COPYRIGHT AND CITATION CONSIDERATIONS FOR THIS THESIS/ DISSERTATION

○ Attribution — You must give appropriate credit, provide a link to the license, and indicate if changes were made. You may do so in any reasonable manner, but not in any way that suggests the licensor endorses you or your use.

○ NonCommercial — You may not use the material for commercial purposes.

○ ShareAlike — If you remix, transform, or build upon the material, you must distribute your contributions under the same license as the original.

How to cite this thesis
NANOINDENTATION STUDIES ON TITANIUM NITRIDE NANOCERAMIC REINFORCED TITANIUM-ALUMINIUM-VANADIUM ALLOYS

MOSIMA EDITH MAJA (200927491)

Submitted in partial fulfilment of the requirements for the degree

Masters of Technology

In the
Department of Chemical Engineering Technology

FACULTY OF ENGINEERING AND THE BUILT ENVIRONMENT
DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF JOHANNESBURG

Supervisor: Prof. P.A. Olubambi
Co-Supervisor: Dr. B.A. Obadele

22 March 2018
DECLARATION

I hereby declare that the dissertation submitted for Masters of technology in Chemical Engineering Technology, at the University of Johannesburg, is my original work, apart from the valuable inputs of my supervisors. This dissertation is not submitted to any other institution of higher education. I further declare that all sources cited or quoted, are indicated and acknowledged by means of a comprehensive list of references.

Mosima Edith Maja
Date: 22/03/2018
This study is dedicated to my late Ramokgolo, Mr Frans Matsobane Maja.
ACKNOWLEDGEMENTS

Firstly, I want to thank the Almighty God, the giver of life, the privilege to study masters in chemical engineering and the ability to complete this phase.

I would like to acknowledge with gratitude the following people:

My supervisor Prof. P.A Olubambi, for his continuous encouragement, support, and contribution to make this research work a possibility, it has been an honor to work with a highly experienced and educated mentor. My co-supervisor Dr. B.A Obadele, for believing in me, supervision, assistance and guidance in my masters work. I pray that God continues to bless you. My mentor O.E Falodun, for his support, guidance and always availing himself to assist. You are highly appreciated.

I would like to thank the University of Johannesburg for granting me the opportunity to carry out my studies and National Research Foundation for the financial support. Anton Paar Tritec Switzerland and Mintek, for training on nanoindentation and use of optical microscope respectively. My research group members for their support and contribution of ideas: Dr Oladeji Oluremi Ige, Dr Ajibola, Samuel Ranti Oke, Mahlatse Rami Mphahlele and Marcia Ramokone Mafafo, I appreciate you all.

Family, Special thanks to my parents, Isaac Maja and Noko Maja for their prayers and support. My siblings: Ntologane, Tlou and Phuti for the wonderful roles they playing in my life, you are simply the best.

To my partner Tshegofatso Galane thanks for the undying encouragement and support.
ABSTRACT

Recent development in nanoindentation techniques has enabled investigations on the mechanical properties of materials under dynamic conditions as the technique offers unique capabilities for direct measurement of hardness, modulus of elasticity and contact stiffness among other properties. In this study, ultra nanoindentation (UNHT) technique was used to investigate the mechanical properties of spark plasma sintered Ti-6Al-4V reinforced with 1 to 4 vol% TiN nanoparticles. The morphology and microstructure of the as-sintered samples were examined using field emission scanning electron microscopy (FESEM) equipped with energy dispersive X-ray spectroscopy (EDS) and Electron Backscattered Diffraction (EBSD). The hardness, modulus of elasticity and creep properties were examined using Berkovich diamond indenter which is equipped with a three-sided pyramid. Microstructural results indicated that sintered samples containing 1 vol % of TiN nanoparticles was fully transformed from lamellar to bimodal and duplex structures. It was also observed that TiN nanoparticles segregated at the grain boundaries of the Ti-6Al-4V matrix. Results obtained from the EBSD revealed that α phase, hexagonal close packed (HCP) was stabilised at the expense of β phase Body centered cubic crystal structure (BCC). The nanoindentation results showed that both hardness and modulus of elasticity depend on the presence of volume fraction of TiN in Ti-6Al-4V matrix. There was significant increase in bulk hardness, modulus of elasticity while subsequently decreasing the contact depth and maximum depth of the indentation with increase in volume fraction of TiN. The mechanical properties (hardness and modulus of elasticity) of each phase (α and β) were derived from the grid indentation technique, where the β phase exhibited the highest hardness against α phase and the grain boundary, which may be due to uniform distribution of TiN along the grain boundary and β phases were found along the grain boundary. Optimum properties were obtained with the addition of 2 vol % of TiN which had highest creep resistance compared with that of Ti base alloy.
JOURNAL PAPERS


CONFERENCES

Mosima Edith Maja, Oluwasegun Eso Falodun, Babatunde Abiodun Obadele, Samuel Ranti Oke, Oladeji Oluremi Ige and Peter Apata Olubambi, 2017. Nanoindentation studies on TiN nanoceramic reinforced Ti-6Al-4V matrix composite. International Conference on Fracture (ICF 14), 18-23 June 2017, Rhodes, Greece

Nanoindentation studies on TiN nanoceramic reinforced Ti-6Al-4V matrix composite

Mosina Edith Maja, Olusasegun Eso Falodun*, Babatunde Abiodun Obadele, Samuel Ranti Oke, Peter Apata Olubambi

Cermics International 40 (2018) 4610–4625

ARTICLE INFO

Keywords: Ti-6Al-4V; spark plasma sintering; Nanoindentation; Hardness; Modulus of elasticity

ABSTRACT

The technological advancement in nanoindentation development has enabled investigations of material under dynamic conditions, which offer direct measurement of hardness, modulus of elasticity and contact stiffness among others. In this study, mechanical properties of sintered Ti-6Al-4V reinforced with 1–4%vol TiN was investigated by ultra-nanoindentation (UNIH) technique. It was revealed that the presence of reinforcing controls the grain morphology of the microstructure, thus an improvement in the mechanical properties of the sintered compact. Furthermore, from the nanoindentation results, it was evident that both hardness and modulus of elasticity depend on the presence of TiN in Ti-6Al-4V matrix. Sintered compact with 4vol% TiN had the highest indentation hardness value of 75.57GPa (696 H) and modulus of elasticity of 156 GPa as compared with that of Ti-6Al-4V alloy. Also sintered nanocomposites exhibited higher hardness with the decrease in maximum indentation depth and possibly lower wear resistance than the Ti-6Al-4V alloy. This shows the influence of hard phase, reinforcement on the mechanical properties of the sintered nanocomposites.

1. Introduction

Ti-6Al-4V alloy represents an important class of material which is widely used in the aerospace, biomedical and automotive industry due to its unique properties such as high-strength-to-weight ratio, low density and excellent corrosion resistance [1,2]. Ti-6Al-4V matrix is a two phase alloy comprising alpha and beta phases which are metastable and include the combination of both alpha and beta stabilizers, i.e., aluminium (alpha phase) and vanadium (beta phase) [3,4]. However, there are significant applications in many engineering industries are limited due to low wear resistance [5] and poor mechanical strength at high temperatures. Furthermore, research on improvement of the mechanical properties at elevated temperatures have led to modifications on Ti-6Al-4V (alpha & beta phase) alloy by reinforcing with hard particles such as zirconia [6] and perhaps titanium nitride (TiN).

TiN has been reported to possess good thermal and chemical compatibility and are more stable at high temperatures with sufficient diffusivity at the interface which creates effective bonding and results in high strength, stiffness and creep resistance [7].

Alloys alone are not capable of providing strength and stiffness to structure simultaneously, it is therefore expected that metal matrix composites (MMCs) could provide reinforcement to deliver strength and stiffness while the matrix material deliver ductility and strength to the composite structure [8–10]. Thus reinforcing with nanometer dimension could contribute to improvement in the mechanical properties due to the size range, fine grain, phase and strength of the nano-sized material [11,12].

Among various techniques available for fabricating TiN reinforced Ti-6Al-4V, spark plasma sintering (SPS) is identified as the most promising and near-net-shape technique for fabricating MMCs. Musti et al. [13] showed that SPS provides benefits over other traditional methods of sintering such as hot pressing (HP), hot isostatic pressing (HIP) and microwave sintering. These advantages include lower sintering temperature, shorter processing times, higher densified densities, minimal material loss during sintering and limited grain growth, as well as the reported improvement in comparative properties [14]. The mechanical properties of TiN reinforced Ti-6Al-4V alloy were investigated using the nanoindentation technique, a promising technique that measures the mechanical properties of engineering materials at small and nano scale. Nanoindentation can measure continuously force and displacement as an indentation is made, and the data obtained could be used to determine hardness, modulus of elasticity and other mechanical properties. The advantage of using nanoindentation compared to other conventional testing methods is its capability of in-situ measurement of material properties without disrupting their microstructure and considerably damaging them [15].

*Corresponding author.

