1.42	62.48
7	0.81	54.25	5.76	0.04	0.08	0.11	<0.01	0.14	0.03	0.03	<0.01	<0.01	1.54	62.79
11	0.85	58.97	6.14	0.03	0.08	0.15	<0.01	0.17	0.03	0.03	<0.01	<0.01	0	66.45
Method:														
XRF analyses were performed using a PANalytical Epsilon 3 XL ED-XRF spectrometer, equipped with a 50kV Ag-anode X-ray tube, 6 filters, a helium purge facility and a high resolution silicon drift detector, calibrated using a number of international and national certified reference														

Appendix IX XRF results (trace elements) acquired commercially from an external service provider (1)

2 XF02 – Trace Element Analysis

Code: XF02																																							
Sample Name	Ag	Ba	Bi	Br	Cd	Ce	Cl	Co	Cu	Ga	Ge	Hf	Hg	La	Lu	Mo	Nb	Ni	Pb	Rb	Sb	Se	Sn	Sr	Ta	Tb	Ti	U	V	W	Y	Zn	Zr						
Unit	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm					
Sample Results																																							
Patrick 8	<5.00	23.7	<1.00	1.29	<5.00	<5.00	36.6	<5.00	1.45	<5.00	68.8	<5.00	2.37	1.20	555	<1.00	9.74	2.58	<5.00	<5.00	<5.00	8.00	3.17	53.8	4.19	18.6	5.28	<5.00	4.08	34.9	6.21	4.53	14.9	<0.01	<5.00	1.35	38.1	10.6	15.3
Patrick 6	<5.00	14.6	<5.00	1.70	40.3	<5.00	1430	<5.00	<1.00	<5.00	75.0	<5.00	8.14	1.97	2938	<1.00	20.3	3.02	173	<5.00	74.0	2.91	3.94	42.2	<1.00	30.8	2.83	<5.00	5.49	34.6	11.7	7.73	14.1	1.88	<5.00	2.36	39.2	<5.00	<5.00
Patrick 4	<5.00	15.3	<5.00	1.81	37.0	<5.00	1340	<5.00	1.50	246	68.6	<5.00	<5.00	1.88	1943	<1.00	22.2	5.54	171	124	57.0	3.07	5.83	44.9	1.93	22.9	4.80	<5.00	10.7	22.3	11.6	7.28	10.9	1.40	<5.00	2.41	42.1	<5.00	6.84
Patrick 2	<5.00	17.2	<5.00	1.86	39.2	<5.00	1320	<5.00	1.78	30.4	75.5	<5.00	2.74	2.16	2574	<1.00	43.4	5.25	159	<5.00	38.1	3.90	4.04	44.8	2.07	29.3	6.28	<5.00	4.21	22.6	9.01	7.69	12.9	1.67	<5.00	2.24	39.0	<5.00	214
1	<5.00	23.3	<5.00	1.74	40.6	<5.00	1400	<5.00	1.53	<5.00	67.9	<5.00	<5.00	1.96	2734	<1.00	41.2	8.96	271	<5.00	67.2	3.86	4.12	44.2	<1.00	31.8	8.91	<5.00	4.99	22.8	11.9	7.86	13.9	1.67	<5.00	2.24	40.2	<5.00	<5.00
8	<5.00	<5.00	<5.00	1.80	38.7	<5.00	1416	<5.00	<5.00	3.56	76.8	<5.00	3.56	1.93	3473	<1.00	47.9	3.90	152	<5.00	71.7	3.64	<1.00	46.7	1.00	19.9	6.79	<5.00	5.78	23.6	11.4	7.94	11.9	1.62	<5.00	2.29	39.6	<5.00	246
Patrick 11U	<5.00	16.1	6.78	1.52	32.8	<5.00	807	<5.00	1.63	<5.00	52.6	<5.00	6.41	1.17	1556	<1.00	16.8	8.83	119	1.58	<5.00	<1.00	<5.00	48.6	1.47	18.0	<5.00	<5.00	6.02	19.2	<5.00	5.47	7.32	1.17	<5.00	2.76	38.8	<5.00	<5.00
Patrick 8	<5.00	19.1	<5.00	1.74	37.0	<5.00	1504	<5.00	1.68	6.62	68.3	<5.00	1.98	1.88	3474	<1.00	51.5	3.69	131	<5.00	51.1	2.77	<1.00	48.3	1.76	23.6	8.89	<5.00	6.33	21.2	11.0	7.40	11.2	1.46	<5.00	2.05	39.1	<5.00	<5.00
Patrick 12	<5.00	24.9	<5.00	1.78	41.6	<5.00	1388	<5.00	1.03	<5.00	72.7	<5.00	1.47	2.02	2775	<1.00	16.9	3.89	302	<5.00	66.2	3.39	<1.00	41.1	<1.00	33.6	5.81	<5.00	8.54	20.1	11.1	7.16	12.3	1.80	<5.00	2.57	39.1	<5.00	<5.00
10	<5.00	6.97	<5.00	1.70	36.6	<5.00	1546	<5.00	<1.00	21.4	70.7	<5.00	3.35	1.87	3449	<1.00	21.6	18.0	193	44.0	44.7	3.66	15.8	46.3	1.54	20.4	23.1	<5.00	7.22	21.0	11.1	8.22	11.4	1.42	<5.00	1.96	40.8	<5.00	7.28
7	<5.00	12.8	<5.00	1.76	40.0	<5.00	1476	<5.00	1.13	<5.00	74.8	<5.00	4.52	1.96	2392	<1.00	61.1	3.38	234	<5.00	55.5	3.92	2.86	47.0	1.70	27.4	13.4	<5.00	5.37	22.0	11.2	7.40	11.6	1.64	<5.00	2.00	37.9	<5.00	<5.00
Comments:																																							
* determined semi-quantitatively																																							
Method:																																							