E-mail addresses: apgy20@gmail.com, obadele1@gmail.com (O. E. Falodun)

Received 16 October 2017; Revised 16 November 2017; Accepted 5 December 2017
Available online 16 December 2017
0272-8842/ © 2017 Elsevier Ltd and Techna Group Srl. All rights reserved.
## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>II</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>IV</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>V</td>
</tr>
<tr>
<td>PUBLICATIONS / CONFERENCES</td>
<td>VI</td>
</tr>
<tr>
<td>CHAPTER ONE</td>
<td>1</td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1. Problem Statement</td>
<td>2</td>
</tr>
<tr>
<td>1.2. Aim and Objectives</td>
<td>3</td>
</tr>
<tr>
<td>1.3. Justification for the study</td>
<td>4</td>
</tr>
<tr>
<td>1.4. Gap of knowledge</td>
<td>4</td>
</tr>
<tr>
<td>1.5. Scope of the work</td>
<td>5</td>
</tr>
<tr>
<td>1.6. Structure of the dissertation</td>
<td>5</td>
</tr>
<tr>
<td>CHAPTER 2</td>
<td>6</td>
</tr>
<tr>
<td>2. LITERATURE REVIEW</td>
<td>6</td>
</tr>
<tr>
<td>2.1. Titanium alloys</td>
<td>6</td>
</tr>
<tr>
<td>2.1.1. Ti-6Al-4V</td>
<td>9</td>
</tr>
<tr>
<td>2.2. Metal Matrix composite</td>
<td>9</td>
</tr>
<tr>
<td>2.3. Reinforcement</td>
<td>10</td>
</tr>
<tr>
<td>2.4. Spark Plasma Sintering</td>
<td>11</td>
</tr>
<tr>
<td>2.5. Nanoindentation</td>
<td>13</td>
</tr>
<tr>
<td>2.5.1. How it works</td>
<td>13</td>
</tr>
<tr>
<td>2.5.2. Indenter tip geometry</td>
<td>15</td>
</tr>
<tr>
<td>2.5.3. Mechanical properties extracted from the nanoindentation test</td>
<td>18</td>
</tr>
<tr>
<td>2.5.4. Limitations of Nanoindentation</td>
<td>22</td>
</tr>
<tr>
<td>2.5.5. Study on nanoindentation of Titanium alloys</td>
<td>26</td>
</tr>
<tr>
<td>2.6 SUMMARY</td>
<td>27</td>
</tr>
<tr>
<td>CHAPTER 3</td>
<td>28</td>
</tr>
<tr>
<td>3. EXPERIMENTARY PROCEDURE</td>
<td>28</td>
</tr>
<tr>
<td>3.1. Materials</td>
<td>28</td>
</tr>
<tr>
<td>3.2. Sample Preparation</td>
<td>28</td>
</tr>
<tr>
<td>3.3. Microstructural Characterisation</td>
<td>29</td>
</tr>
<tr>
<td>3.3.1. Sample preparation for EBSD</td>
<td>29</td>
</tr>
<tr>
<td>3.4. Mechanical Characterisations</td>
<td>31</td>
</tr>
<tr>
<td>3.4.1. Conventional Micro-hardness testing</td>
<td>31</td>
</tr>
<tr>
<td>3.4.2. Nanoindentation</td>
<td>32</td>
</tr>
<tr>
<td>3.4.3. Nanoindentation Mapping</td>
<td>33</td>
</tr>
<tr>
<td>3.4.4. Nanoindentation Creep test</td>
<td>34</td>
</tr>
<tr>
<td>CHAPTER 4</td>
<td>36</td>
</tr>
<tr>
<td>4. RESULTS AND DISCUSSION</td>
<td>36</td>
</tr>
<tr>
<td>4.1. Microstructural Analysis</td>
<td>36</td>
</tr>
<tr>
<td>4.1.1. Optical Microstructure</td>
<td>36</td>
</tr>
<tr>
<td>4.1.2. Scanning Electron Microscope (EDS)</td>
<td>38</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2.1. Crystal structures of titanium as (a) hcp α phase and (b) bcc β (Ducato et al, 2013; Lutjering, 2008). ..........................................................7

Figure 2.2. Optical micrograph of Ti-6Al-4V a) Bimodal, b) Lamellar (Nalla et al., 2002) and c) Equiaxed microstructure (Leyens and Peters 2003). ..............................................8

Figure 2.3. Schematic illustration of the spark plasma sintering process (courtesy of substech) .............................................................12

Figure 2.4. Typical load displacement curve (Barbakadze et al., 2006) ..................................................14

Figure 2.5. Basic indenter tips (courtesy of surface-tec) .................................................................16

Figure 2.6. Indentation creep graph (courtesy of Anton Paar) ..........................................................22

Figure 2.7: Photographs showing sink in and pile up (courtesy of Anton Paar Tritec) ..................24

Figure 3.1: Field Emission Scanning Electron Microscope (FESEM, JoelTM, model JSM-7600F) ..........................................................29

Figure 3.2: Field Emission Scanning Electron Microscope equipped with Energy Dispersive X-ray Spectroscope (EDS) and Emission Backscatter Scanning Diffraction (EBSD) ....31

Figure 3.3: Micro-hardness tester (Innovatest Falcon 500) ...............................................................32

Figure 3.4: Ultra-Nanoindentation (UNHT) system .................................................................33

Figure 3.5: Typical load-displacement curve ..................................................................................34

Figure 4.1. Optical micrograph of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN. .........................................................37

Figure 4.2. SEM and point EDS of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN .................................................................................40

Figure 4.3. SEM Micrograph of Ti–6Al–4V + 1vol% TiN (1µm) ..................................................40

Figure 4.4. Micrograph of Ti–6Al–4V + 2vol% TiN (2µm) ...........................................................41

Figure 4.5 EBSD phase maps for of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN .........................................................................42

Figure 4.6. Grain size distribution of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN .........................................................................45

Figure 4.7: Average grain size as a function of vol% TiN ..............................................................45

Figure 4.8: Load displacement curve of Ti–6Al–4V with reinforced 1–4 vol% TiN ..........46

Figure 4.9: Depth as a function of Time for Ti–6Al–4V with reinforced 1–4 vol% TiN. ......47

Figure 4.10: Effect of vol. % TiN volume on: (a). Hardness, (b). Modulus of elasticity, (c). Contact depth and (d). Maximum depth. .................................................................48

Figure 4.11: Hardness and elastic modulus (H/Er) and H^3/Er^2 ratios of Ti–6Al–4V with volume fraction of TiN. .................................................................49

Figure 4.12: Micro-Hardness measurements of Ti-6Al-4V without and with TiN .................51
Figure 4.13: Effect of TiN on hardness ................................................................. 53

Figure 4.14: Hardness distribution of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN ........................................................................................................................ 55

Figure 4.15: Effect of TiN on modulus of elasticity .................................................... 56

Figure 4.16: Modulus of elasticity distribution of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN ..................................................................................................... 58

Figure 4.17: Load displacement curve of Ti–6Al–4V with reinforced 1–4 vol% TiN at; a.5mN, b. 23mN & 80mN ........................................................................................................ 60

Figure 4.18: Creep depth and time curves for Ti–6Al–4V and Ti–6Al–4V with 1-4vol% TiN at; a.5mN, b. 23mN & 80mN ................................................................. 62

Figure 4.19: Logarithmic stress and strain rate graphs ............................................ 62
LIST OF TABLES

Table 2.1. Titanium alloy (Ti-6Al-4V) chemical composition .................................................. 9
Table 2.2. Indenter type and geometry (Fischer-Cripps, 2002) ............................................. 16
Table 4.1. Phases and crystal structures of Ti-6Al-4V ............................................................ 41
Table 4.2. Measured phases and unresolved phases of Ti-6Al-4V and Ti-6Al-4V reinforced (1-4vol %) TiN ................................................................................................................. 43
Table 4.3: Nanoindentation values of Ti-6Al-4V reinforced with 1-4 vol. % of TiN .......... 46
Table 4.4: Micro-Hardness vs. nano-indentation results ......................................................... 51
## LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BCC</td>
<td>Body Centred Cubic</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscatter Diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive spectroscopy</td>
</tr>
<tr>
<td>HCP</td>
<td>Hexagonal Close Packed</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrogen Fluoride</td>
</tr>
<tr>
<td>GPa</td>
<td>Giga Pascal</td>
</tr>
<tr>
<td>MMC</td>
<td>Metal Matrix Composite</td>
</tr>
<tr>
<td>mN</td>
<td>Mill-Newton</td>
</tr>
<tr>
<td>MPA</td>
<td>Mega Pascal</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark Plasma Sintering</td>
</tr>
<tr>
<td>TiN</td>
<td>Titanium Nitride</td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>Titanium, 6Aluminium, 4Vanadium</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate Tensile Strength</td>
</tr>
<tr>
<td>α</td>
<td>Alpha Phase</td>
</tr>
<tr>
<td>β</td>
<td>Beta Phase</td>
</tr>
</tbody>
</table>
CHAPTER ONE

1. INTRODUCTION

Ti-6Al-4V alloys represent an important class of material that is widely used in the aerospace and automotive industry, for the reason that it possesses unique thermo physical and mechanical properties which includes high-strength-to-weight ratio and excellent corrosion resistance (Kumar, 2012; Kondoh, 2012). Ti-6Al-4V matrix is a two-phase alloy consisting of alpha and beta alloy which are metastable and include combination of both alpha and beta stabilizer (Pederson, 2002). However, this alloy loses significant strength and stiffness at elevated temperatures which limits their applications in some extreme conditions (Zhang et al., 2008). These shortcomings restrict their full potential not only in structural applications but also in other industries.

The required improved mechanical properties at high temperatures have led to modifications on Ti-6Al-4V alloy by reinforcing with high strength and high stiffness titanium nitride (TiN) nanoceramic. Camargo et al. (2009) stated that TiN reinforcements are incorporated mainly into the matrix for their good thermal and chemical compatibility and are more stable at high temperatures with sufficient diffusion at the interface, which creates effective bonding, and results in high strength, stiffness and creep resistance. Ti-6Al-4V is not able to provide both strength and stiffness at elevated temperatures, so the reinforcement is expected to assist in providing strength and stiffness to the composite structure (Tjong, 2007; Munir et al., 2015; Agarwal et al., 2016). Thus reinforcing with nanometer dimension contributes to improvement in mechanical properties due to the size, strength, fine grain and phase of the nanosize material (Suryanaranya, 2011; Saheb et al., 2012). Ti-6Al-4V alloy reinforced with TiN can be designed for metallurgical stability at elevated temperature and wear resistant applications in the aerospace industry focusing mainly on rotating components such as the aero-engine fan blades and other automotive components such as disc brakes and engine. The desired properties of this lightweight material could include high strength, high stiffness, high specific modulus, thermal stability, low creep rates and low-cycle fatigue.

Among various techniques for fabricating TiN reinforced Ti-6Al-4V, Spark Plasma Sintering (SPS) is the most promising technique in fabricating MMCs. Munir et al. (2006) showed that SPS method has the added advantage of sintering at lower temperatures in shorter processing times, and improved properties compared to the traditional sintering processes. The mechanical properties of these TiN reinforced Ti-6Al-4V alloys were investigated using
nanoindentation technique, due to advances made in the past years to develop a technique, which continuously measures force, and displacement as an indentation is made, and the data was used to determine hardness, modulus of elasticity and other mechanical properties. The advantage of using nanoindentation over the conversional testing methods is its ability to measure the mechanical properties at a small scale without disturbing their microstructure and considerably damaging them (Sattler, 2010).

In the present study, Ti-6Al-4V reinforced with TiN was synthesized using spark plasma sintering technique and the mechanical properties of the metal matrix composite were investigated using the nanoindenter. The research was centered on microstructural evaluation and nanoindentation studies of Ti-6Al-4V reinforced with (1-4 vol. %TiN), focusing mainly on the grain size and shape, crystallographic orientation, micro-hardness, nanoindentation hardness, modulus of elasticity of each phase and the creep properties. All the MMCs results were compared to the results obtained for Ti-6Al-4V alloy.

1.1. Problem Statement

Ti-6Al-4V matrix is often used for structural application in the aerospace and automotive industry. Unfortunately, the applications in these industries are limited due to low wear resistance and decreased mechanical strength and stiffness at high temperatures (U.S. Congress, 1998). Blade and disk, which are inside the engine case, generates localised heating on the tips of the blades and this deteriorates the mechanical properties at elevated temperatures.

The above has resulted in the development of reinforced composites that are well known for weight reduction, increased temperature capability in specific performance improvements. Reinforcing Ti-6Al-4V with TiN nano particle using spark plasma sintering technique present significant challenges and is a research area of interest. The challenges involves appropriate blending of either the ceramic or the metal powders into the metal matrix and selecting the suitable process parameters such as; the heating rate, holding time and sintering temperature to development a fully dense metal matrix composite (Kainer, 2006; Oke et al., 2017). Sintered compacts that are not fully dense results in unwanted pores and cracks which could be detrimental to the mechanical properties. Thus, it is important to mix the powders well and produce homogenized sintered compacts.
The mechanical properties of this newly developed nanocomposite material are not yet explored and well understood and for those reasons, the material is not used to the best of its ability (fully optimised). To optimise this composite, the mechanical properties need to be investigated. Despite the increasing importance of using nanoindentation techniques, there are a few aspects of the technique that if not addressed correctly, can lead to erroneous results. Surface roughness is extremely important because mechanical properties of the tested sample are calculated on the assumption that the sample is clean, flat and smooth. Secondly, the Indenter geometry is also important in selecting the correct indenter tip for specific application to ensure that the indenter receives the least amount of damage possible. Lastly, thermal drift which results from expansion or contraction of samples responding to change in thermal gradients (Maxwell and Alvarez, 2001). These problems highlighted will be addressed by appropriate selection of the optimal powder mixing parameters and controlled indentation testing, which improved the microstructure and the mechanical properties of the metal matrix composite.

1.2. Aim and Objectives
The main aim of this study is to investigate the mechanical properties of TiN reinforced Ti-6Al-4V in order to optimise the performance and widen the application in aerospace and automotive industry. The research is centered on nanoindentation studies, which measures the hardness, modulus of elasticity, creep properties and grid indentation (mechanical properties of each phase) at ambient temperatures. The research aim is achieved through the following objectives:

- Evaluate the microstructure of Ti-6Al-4V and Ti-6Al-4V reinforced with TiN.
- Study the effect of grain size on the mechanical properties of Ti-6Al-4V reinforced TiN.
- Investigate the mechanical properties (hardness and modulus of elasticity) of each phase by mapping the surface of the composite.
- Compare micro-hardness and nanoindentation techniques.
- Investigate the creep behaviour of Ti-6Al-4V and Ti-6Al-4V reinforced with TiN at ambient temperature.
1.3. Justification for the study
Ti-6Al-4V is an important class of titanium alloys, which is often used for structural applications in the aerospace and automotive industry due to its high strength to weight ratio, low density and high corrosion resistance. In these applications, the alloy is exposed to high stresses, high vibrations and high temperatures, which results in failures. For these reasons, the applications in these industries are limited.

Numerous research studies have been reported on modification of Ti-6Al-4V alloys; by heat treatment and coatings (Morita, 2005; Krishna, 2008; Venkatesh et al., 2009; Wu et al., 2009; Becker et al., 2014; Xu et al., 2015; Yang et al., 2016; Xu et al., 2017). However, there is no work reported on reinforcing Ti-6Al-4V with TiN using spark plasma sintering process, which result in no published data on the mechanical behaviour and microstructural evolution of these MMCs. Studies on Ti-6Al-4V reinforced with varying additions of TiN nano composite and the relationship between microstructure and mechanical properties is not yet reported. This study will assist in generating data, understanding the behaviour of the titanium matrix composite, which would widen the application and ultimately longer life span.

1.4. Gap of knowledge
The following gaps have been recognised by the study:
- There is not much work reported on nanoindentation behaviour of titanium alloys reinforced with nanoceramic at ambient temperature however, the study is expected to bridge the gap to benefit the structural component industry.
- Metal matrix composites (MMC) are still in the developmental stage and there are no industry standards, which explain the difference in published paper data for MMC. Working on MMC will increase the chances of industry standards.
- Ti-6Al-4V reinforced TiN will improve the strength, but the basic mechanism of strengthening is not yet well understood.
- The current level of developing MMC is insufficient to bring about commercialization.
1.5. **Scope of the work**
This study on metal matrix composite was carried out at the University of Johannesburg and Tshwane University of Technology. Spark plasma sintering technique was used to synthesize Ti-6Al-4V powders together with different volume percentage of TiN. The sintered compacts were analysed in terms of phase, microstructure and mechanical properties. The mechanical properties that were studied extensively include; hardness, modulus of elasticity of each phase present and the creep properties.

1.6. **Structure of the dissertation**
**Chapter One** introduces the study, research problems, aim and objectives, justification, gap of knowledge and the scope of research. **Chapter Two** covers literature review on Ti-6Al-4V matrix, reinforcement TiN, metal matrix composites, spark plasma sintering and microhardness and nanoindentation. **Chapter Three** describe methods used for the experiment. Results obtained are discussed in **Chapter Four**, from the density of the sintered compacts, microstructural evolution and nanoindentation results. **Chapter Five** contain the conclusions, contribution to knowledge and recommendations drawn in this study.
CHAPTER 2

2. LITERATURE REVIEW
The nanoindentation behaviour of Ti-6Al-4V reinforced with TiN using spark plasma sintering technique is a new and novel research area, which is currently investigated due to the increasing need to produce lightweight and high strength materials. Metal matrix composites (Ti6Al4V reinforced TiN) find use in structural applications such as aerospace and automotive industry. This chapter gives an overview of the past, present and possible future of nanoindentation study of Ti-6Al-4V alloy, metal matrix composites and reinforcement (modifications) of the Ti6Al4V matrix.

2.1. Titanium alloys
Titanium is one of the most abundant elements in the earth’s crust and it forms part of the fourth most abundant structural metal (Lehmhus et al., 2013). This titanium and its alloys are one of the most important nonferrous, lightweight, advanced materials. Their strength to weight ratio, wear resistance and outstanding non-corrosive characteristics are highly appreciated in structural materials for a wide range of applications in the aerospace, automotive, military, chemical and biomedical industry (Leyens and Peters, 2003; Welsch, 2007; Boyer, 2010). Approximately 80% of titanium alloys are used in the aerospace industry, while the remaining 20% is used for aerospace industries, such as pumps, valves, and heat exchanger (Myrick, 2005). Titanium is also used in human implants, due to its compatibility with the human body. Ti alloys are significantly important for the fact that they are energy saving and fuel consumption (low density), when they are applied in those industries.

Titanium alloys generally have a relatively low density of 4.506 g/cm³, comparing it to 7.9 g/cm³ density of steel. (Leyens and Peters, 2003) stated that the excellent corrosion resistant properties are caused by titanium’s high affinity for oxygen at both ambient and elevated temperatures, which forms a thin oxide layer of (TiO2) on the metal surface. Titanium like other metals, crystallise into various crystal structures and is it stable at specific temperature range (Peters, 2003). Pederson (2002) mentioned that the crystal structure of titanium is a close-packed hexagonal (α phase) at low temperature and pressure, then transforms to a body-centered cubic β phase at about 890 °C, which remains stable to the melting temperature (shown in Figure 2.1).
This alloy is usually tailored to achieve specific properties by changing the alloying and processing parameters, which changes the microstructure, and ultimately the mechanical properties. The change may be due to phase transformations in the alloy system (Vydehi, 2006).