Appendix X XRF results acquired from an external service provider (2)

	sample																	
	1	2	3	4	5	6	7	8	9	10	11	12	Certified	Result	Certified	Result	Certified	Result
SiO ₂	-			-	-								45.42	42.85	13.43	15.21	42.38	43.52
TiO ₂	95.2			92.4	95.9	99.8	92.1		93.5	93.7	93.5	91.7	1.54	1.96	1.9	1.84	2.39	2.30
Al ₂ O ₃	-			2.90	-	-	3.63		1.81	1.66	1.93	3.55	16.62	20.16	48.8	47.41	39.23	38.96
Fe ₂ O _{3 (t)}	-			0.04	0.14	-	0.03		0.04	0.07	0.03	0.08	9.73	13.84	7.14	7.07	1.188	1.24
MnO	-			-	-	-	-		-	-	-	-	0.180	0.18	0.11	-	0.0061	-
MgO	-			-	-	-	-		-	-	-	-	8.15	-	0.085	-	0.187	-
CaO	-			-	-	-	-		-	-	-	-	10.93	17.58	0.130	-	0.035	-
Na ₂ O	-			-	-	-	-		-	-	-	-	3.65	-	0.025	-	0.066	-
K ₂ O	-			-	-	-	-		-	-	-	-	0.70	0.51	0.068	-	0.618	0.310
P ₂ O ₅	-			-	-	0.08	-		-	-	0.07	0.08	0.259	-	0.118	0.24	0.05	-
Cr ₂ O ₃	-			-	-	-	-		-	-	-	-	0.074	0.04				
V ₂ O ₅	4.78			4.70	3.89	-	3.96		4.56	3.79	4.38	3.45						
Total	99.99			100.00	99.96	99.88	99.73		99.92	99.21	99.86	98.9	99.75	99.80	99.01	98.97	99.45	99.63
L.O.I.	-37.74	-37.08	-56.97	-34.98	-34.52	-34.73	-36.95	-47.92	-36.32	-40.20	-36.43	-42.83	2.50	2.68	27.2	27.2	13.3	13.30
H ₂ O ⁺	0.22	0.19	0.14	0.11	0.17	0.09	0.17	0.17	0.07	0.16	0.08	0.05		-	-	-	-	-