![Phase Transformation Diagram](image)

Figure 2.1. Crystal structures of titanium as (a) hcp α phase and (b) bcc β (Ducato et al, 2013; Lutjering, 2008).

The microstructure of titanium alloys is usually defined by the arrangement, size and shape of α and β phases (Peters, 2003). Lamellar and equiaxed microstructure are the two defined extreme phase arrangements generated during cooling and recrystallization process respectively for titanium (Fan et al., 2016). These two extreme phase arrangements can have both fine and coarse arrangement. Nalla et al. (2003) stated that the lamellar microstructure (shown in Figure 2.2a) is associated with high strength due to the size of α phase, which result in low ductility. Equiaxed microstructure (shown in Figure 2.2b) has improved elastic modulus, high ductility and fatigue strength. The titanium alloy can also have a bimodal microstructure (shown in Figure 2.2c), which has the added advantage of both lamellar and equiaxed structure properties. Fan et al. (2016) mentioned that the combination of lamellar and equiaxed microstructure possess excellent mechanical properties.
These titanium alloys are typically classified into three major groups, namely α-alloys, β-alloys and α-β-alloys.

- **Alpha alloys**
The alpha alloys consist of pure titanium and alpha stabilizers (aluminium, oxygen and nitrogen) or neutral elements such as tin (Leyens and Peters, 2003). These alloys have low strength, good toughness and are non-heat treatable (Mazzolani, 2002).

- **Beta alloys**
The beta alloy comprises of beta stabilizers such as molybdenum, silicon and vanadium. They maintain the beta phase when quenched. These alloys have high strength, good creep resistance and high strength.

- **Alpha beta alloys**
The alpha-beta alloys are the most widely used alloys and include combination of both alpha and beta stabilizers such as Ti-6Al-4V. They possess are metastable, have medium to high strength and are heat-treatable.
2.1.1. Ti-6Al-4V
Ti-6Al-4V is a multiphase material, which has more than one material merged on a macroscopic scale to form desired material (Shivakumar and Doddamani, 2009). Typical chemical composition of Ti-6Al-4V is given in Table 2.1. This two-phase alloy consists of alpha and beta stabilizer where aluminium is an alpha stabilizer and vanadium is a beta stabilizer, which are metastable (Pederson, 2002). The β phase is harder while α is a softer phase which gives strength and workability respectively (Majorell et al., 2002). This mixture undergoes precipitation strengthening.

Ti-6Al-4V is extensively used in aerospace, medical, marine and chemical processing plant. It is used for aero engine fan blades because it has higher strength than titanium while it also has the same stiffness and thermal properties of titanium (Russel and Cohn, 2012). This alloy has density of 4420 kg/m³, Young's modulus of 110 GPa, and tensile strength of 1000 MPa, which are greater than those of titanium acting independently. However, this alloy is used in application up to 400°C and retains more than 50% of its yield strength at 300°C. Applications of this alloy are limited in some extreme conditions. The required improved mechanical properties at high temperatures have led to modifications on Ti-6Al-4V alloy by reinforcing with high strength and high stiffness titanium nitride TiN to form a metal matrix composite.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al</th>
<th>V</th>
<th>Fe</th>
<th>O₂</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. %</td>
<td>6</td>
<td>4</td>
<td>0.2</td>
<td>0.2</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2. Metal Matrix composite
The monolithic materials (matrix) have limitations in achieving high strength, stiffness and toughness simultaneously. These shortcomings are overcome by introducing composites materials. Metal matrix composite (MMCs) is a mixture of composite material, constituent metal with a different metal or material, such as a ceramic. The reinforcement is usually dispersed (embedded) into the matrix, which is monolithic to produce the MMCs (Kainer, 2006). In structural applications, the matrix is expected to be lighter but still be able to provide satisfactory support for the reinforcement (Senthilkumar and Senthil, 2015). Titanium matrix composites (TMCs) are novel composites in engineering materials for advanced design which extend the application of titanium alloys in automotive, biomedical
and aerospace. They are used due to their superior mechanical properties, such as high specific strength to weight ratio, high stiffness, good wear resistance and favourable high temperature durability (Tjong and Mai, 2008). The reinforcement that is embedded on the matrix alters wear resistance and thermal conductivity (Etemadi et al., 2018). The reinforcement can be either continuous, or discontinuous. Continuous reinforcement uses monofilament wires or fibers, where the fibers are embedded into the matrix, which results in an anisotropic structure. Discontinuous MMCs are isotropic and they are produced by powder processing techniques. Mercier et al. (2002) stated that the properties of MMCs are a function of: constituent, geometry of the dispersed phase & distribution of the phases.

2.3. Reinforcement
Discontinuous particulate TiN reinforcement are incorporated mainly into the matrix for their good thermal and chemical compatibility and are more stable at high temperatures with sufficient diffusion at the interface which creates effective bonding and results in high strength, stiffness and creep resistance (Camargo et al., 2009). TiN is an extremely hard ceramic with a density of 5.40 g/cm$^3$, Vickers hardness of 18-21 GPa, Modulus of elasticity of 251GPa (Russel and Cohn 2012). The nitrogen in TiN is an interstitial element that extends $\alpha$ phase which develops two phases $\alpha+\beta$ field; raise the transus temperature and ultimately increasing the strength.

It has recently received intense attention due to its superior properties such as improved mechanical properties, wear properties and good thermal stability (Zhen et al., 2017). TiN is used extensively as a coating to protect the surface of a substrate but in this study, it has been dispersed into titanium matrix as reinforcement. TiN has recent been reported as a reinforcement in metal matrix such as aluminium, steel and Ti-6Al-4V (as a coating) to improve the properties of the matrix. TiN reinforced Al$_2$O$_{24}$ showed improved yield and ultimate strength, which were 185% and 35% higher than those without TiN and still maintain 10% engineering strength (Li et al., 2017). Hussain et al. (2017) fabricated TiN particulates reinforced with SS316 metal matrix and they concluded that the wear and hardness increased with increasing weight % of TiN. Balla et al. (2011) reinforced Ti-6Al-4V with TiN coating to improve the wear properties for implants applications, the surface hardness of TI-6Al-4V increased with TiN reinforcement and the wear rate decreased to 1.04 x 10$^{-5}$ mm$^3$/Nm. Bailey et al. (2011) concluded that TiN is an excellent corrosion resistant, very hard and wear resistant material. The results indicated that mechanical properties of
metal matrix composites can be improved by additions TiN (Zhen et al., 2017). Munir (2014) stated the important parameters, which play a major role in reinforcements, include volume fraction, distribution, geometry and orientation of reinforcement. Shivakumar-Aradhya and Doddamani (2009); Zhen et al. (2017) explained that the distribution of reinforcement affects the homogeneity of the material.

1%-4 vol. % TiN of reinforcement was used to stabilize and strengthen Ti-6Al-4V. Reinforcement of more than 10 vol. % TiN is known to saturate the grain boundary, which ultimately makes the composite brittle. MMCs have disadvantage like metals. It is expensive to fabricate high-performance MMCs and there is a significant difference in published data for MMCs, because there are no industry standards, compared with metals. The combination of both the reinforcement and the matrix which forms metal matrix composites (MMCs) promises to offer high strength and stiffness at elevated temperature, and the ability to be tailored for a particular application. In this study, the powders were prepared by powder metallurgy process.

2.4. Spark Plasma Sintering
Among various techniques for fabricating TiN reinforced Ti-6Al-4V, Spark Plasma Sintering (SPS) is generally accepted as the most promising technique. This process involves heating and consolidation of powders below their melting point, for effective bonding by diffusion to form dense compact. Frage et al. (2007) indicated that this technique takes a few minutes to complete the entire process because of its high heating rates, reduced time due to small holding time, and has the ability to control the unwanted sintering reactions in reactive systems. The heating rates in conventional furnaces are usually 5 to 8°C/min - 10°C/min that would take 2 to 4 hours to reach temperature of 1200°C, whereas in SPS the heating rate is more than 300°C/min and takes only about 4 minutes to reach temperature of 1200°C.

The basic principle of SPS is shown in Figure 2.3. It consists of graphite punches (pressing device) which also serve as electrodes, a water-cooled reaction chamber, a gas atmosphere (vacuum/air/argon) control mechanism, a pulsed DC generator, and position temperature, and pressure regulating systems (Aalund, 2008; Saheb et al., 2012). SPS technique applies the uni-axial force and a direct electrical current to perform high-speed consolidation of the powder. Low voltages <10 V are used to produce high currents 1-10 kA, which are enabled by good electrical conductivity of the tooling materials (Guillon et al., 2014; Matizamhuka,
Heating rates of up to 1000°C/min have been reported, making it possible to sinter within very short durations, saving on energy costs (Suárez et al., 2010). The densification process is enhanced by loads of typically 50-250 kN under vacuum at atmospheric pressure.

Figure 2.3. Schematic illustration of the spark plasma sintering process (courtesy of substech). The SPS method is used to consolidate different materials, which were considered difficult to consolidate (difficult to densify) without melting the particles (Liu et al., 2007). Adebenjo et al. (2017) fabricated graphitized multi-walled carbon nanotube-reinforced Ti-6Al-4V using SPS, which resulted in enhanced relative density and hardness of the sintered composites. In-situ TiB-reinforced Ti-6Al-4V composite were processed by SPS and it was concluded that increased sintering temperature, leads to the formation of in-situ TiB whiskers with reduced porosity (Tong and Mai, 2008). Mehdi et al. (2017) studied the effects of sintering temperature on microstructure and mechanical properties of spark plasma sintered titanium and fully dense sample with highest mechanical performance was obtained at 1200 ºC.

Garbiec et al. (2016) investigated the microstructure, mechanical properties of spark plasma sintered Ti-6Al-4V and the results showed increased grain size and improved hardness, compressive strength and elastic modulus. Aalund 2008; Kessel et al. 2009; Rajeswari et al. 2010; Saheb et al. 2012, Illustrated that SPS is capable of achieving 100% theoretical density in most materials without the use of binders and higher purity materials through the
vaporization of impurities in the voids between powder particles. The review paper by Munir et al. (2006) showed that SPS method has the added advantage of sintering at lower temperatures in shorter processing times, and improved properties compared to the traditional sintering processes.

2.5. Nanoindentation
Nanoindentation test has been used to characterise mechanical properties of materials from 1970 and it has since received attention from scientists and engineers. Oliver and Pharr 1992; Hay et al., 1999; Li and Bushan 2002; Oliver and Pharr 2004; Fischer-Cripps 2010; Diez-Pascual et al. 2015, have improved nanoindentation test by developing advanced testing instruments, techniques and analysis. The new developments have since enabled nanoindentation test to be a well-established experimental means to measure the mechanical properties of different materials, coatings, biomaterials and thin films (Biswas et al., 2014).

Nanoindentation is defined as a universal technique, used to record nanoscale amounts of material, thin films, single grains and individual phases of composites while maintaining the precision and high accuracy (Trenkle et al., 2010). This technique has the added advantage of measuring the mechanical properties of different layers of coatings on the substrate and how each coating influences the substrate and how the substrate influences the coating. Fischer-Cripps (2010) stated that the nanoindentation test measures the elastic modulus, hardness, fracture toughness, creep and dynamic properties. Schuh (2006) stated that dislocation, shear instability initiation, and phase transformations can be detected from load-displacement data during nanoindentation. Nanoindentation instrument provides a certified approach to investigate mechanical properties of a solid material, required to design structural components in both the micro- and nanoscale devices. The nanoindentation technique is considered as a nondestructive test because it leaves small imprint.

2.5.1. How it works
A set load is applied to an indenter, which comes in contact with a sample. The depth of penetration is measured as the load is applied. The contact area is then determined from the impression made (depth) and the indenter angle at the maximum load (Hainsworth and Chandler, 1996). Oliver and Pharr (2004) stated that advances made to measure force and displacement as an indentation is made have increased the use of indentation. Material properties are extracted from the curve that is divided into two categories; the loading and
unloading curve (load-displacement curve) shown in Figure 2.4. The unloading curve describes the elastic region of the indentation while the loading curve describes the plastic region of the indentation. Both the loading and unloading response in the curve, describes different parameter by using simulations to match experimental data with the simulations (Heinrich, et al., 2009). The curve permits the opportunity to measure four important quantities; the maximum load, $F_{\text{max}}$, the maximum displacement, $h_{\text{max}}$, the elastic unloading stiffness and the final depth, $h_{\text{f}}$, $S = dP/dh$, defined as the slope of the upper portion of the unloading curve which is also called the contact stiffness (Oliver and Pharr, 2004). It is important to accurately measure the four quantities, as they affect the hardness and modulus of elasticity measurements.

![Typical load displacement curve](image)

Figure 2.4. Typical load displacement curve (Barbakadze et al., 2006)

This test relies on high-resolution instrument that carefully measures the loads and displacements of an indenter as it is pressed into and removed from a sample (Xu and Xiaodong, 2005). Nanoindentation test also rely on a method introduced by Oliver and Pharr (1992). The method uses the analytical solution of a punch in an infinite elastic half space, while the analytical solution is derived by Sneddon (1965). This is described by the relationship between force, displacement and the contact area of the punch for a linear elastic material (Heinrich et al., 2009).
Nanoindentation test can also help determine the dynamics effects such as pop in and pop-out phenomenon. In metals, if you apply load, dislocations generate and they are arrested at the grain boundary and there is a sudden burst of dislocation during loading which is called pop-in phenomenon. When the load is realized during unloading, there might be some stress-associated relaxation in the middle of called pop out. There are no reports on nanoindentation studies of Ti-6Al-4V reinforced with particulate material, however there are considerable reports on nanoindentation studies of different titanium alloys and on other metal matrix composite. Isaza Merino (2017) investigated the mechanical properties of metal matrix composites reinforced with carbon nanotubes by a different technique (tensile and nanoindentation). From the work, it was concluded that the yield and ultimate strengths, elastic modulus and hardness were increased with respect to the unreinforced material.

Aniruddha et al. (2013) examined mechanical properties of MWCNT/aluminum alloy 6061 nanocomposite using a nanoindenter technique and it was concluded that addition of 1 wt. % and 2 wt. % copper coated MWCNTs increase hardness and modulus of elasticity respectively. The experimental values and theoretical models were used to measure and compare micro-hardness and nano-hardness. Fale et al. (2014) studied the ex situ AlN/Al metal matrix nanocomposite using nanoindenter and the load-displacement curve showed that oxide phases and AlN particle have an effect on the penetration depth. Mallikarjuna et al. (2017) reported nanoindentation and wear behavior of copper-based hybrid composites reinforced with SiC and MWCNTs fabricated using by SPS process. It was concluded that the nanohardness and modulus of elasticity for copper-based reinforced MWCNTs, increased with an increase in MWCNTs content, suggesting better effective bonding.

2.5.2. Indenter tip geometry
There are various types of nanoindenter with different geometries for the indenter shape. The different geometries shown in Table 2.2 include; three sided pyramids, four sided pyramids, wedges, cones, cylinders or spheres with accepted tolerance defined by ISO 14577-22. The tip of the indenter can be made sharp, rounded to a cylindrical or spherical shape (Sushko et al., 2013; Dey and Mukhopadhyay, 2014) presented in Figure 2.5. The sapphire and diamond are the two widely used materials for most nanoindenter tips. Quartz, steel, tungsten carbide and almost any other hard metal or ceramic can be used as indenter tip material (Briscoe and Sebastian 1996; Dey and Mukhopadhyay, 2014). Single crystal diamond is the most commonly used material for nano-indentation because of its, excellent hardness properties.
extracted from the covalent bond and thermal conductivity, which are usually not found in other known material. It also does not have impurities or inclusions. The Sapphire is used because it can be shaped to sharp points and edges. 

(www.microstartech.com/index/nanoindenters.pdf)

Table 2.2. Indenter type and geometry (Fischer-Cripps, 2002)

<table>
<thead>
<tr>
<th>Indenter type</th>
<th>Projected area</th>
<th>Semi angle (θ)</th>
<th>Effective cone angle (α)</th>
<th>Intercept factor</th>
<th>Geometry correction factor (β)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>$A = \pi 2R h_p$</td>
<td>N/A</td>
<td>N/A</td>
<td>0.75</td>
<td>1</td>
</tr>
<tr>
<td>Berkovich</td>
<td>$A = 3 h_p^2 \tan^2 \theta$</td>
<td>65.3°</td>
<td>70.2996°</td>
<td>0.75</td>
<td>1.034</td>
</tr>
<tr>
<td>Vickers</td>
<td>$A = 4 h_p^2 \tan^2 \theta$</td>
<td>68°</td>
<td>70.32°</td>
<td>0.75</td>
<td>1.012</td>
</tr>
<tr>
<td>Knoop</td>
<td>$A = 2 h_p^2 \tan \theta_1 \tan \theta_2$</td>
<td>$\theta_1=86.25°$</td>
<td>$\theta_2=65°$</td>
<td>0.75</td>
<td>1.012</td>
</tr>
<tr>
<td>Cube Corner</td>
<td>$A = 3 h_p^2 \tan^2 \theta$</td>
<td>35.26°</td>
<td>42.28°</td>
<td>0.75</td>
<td>1.034</td>
</tr>
<tr>
<td>Cone</td>
<td>$A = \pi h_p^2 \tan^2 \alpha$</td>
<td>$\alpha$</td>
<td>$\alpha$</td>
<td>0.72</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 2.5. Basic indenter tips (courtesy of surface-tec)

**Sphere indenter**

The sphere indenter determines wide range of mechanical properties such as material response in the elastic regime for bulk and thin films, elastic limit and indentation stress-strain curve using appropriate techniques (Bushby and Niggel, 2001). However, a truly spherical tipped cone is difficult to fabricate at nanometer scale. In practice, a rounded cone
may have geometry similar to sphere tip. The tip is spherical at the apex but has a transition section, which is neither part of the sphere nor the cone. It was discovered that deeper indentations require, precise definition of the area function.

**Berkovich indenter**

E.S. Berkovich invented the Berkovich indenter in 1950. This indenter is a three-sided indenter, with sharp and well-defined tip geometry. The angle between the centreline and the three faces is 65.3°, angle of 142.3°, which is responsible for reduced friction (Kothari and Luckham, 2016). Hardiman et al. (2017) stated that the Berkovich indenter and Vickers indenter tip have same area-to-depth ratio. It is easier to manufacture and it is not easily damaged as compared to the Vickers indenter. It is preferred for measuring modulus and hardness on hard materials. (www.toyo.co.jp/files/user/img/product/microscopy/pdf/5990-4907EN.pdf).

**Vickers indenter**

The Vickers tip is a four-sided pyramid, with an offset of 0.5 µm, centreline-to-face angle of 68°. Hardiman et al. (2017); Adonias et al. (2004), mentioned that the slight offset is the main reason why the Vickers tip is not used in indentation machines.

**Knoop indenter**

The Knoop indenter is a rhombic-based pyramidal shape which was first developed in the 1930. The Knoop indenter is used for studying very hard materials because of its elongated shape. This tip makes it easy for the diagonal of the residual impression to be measured (Fisher-Cripps, 2004).