Appendix XI Particle density obtained using a pcynometer

	SAMPLE WEIGHT IN GRAMS											
Masses	1	2	3	4	5	6	7	8	9	10	11	12
M ₁	31.28	31.28	32.22	31.28	31.28	30.58	31.28	31.28	31.28	31.28	31.28	31.28
M ₂	36.7	37.80	38.38	38.09	38.01	37.40	37.87	38.01	38.53	38.37	38.12	38.15
M ₃	85.30	86.07	86.37	86.29	86.24	85.56	86.15	86.24	86.62	86.49	86.33	86.36
M ₄	81.23	81.16	81.74	81.16	81.16	80.43	81.16	81.16	81.16	81.16	81.16	81.16
$\rho = \frac{M_2 - M_1}{(M_4 - M_1) - (M_3 - M_2)} \times \rho_w$ in g/cm ³	4.09	4.05	4.03	4.05	4.08	4.04	4.12	4.08	4.05	4.03	4.10	4.11

Appendix XII Computation of theoretical density.

EL	PD	S1	p	S2	p	S3	p	S4	p	S5	p	S6	p	S7	p	S8	p	S9	p	S10	p	S11	p	S12	p	G5	p
AL	2.70	1.67	4.50	3.60	9.72	3.65	9.85	3.45	9.30	3.43	9.25	0.00	0.00	3.57	9.64	3.53	9.53	3.55	9.59	3.05	8.24	3.74	10.10	4.08	11.02	5.5	14.9
V	6.11	0.00	0.00	4.14	25.28	4.71	28.79	4.21	25.73	4.53	27.65	0.00	0.00	3.13	19.12	3.59	21.93	3.17	19.37	4.24	25.91	4.00	24.44	4.19	25.60	3.4	20.8
Fe	7.87	0.00	0.00	0.27	2.13	0.24	1.86	0.00	0.00	0.25	1.96	0.00	0.00	0.00	0.00	0.18	1.39	0.00	0.00	0.00	0.00	0.00	0.00	0.21	1.63	0.19	1.5
Si	2.33	1.46	3.40	1.31	3.05	1.21	2.83	1.32	3.07	1.18	2.74	1.61	3.75	1.25	2.91	1.18	2.75	1.42	3.31	1.40	3.26	1.27	2.96	1.20	2.80	0	0.0
O	1.43	0.35	0.50	0.28	0.40	0.34	0.49	0.36	0.51	0.26	0.37	0.17	0.24	0.23	0.33	0.25	0.36	0.23	0.33	0.20	0.29	0.17	0.24	0.10	0.14	0.12	0.2
C	2.26	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.0
N	1.25	0.15	0.19	0.21	0.26	0.18	0.23	0.32	0.40	0.23	0.29	0.12	0.15	0.06	0.08	0.10	0.12	0.16	0.20	0.27	0.34	0.11	0.14	0.13	0.16	0.01	0.0
H	0.09	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.02	0.00	0.01	0.00	0.02	0.00	0.03	0.00	0.02	0.00	0.01	0.00	0	0.0
Cl	3.21	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.09	0.01	0.03	0.00	0.00	0.00	0.00	0.02	0.05	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0	0.0
K	1.78	0.10	0.17	0.07	0.13	0.06	0.11	0.07	0.13	0.08	0.14	0.06	0.10	0.07	0.12	0.07	0.13	0.08	0.14	0.09	0.15	0.06	0.11	0.06	0.11	0	0.0
S	2.07	0.00	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0	0.0
Ti	4.43	96.28	426.50	90.11	399.20	89.58	396.84	90.23	399.71	90.02	398.80	98.03	434.29	91.67	406.12	91.08	403.47	91.36	404.74	90.72	401.91	90.61	401.42	90.02	398.78	90.8	402.1
	100.00		435.25	100.00	440.17	100.00	441.03	100.00	438.96	100.00	441.26	100.00	438.54	100.00	438.32	100.00	439.73	100.00	437.70	100.00	440.10	100.00	439.44	100.00	440.24	100	439.4
p			4.35		4.40		4.41		4.39		4.41		4.39		4.38		4.40		4.38		4.40		4.39		4.40		4.4

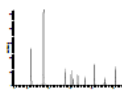
EL - Element, PD - Particle Density, p - Sample Theoretical Density

Appendix XIII XRD results acquired from an external service provider (2)



Council for Geoscience

Private Bag X112 Pretoria 0001 SOUTH AFRICA 280 Pretoria Street Silverton Pretoria
Reception: +27 (0) 12 841 1911 Internet: <http://www.geoscience.org.za>



X-Ray Diffraction Laboratory

Supply to: Prof P. Mendonidis / Patrick Nziu, Vaal University of Tech.