**Cube corner indenter**

Cube corner is a three-sided pyramidal tip with perpendicular faces similar to the corner of a cube. It has centreline-to-face angle of 35.3, with a sharp tip which produces higher stresses and strains around the contact area. It is used to measure the fracture toughness of material (Chudoba et al., 2005). It is very fragile and can be easily broken.
Cone indenter

The cone indenter tip is a sharp, self-similar geometry, with a cylindrical symmetry which makes it attractive for modeling purposes. However, there is very little test conducted with cones because of the difficulties of producing a sharp conical diamond shape tip. (www.toyo.co.jp/files/user/img/product/microscopy/pdf/5990-4907EN.pdf)

Indentation tip characterization is very important for quantitative analysis in nanoindentation and it makes it easy to select the correct indenter tip for a specific material property. The four-sided pyramidal Vickers tip, is the most commonly used indenter geometry for the conventional hardness testing at the macro and micro-scales. However, for nanoscale measurements, the three-sided pyramid shape of the Berkovich indenter is the most preferred. Bushby and Niggel (2001) stated that the successful application of indentation technique requires accurate calibration of the indenter tip geometry.

2.5.3. Mechanical properties extracted from the nanoindentation test

The increasing need of designing reliable structures have led to the use of nanoindentation technique which measures the mechanical properties of material at a nanoscale. It is known that most material properties are size-dependent and these properties are not yet well characterized. Indentation measurements are already standardised by the ISO 14577 (Fischer-Cripps, 2002).

Hardness

Hardness testing started as early as in the 1890s by Huygens in his Traite` de la Lumie`re (Albury, 1971), who described the difference in scratching of Iceland spar by a knife (Huygens, 1690; Huygens, 1912; Walley, 2012). In 1730, Sir Isaac Newton has noticed the difficulties of polishing a ductile material than a brittle glass (Biswas et al., 2014). The ten stage hardness scale and instrumentation was introduced in 1822 by Mohr, but the first machine for measuring indentation hardness was in 1850. Hardness machines for measuring hardness under static and dynamic conditions were made available in 1990 (Walley, 2012; Calvert and Johnson, 1859) In the early 1900s, Brinell ball test was the first approved and standardised hardness tester, however the one problem with the hardness value increase with increase in the load (Walley, 2012).
As time progressed, new technologies and innovations were required which lead to the development of the Vickers hardness test by Smith and Sandland in 1924, which is more refined (uses pyramid shaped diamond) than the Brinell. Rockwell and Rockwell (1919) commercialised the conical diamond indentation test (Rockwell) which is required for small area of indentation. In 1939, Fredrick Knoop introduced the Knoop test, which uses elongated diamond pyramid. After significant improvements, depth sensing nanoindentation tester was developed.

Hardness measurement has been known for years, but the use of nanoindentation to measure hardness of a material has gained new popularity over the last decades. One of the most common uses of nanoindentation is for the measurement of hardness. Hardness is defined as resistance of a material to plastic deformation therefore, as hardness increases; the strength also increases (Bhandarie, 2007). Hardness is measured from the load–displacement curve obtained during nanoindentation test. Oyen (2006) and Walley (2012) observed that during nanoindentation test, the indentation impression is often too small to be measured optically, but there is an assumption that the residual area is the same as the contacted area at maximum load. The elastic and plastic deformation contributes to the total contact area at maximum load (Oliver and Pharr, 1992; Sakai, 1999).

The test follows the Oliver and Pharr (OP) method (Oliver and Pharr, 1992, 2004).

\[
H = \frac{P_{\text{max}}}{A_c(h_c)}
\]  

\[
h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}
\]

Where \( P_{\text{max}} \) is the peak indentation load, \( A_c \) is the projected contact area of impression and \( h_c \) denotes the contact depth, \( \varepsilon \) is different depending on the indenter and \( S \) is contact stiffness. The \( P_{\text{max}} \) is measured from the load-displacement curve, while the contact area is measured from contact depth.

**Modulus of Elasticity**

Modulus of elasticity also called Young’s modulus is one of the most common material properties measured by the nanoindenter. This material property is an important material constants related to the microstructure and mechanical performance of the material. This material property is defined as the measure of stiffness of a material, which ultimately defines the relationship between stress/strain in a material. Since 1992, Oliver and Pharr analysis method has been employed to determine the modulus of elasticity from the indentation load-
displacement curves focusing on the slope of the unload curve which is known for extracting the elastic modulus. The indentation modulus of elasticity of a material can be extracted without the image of the indentation (Li and Vlassak, 2009).

\[ E_r = \frac{\sqrt{\pi} S}{2\beta \sqrt{Ac}} \]  \hspace{1cm} (2.3)

Where \( E_r \) is the reduced modulus, \( S = \frac{dp}{dh} \) is the initial unloading contact stiffness, \( Ac \) is the projected area of contact and \( \beta \) is a dimensionless parameter that depends on the indenter geometry. The equation was derived from the Hertzian theory of contact mechanics (Fisher-Cripps, 2002).

The modulus, of the sample is determined from the following equations:

\[ \frac{1}{E_r} = \frac{(1-v^2)}{E} + \frac{(1-v_1^2)}{E_1} \]  \hspace{1cm} (2.4)

Where \( E_r \) is the reduced modulus, \( E \) is the indenter modulus, \( v \) is the sample Poisson’s ratio and \( v_1 \) is the indenter Poisson’s ratio.

\[ Ap = C_0 \cdot hc^2 + C_1 \cdot hc \]  \hspace{1cm} (2.5)

The Hertzian method requires the projected area at the maximum load (Shuman, 2007). To determine the projected contact area, contact depth needs to be determined (Li and Vlassak, 2009).

Where \( Ap \) is the projected area, \( hc \) is the contact depth and \( C_0 & C_1 \), are two term equations.

\[ E = \frac{(1-Vs^2)}{2\sqrt{C_0 hc^2 + C_1 hc}} \frac{am(h_{max}-hf)^{m-1}}{am(h_{max}-hf)^{m-1} \sqrt{\pi}} \]  \hspace{1cm} (2.6)
Creep

Nanoindentation creep behaviour of structural materials and thin films has recently received intense attention at ambient temperature (Wang et al., 2004; Chatterjee et al., 2013; Kaur and Kaur, 2014). Manas et al. (2017) mentioned that the creep phenomenon is the change in indentation depth when the maximum force is kept constant. Nanoindentation creep test provides important mechanical behavior of a material especially when the measurement data is limited to a small area. Accuracy of this test is highly dependent on precise control of applied force and sensitivity in measuring small changes in probe displacement. (https://www.hysitron.com/techniques-properties/mechanical-properties/creep)

Various methods have been proposed for the evaluation of creep parameters. However, there is no universal method and numerous papers have highlighted this point (Cheng et al., 2001; Goodall and Clyne, 2006). There is no universal method because of the lack of reliability of the results, which focus on secondary creep stage with the assumption of eliminating influence of primary creep. This assumption is easily made for the conventional method but for the nanoindentation method is impossible since the regions of the sample undergoes primary creep, which affects the indenter response (Takagi et al., 2008; Stone and Elmustafa, 2008). Most researchers are aware of the unreliability (difficulties) of extracting creep properties from indentation, but there have been reported success in extraction of creep properties from indentation data (Fujiwara and Otsuka, 2001; Liu et al., 2007). The correlation between creep parameters obtained by indentation and by conventional testing was discussed by Goodall and Clyne (2006).

In nanoindentation creep test, the creep stress exponent ($n$) is calculated from the steady stage at the maximum force and stress exponent are usually comparable with those obtained by conventional methods (Liu et al., 2007; Wang et al., 2010; Su et al., 2013). The maximum force is held between 1 min and 1 h, while the indentation depth is observed as a function of time (Poisl et al., 1995; Lucas and Oliver, 1999; Stone et al., 2010; Choi et al., 2012; Maier et al., 2013). The creep behavior is extracted from the apparent change in displacement shown in (Figure 2.6), but these results are affected negatively by thermal drift especially at elevated temperatures. Thermal drift was also found to affect the holding times, which resulted in shorter holding times to avoid thermal drift. Chudoba and Richter (2001) and Dean et al. (2013); suggested that the holding times should be extended for correct analysis of creep results.
Where $C_IT$ is the creep, $h_1$ is the initial indentation depth and $h_2$ is the final indentation depth.

Researchers have carried out studies on creep phenomenon at ambient-temperature of titanium and its alloys (Neeraj et al., 2001; Viswanathan et al., 2002). These tests have been conducted on titanium and its alloys because it has been observed that there is an increase in penetration depth even after the loads are constant. The studies have revealed that ambient-temperature creep mechanisms of Ti alloys were aligned with dislocations slip (Liu et al., 2007). It is also expected for texture, TiN reinforcement, precipitate particles and grain size to have an influence on the nanoindentation creep behaviour.

2.5.4. Limitations of Nanoindentation

Nanoindentation test is widely used to measure different mechanical properties of a material at small scale and does not require machining. The test measures the material properties from the load displacement curve and a basic formula is used to assume the material response, which is accurate for specific conditions (Mencik, 2012). For this reason, the behaviour of the material to be tested needs to be known prior to testing, to ensure precise measurement of the mechanical properties. Nanoindentation is known to work best on homogenous materials as compared to heterogeneous material. Despite the increasing need of indentation at small scale, there are many aspects of the technique such as; indenter geometry, thermal drift, pile-
up and surface roughness (surface preparation) that if not addressed correctly can lead to erroneous results (Maxwell and Alvarez, 2001).