16 August 2013

Order No: Cash

JOB No: 130127

Project No: 5036

Mineralogical results

X-Ray Diffraction (XRD) analysis of 12 samples was performed and the results are explained below. Diffraction measurements were performed on a BRUKER D8ADVANCE instrument with 2.2kW Cu long fine focus tube (Cu K α , $\lambda=1.54060$) and 90 position sample changer. The system is equipped with LynxEye detector with 3.7° active area. Samples are scanned from 2 to 70° 2 θ at a speed of 0.02° 2 θ steps size/1 sec and generator settings of 40 kV and 40mA. Phase identification is based on BRUKER DIFFRAC^{Plus} - EVA evaluation program. Quantitative XRD analyses by Rietveld method are performed using DIFFRAC^{Plus} - TOPAS software with accuracy in the region of $\pm 1\%$.

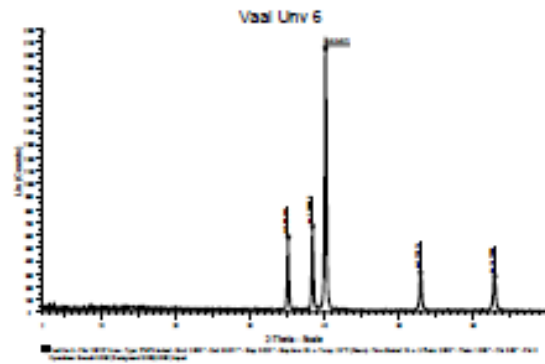
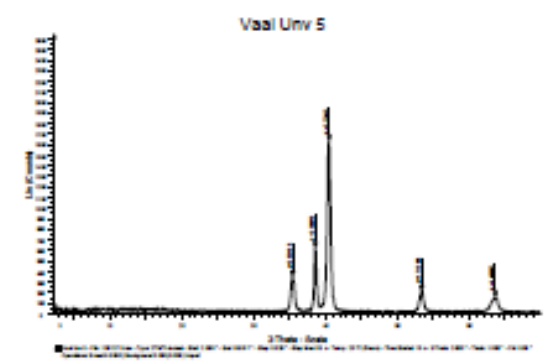
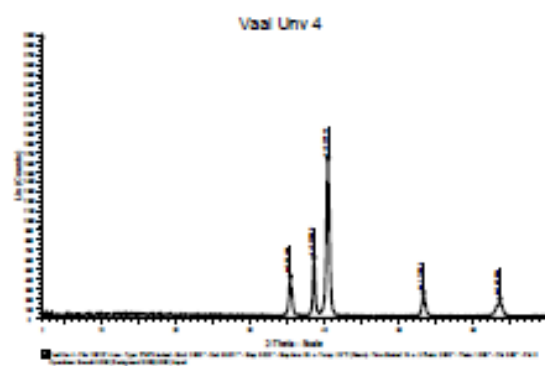
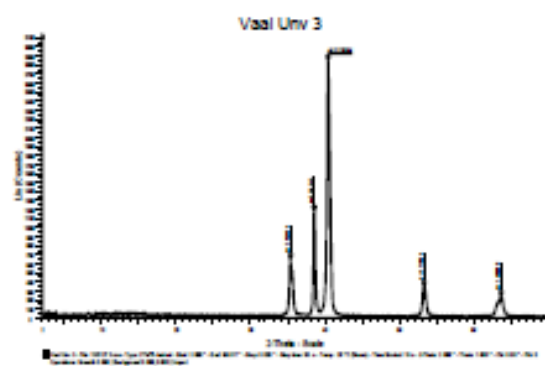
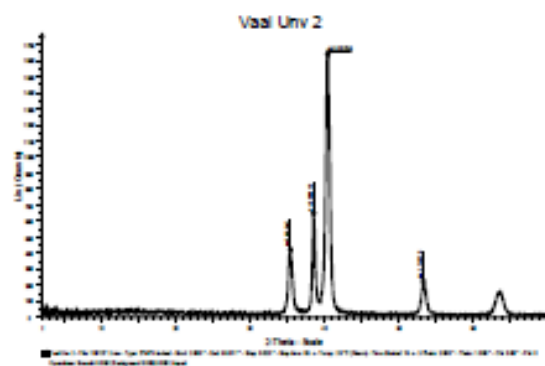
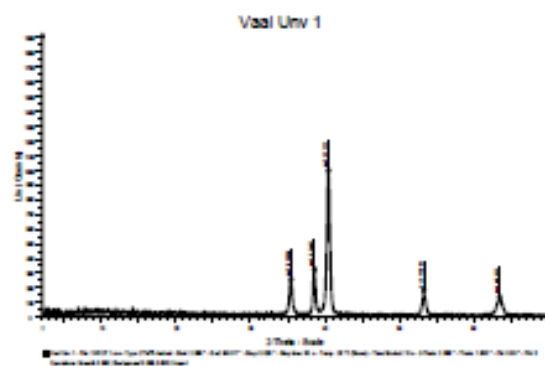
The results show five major reflections in the region 2-70° 2 θ closely overlapping with slight shift for most of the samples with the exception of Sample 6 where the shift towards lower angles is more pronounced. The following Ti containing phases could be identified that showed best match with the raw diffraction data: Ti-alpha_99778, Ti-alpha_43416, Ti-beta-76165 and Ti2VA1-185875. The relative proportions of these phases have been determined by Rietveld refinement and the results are included on p.2.

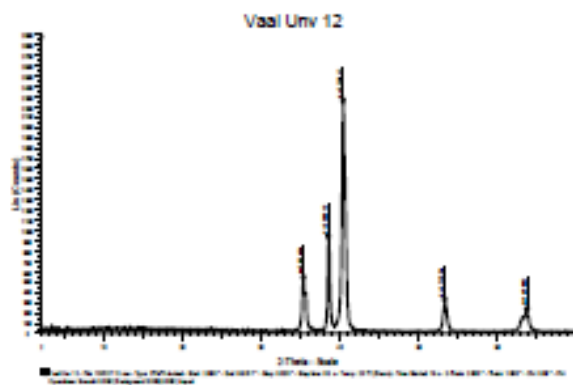
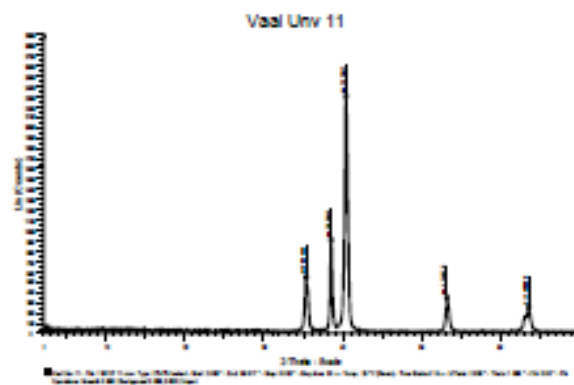
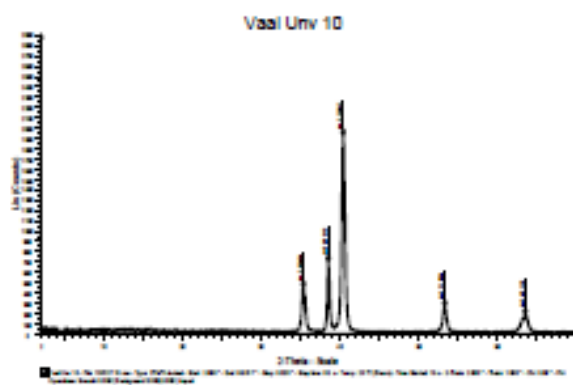
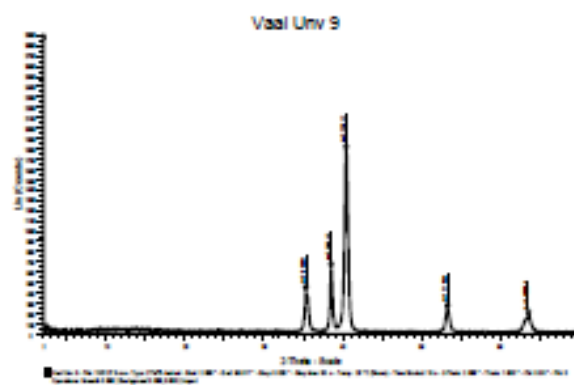
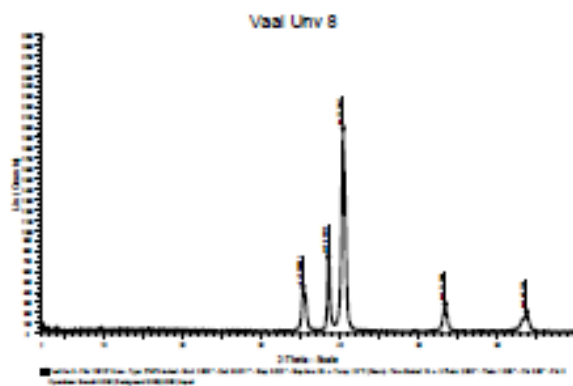
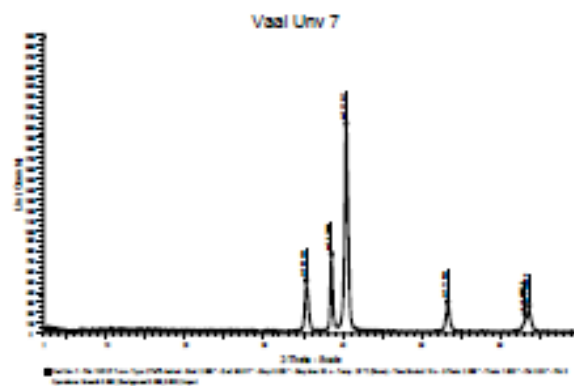
Note:	Approved by:
• results relate only to items tested	M. Atanasova
• (-) not detected	Tel: 012 841 1288
• samples will be discarded after 3 months in storage	Email: mtg@geoscience.org.za