**Indenter Geometry**

The accurate determination of mechanical properties by any indenter is highly depended on the information of its geometry. There are several indenter tips, which have different indenter geometry and are preferred for different tests. For example, the Berkovich indenter is the most used due to its sharp points that ensures precise control than the Vickers indenter, but major problems lies with sphere indenters, where the shape deviates from the sphere shape and the radius is not the constant (Králík and Nemecek, 2014).

One of the main challenges in nanoindentation test is the use of correct tip for the correct application and interpretation of results. The selection of indenter is normally based on the hardest material, to minimize damage that the indenter might experience from the high stresses during indentation (Wheeler et al., 2015). In other words, the material used on the indenter tip and shape should be considered as they play a major role. Material properties vary greatly with changes in temperature. Thus, when characterizing materials, which expand during heating or react with the indenter at high temperatures, they must be treated with care, so that the test conditions mimic in-service conditions as closely as possible. The geometry of the tip has an effect on the load displacement results and ultimately the hardness measurements (Mirshams et al., 2006). Therefore, calibration of the tip is required for correction determination of material response. In sphere indenters, suggestions have been made to image using scanning or atomic force microscope to measure the contact area.

**Thermal Drift: temperature change**

Thermal drift is a time-dependent error that occurs when any part in the load frame (sample, indenter or sample holder) expands due to changing temperatures (Maxwell and Alvarez, 2001). Thermal drift is divided into frame drift and contact drift and it is important to know which of the two is causing the drift. Wheeler et al. (2015) explained the frame drift to occur at ambient temperatures because of the atmospheric differences in the nanoindentation system’s frame and when there is no contact. The frame drift can sometimes occur at elevated temperature which is due to thermal gradients on the heated and cooled components. Contact drift is insignificant at ambient temperature, but at elevated temperatures it occurs
due to difference in temperature, (Wheeler et al., 2015). The thermal drift affects the displacements of the indenter into the specimen and accuracy of the results.

The thermal drift can be minimised by running the test for short periods, to avoid time dependent properties such as creep, as they affect modulus of elasticity and hardness. Working in controlled (enclosed) environments like vacuum conditions eliminates frame drift. This thermal drift can be measured after the system stabilizes which normally takes long and the drift can ultimately be corrected, but is not recommended on viscoelastic material. However, the effect of thermal drift may be minimised to a certain extent, but not eliminated https://www.azonano.com/article.aspx?ArticleID=3228.

**Pile-up and Sink-In**

Pile-up and sink-in shown in Figure 2.7 are important deformation features of material around the contact area. Pile-up causes underestimation while sink-in causes overestimation of the contact area (Bull, 2014). The Oliver and Pharr method does not measure pile-up and sink-in, which result in erroneous mechanical properties. Pile-up and sink-in have been studied by a number of researchers where most have correlated the form of pile-up and sink-in with crystallography and grain orientation (Wang et al., 2004; Chen et al., 2007; Gerday et al., 2009). Bucaille et al. (2003) and Liu et al. (2005); mentioned that friction also to affect pile-up and sink-in. Lower coefficient of friction, result in higher height pile-up patterns (Bocciarelli et al., 2005). Tsui (1997) stated that the amount of pile-up is highly depended on the indenter geometry and the Vickers indenter was found to generate more pile-up than the Berkovich indenter for both monolithic material and soft films on hard materials.

![Figure 2.7: Photographs showing sink in and pile up (courtesy of Anton Paar Tritec)](image-url)
Pile-up and sink-in deformation modes result in erroneous measurements of the hardness and modulus of elasticity. Pile-up and sink-in occurs when the true contact area between the sample and the indenter increases and decreases when the sinking-in occurs respectively (Ma et al., 2014). The elastic equations of contact assume that the contact area is underneath the sample surface. Depending on the ratio of modulus of elasticity and hardness of the sample, the material may be pushed up towards the indenter or sinking-in the material may be pushed up towards the indenter and be “piled-up” on the edges of the indentation (Bhattacharyya, 2006). In monolithic material, the material with lower modulus of elasticity to hardness is less likely to experience pile-up and the material with higher modulus of elasticity to hardness (large plastic zone) is more likely to pile-up (Ting, 1996).

When pile-up occurs, more material supports the force from the indenter than is expected on the contact equations, which result in specimens appearing stiffer and harder than reality. Bolshakov and Pharr (1996) stated that when pile-up occurs, the contact area is normally estimated by 60% and the behaviour is dependent on the ratio of the reduced modulus of elasticity to the yield stress (Mircea, 2008; Hardiman et al., 2017). Inhomogeneous materials also aggravate pile-up. Zelenak (2011) stated that pile-up could be avoided by using spherical indenters and shallow depths. In 2012, Menčík concluded that pile-up result in higher calculated hardness and elastic modulus than the actual values.

Sample preparation / Surface roughness
Nanoindentation sample preparation is a delicate process; the polishing process can change surface properties of ductile material by raising the residual stresses and the grinding process can damage the thin surface layer in brittle materials (Menčík, 2012). The Nanoindentation test is conducted under the assumption that the sample is flat, clean (with no dust and adhesive particles) and smooth. In reality, there is no smooth surface; the surface has waves of height in nanometres. During indentation, the indenter contacts the highest wave first which result in higher penetration depth and the least calculated hardness. When the indenter contacts the lowest wave, the contact area is underestimated and results in overestimation of hardness value. The rough surface easily causes errors when determining contact area, directly from the depth of penetration (Fischer-Cripps 2002; Chen et al., 2013).
Sample preparation must be carried out using a precise diamond saw, which cuts both the top and bottom parallel. The sample has to be cleaned with pressurised air, ethanol and in an ultrasonic bath.
2.5.5. Study on nanoindentation of Titanium alloys

There are considerable reports on the nanoindentation of titanium and titanium alloys, but not specifically on Ti-6Al-4V. Verkhovtsev et al. (2013) studied the molecular dynamics simulations of the nanoindentation process of titanium crystal using square, conical and spherical shapes indenters. The indenters had different deformation according to their geometry; the spherical indenter had higher dislocation activity against the other indenters, but the hardness and reduced Young’s modulus values were depended on the shape of the indenter. Ehtemam-Haghighi et al. (2017) investigated mechanical properties of Ti based alloys with Fe and Ta additions using nanoindentation technique. From this work, it was concluded that increasing Fe and Ta contents, stabilises the β phase and reduces the modulus of elasticity.

Fizanne-Michael et al. (2014) determined the hardness and modulus of elasticity for polycrystalline commercially pure titanium by both nanoindentation and EBSD. It was revealed that the orientation of the grains affects hardness, as compared to the modulus of elasticity. De Souza et al. (2005) analysed hardness and elastic modulus of ion-nitrided titanium obtained using nanoindentation technique. It was concluded that the presence of nitrogen in a sample treated at 900 °C, increases hardness and modulus of elasticity near the surface. Liu et al. (2016) examined creep properties of ultrafine-grained titanium processed by ECAP using nanoindentation at ambient-temperature. It was reported that that UFG Ti, had high creep stress exponents against that of CG Ti and that the creep resistant properties of UFG Ti could be due to the loading rate and the grain size.
2.6 SUMMARY
Review of literature on nanoindentation studies of TiN reinforced Ti-6Al-4V (MMCs) was reported in this chapter. The survey showed that numerous studies have been conducted on nanoindentation studies of MMCs where, most of them were on aluminium or titanium alloy as the matrix reinforced with multi walled carbon nanotubes (MWCNT) or silicon carbide (SiC) manufactured using different manufacturing processes.

The gap of knowledge observed in the previous work, is inadequate information on the fabrication of TiN reinforced Ti-6Al-4V using spark plasma sintering and nanoindentation analysis on TiN reinforced Ti-6Al-4V. Studies on microstructural evolution and nanoindentation of TiN reinforced Ti-6Al-4V are needed to evaluate the reinforcement on the matrix and add value in the industry. It is vital to study the effect of TiN on Ti-6Al-4V matrix (microstructure) to understand the mechanical properties and ultimately expand the life span of Ti-6Al-4V.
CHAPTER 3

3. EXPERIMENTAL PROCEDURE
This chapter comprises of the materials, methodology and equipment used in this study. The sintering technique and conditions of the samples, metallographic preparations, characterization and nanoindentation testing are described. Spark plasma sintering technique was used to sinter the powders into compacts. Optical microscopy and scanning electron microscopy were used to characterize the morphology and structure of the samples, while the nanoindentation technique and micro-hardness tester were used to extract mechanical properties (hardness, modulus of elasticity of each phase, creep behaviour) and ultimate tensile strength.

3.1. Materials
Sintered compacts of Ti-6Al-4V and Ti-6Al-4V reinforced with (1%-4 vol. %) TiN were supplied by the Centre for Nanoengineering and Tribocorrosion and the initial dimensions of the sintered compacts were 20mm (length), 20mm (breath) by 6mm (thickness). Ti-6Al-4V reinforced with TiN (MMCs) in this study, were sintered using the following parameters: Both powders (Ti-6Al-4V and TiN) were mixed in a Tubular shaker mixer for 6 h at a speed of 49 rpm, in order to have good dispersion homogeneity and good interfacial bonding of the TiN to the matrix. The powders were mixed under high vacuum conditions using graphite die and punch at an applied pressure of 50 MPa, the temperature of 1000 °C, heating rate of 100 °C/min and holding time of 10 min, in reference (Falodun et al., 2017).