Samples scanned from 2 to 70° 2 θ Cu K α radiation at a speed of 0.02° 2 θ steps size/1 sec, LYNXEYE detector and generator settings of 40 kV and 40mA. Phase concentrations were determined by Rietveld quantitative analysis with DIFFRAC^{Plus} - TOPAS software with accuracy in the region of $\pm 1\%$.

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JOB 130127 - Vaal University													
Quantitative Analysis - Rietveld (wt.%)													
	Sample	1	2	3	4	5	6	7	8	9	10	11	12
Phase	ICSD Reference												
Ti-alpha_99778	data_99778-ICSD	43.30(70)	45.80(49)	43.00(21)	42.60(44)	43.90(35)	76.10(99)	38.70(33)	42.80(34)	43.30(39)	46.90(37)	43.30(29)	43.00(21)
Ti-alpha_43416	data_43416-ICSD	56.00(70)	49.80(49)	53.20(21)	55.10(43)	52.00(34)	23.90(99)	58.60(33)	53.20(33)	54.00(38)	50.90(37)	54.50(29)	53.20(21)
Ti-beta-76165	data_76165-ICSD	0.55(35)	1.63(34)	1.20(23)	1.03(30)	0.94(30)	0.08(10)	0.82(30)	1.08(32)	0.96(30)	0.93(34)	0.72(23)	0.85(27)
Ti2VAI-185875	data_185875-ICSD	0.18(86)	2.77(68)	2.59(50)	1.29(69)	3.20(85)	n.d.	1.91(50)	2.86(66)	1.69(67)	1.32(64)	1.46(51)	3.01(59)





Appendix XIV

Dynamic flow energy for all titanium powder samples