3.2. Sample Preparation
Microstructural and mechanical characterisations require several steps of preparation before testing could commence and these steps include cutting, mounting, grinding, polishing and etching of the samples. In this study, the surfaces of the samples were cross-sectioned and ground using silicon carbide paper from 220 to 1200 grade. The samples were then polished with 6 μm-1 μm diamond suspension to produce a smooth surface, washed and cleaned with acetone, distilled water, then dried in air to avoid stains on the surface. Polished samples were etched chemically in a Kroll’s reagent, composed of 92 ml distilled water, 6 ml HNO₃, and 2 ml HF to reveal the microstructure. The exposure time ranged from 5 to 10 s as this process is both time dependant and time sensitive. The Surface finish of the samples needs to be of high quality for both EBSD and nanoindentation tests. Prior to the microstructural and mechanical
characterisations, the samples were stored in a desiccator to avoid reaction of the sample surface with the environment.

3.3. Microstructural Characterisation
The microstructural analysis of the etched samples was carried out using high–resolution optical microscope and a field emission scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) as shown in Figure 3.1 (FESEM, Joel™, model JSM-7600F). The optical microscope was used to analyse the general microstructure and the grain structure at magnification of 10X, 50X and 100X. SEM-EDS analysis of the etched samples was performed to investigate the morphology and elemental composition or the presence of intermetallic particles. Backscattered electron images (BSE) were used to quantitatively analyse the microstructures, phases and morphology of the samples.

Figure 3.1: Field Emission Scanning Electron Microscope (FESEM, JoelTM, model JSM-7600F)

3.3.1. Sample preparation for EBSD
EBDS is a surface sensitive technique, with diffraction signals which requires sample preparation. It is imperative for the surface of the sample to be free from contaminations and damage to obtain accurate EBSD results. The samples were mounted using a conductive mounting resin (no charging) containing graphite powders. Grinding and polishing was performed on fine SiC-Paper and medium soft cloth respectively, applying low pressures and short polishing times to avoid deep deformations. The sample was cleaned after every stage.
to avoid unwanted contaminations. The final polish was carried out with colloidal silica until satisfactory results were obtained. Polished samples were etched chemically in a Kroll’s reagent, composed of 92 ml distilled water, 6 ml HNO3, and 2 ml HF to reveal the microstructure. The prepared sample must be protected to avoid alterations such as dust, dirt and scratches.

Phase identification and grain size were characterised using Field emission scanning electron microscope (FE-SEM) equipped with EDS/EBSD which is presented in Figure 3.2. For crystalline phase analysis, an area of interest was selected from a well prepared sample and the chemistry of the sample was determined by means of the EDS. The samples were tilted at high angles of 70° to maximize the intensity of the backscatter signal and to minimise shadowing effects. Voltage of 20 keV, and Standard EBSD geometry were used. The electron beam strikes the surface of the sample, which causes electrons to travel in all directions to produce the EBSD patterns. Electrons that satisfy the Bragg condition for a crystal plane are channelled and show the Kikuchi bands (Wilkinson and Hirsch, 1997). These diffraction patterns were used to characterise the crystal structure and orientation, which explains the use of high definition software as the basis for determining the relative pattern quality. The Electron Backscatter Diffraction pattern (EBSP) is detected by the camera within a vacuum (phosphor screen). The EBSP is uniquely analysed by the lattice parameters of a crystal and identities and orientations of the crystal, matched to the EBSP.

Grain size was analysed from the changes in crystallographic orientations, while the characteristics of each grain boundary is extracted from the phase and the orientation at the index point. The step size needs to be fixed to obtain accurate results. The linear intercept detection was performed by the data processing software on map grids.
3.4. Mechanical Characterisations

3.4.1. Conventional Micro-hardness testing

Hardness measurements of the etched samples were carried out on an Innova Falcon micro-hardness tester equipped with Vickers, Brinell and Knoop diamond indenters, shown in Figure 3.3. Vickers hardness measurements were conducted at test load of 200 gf and dwelling time of 10 s. The indentations were performed at selected areas on the surface of the samples and a minimum of 8 indents were performed on each sample to validate the results. Vickers diamond indenter tip was used because of its effective cone angle of 70.3°, which is nearly the same with the nanoindenter Berkovich tip indenter (Fischer-Cripps, 2002). Therefore the Vickers and Berkovich indenter tip permits comparable analysis. All measurements were in compliance with ISO 6507, and ASTM E-384 standard.
3.4.2. Nanoindentation

In this study, nano-indentation tests were performed on an Ultra Nano-Indentter (UNHT) presented in Figure 3.4, which is equipped with a three-sided pyramid Berkovich diamond indenter. The tip of the Berkovich indenter was calibrated prior to the measurement on fused silica to maintain accuracy. The loading rate of 6 mN/ min, unloading rate of 6 mN/ min at a maximum load of 3 mN were applied and held for 10 s, to eliminate the time dependent deformation properties. Ten indentations per sample and a spacing of 7 µm between each indent were performed on each sample to maintain the accuracy. The analyses of the tested samples were assessed as the average behaviour of 10 indentations. All the indentation tests were in compliance with ISO 14577.

During nano-indentation test, a described force is applied to an indenter that comes in contact with the sample and creates an indentation, which consists of elastic/plastic deformation. Loading (when the indenter and sample comes in contact) is considered the elastic deformation while the unloading is considered the plastic deformation.
3.4.3. Nanoindentation Mapping

Nanoindentation test (mapping) was performed on an ultra nanoindenter (UNHT) shown in Figure 3.3, according to the ASTM E2546 and ISO 14577 standards. This test was carried on clean and polished surfaces of the Ti-6Al-4V (without reinforcement) and Ti-6Al-4V reinforced with 1-4 vol % TiN samples using a Berkovich diamond tip. The surface area of the samples was carefully selected as it was a representative of the whole sample. The tip was calibrated prior to the measurement on fused silica to maintain accuracy. Surface mapping (grid indentation) measuring mode was applied with a maximum load of 3 mN, with a pause of 10 s to eliminate creep, 100 indents arranged in 10 × 10 square arrays with a distance between the indents of 7 μm to cover several grains with different orientations. All indentations were load controlled, to maintain the same maximum load for all measurements.

Poisson ratios of samples were selected as 0.33, under humidity and ambient temperature of 45% and 24 °C respectively. Standard Oliver and Pharr method was used to estimate the hardness and modulus of both α and β phase individually. This method calculates the hardness from maximum load and contact area, while the modulus of elasticity was calculated from the contact stiffness, Poisson’s ratio and maximum load contact area. The 100 indents data per sample were exported and plotted as histograms.

Figure 3.4: Ultra-Nanoindentation (UNHT) system
3.4.4. Nanoindentation Creep test

Nanoindentation creep tests were performed at ambient temperature using an ultra-Nanoindenter (UNHT) equipped with a three-sided Berkovich pyramid indenter. The Berkovich indenter tip was calibrated prior to the measurement on fused silica to maintain accuracy. The indenter was held for 600 s at different maximum loads of 4 mN, 23 mN, and 80 mN on all the 5 samples. In all the tests, the indenter was unloaded to about 10% of the maximum load and paused for 100 s for the correction of the thermal drift. Six indentation tests were carried out at each maximum load.

Each indentation cycle consisted of four steps: loading to first maximum load (4 mN, 23 mN, and 80 mN), first holding at maximum load for 600 s, unloading to 10% of the maximum load and holding for 100 s shown in Figure 3.5. At each maximum load, the load - displacement curves were recorded in order to determine the hardness and elastic modulus at different maximum load.

Indentation stress is assumed as:

$$\sigma = \frac{F}{Ap}$$  \hspace{1cm} (3.1)

Where $F$ is the load and $Ap$ is projected area of contact, the $Ap$ for a Berkovich indenter is equal to $24.5h_c^2$, (Mulhearn and Tabor, 1961; Kumar et al, 2012)
Indentation strain rate is assumed as:

\[ \dot{\varepsilon} = \frac{1}{h} \frac{dh}{dt} \]  \hspace{1cm} 3.2

Where \( h \) is the instantaneous penetration depth, \( \frac{dh}{dt} \) is rate of change of indentation depth. (Mayo and Nix, 1988; Kumar et al., 2012)

The creep stress exponent is assumed as:

\[ n = \frac{d(\ln \dot{\varepsilon})}{d(\ln \sigma)} \]  \hspace{1cm} 3.3

\( n \) is calculated from the slope of the \( \ln \dot{\varepsilon} \) versus \( \ln \sigma \) graph (Jiangjiang et al., 2017). The creep stress exponent (\( n \)) is used to determine the creep mechanisms and stability (Liu et al., 2016)

Indentation creep rate is assumed as:

\[ \dot{\varepsilon} = A \sigma^n \]  \hspace{1cm} 3.4

Where \( A \) is temperature dependent constant, and \( n \) is described in the equation above (Liu et al., 2016).
CHAPTER 4

4. RESULTS AND DISCUSSION

This chapter presents results obtained from microstructural and mechanical characterisation of the as-received sintered compacts of Ti-6Al-4V and Ti-6Al-4V reinforced with 1%-4 vol. % TiN. This chapter also analyse and discuss the main findings obtained from the S.E.M, EBSD, nanoindentation and micro-hardness test. The lamellar and equiaxed microstructure of α & β alloy are well defined, within different orientation and crystallography. Hardness and modulus of elasticity for each phase within the samples are characterized. The creep mechanism present in Ti-6Al-4V and Ti-6Al-4V reinforced with 1%-4 vol. % TiN are also defined.

4.1. Microstructural Analysis

4.1.1. Optical Microstructure

The microstructure of Ti–6Al–4V is normally described by the arrangement, shape and size of the alpha (α) and beta (β) phases. Figure 4.1 shows the optical images of the sintered sample without and with TiN addition. In Figure 4.1a, sintered Ti–6Al–4V revealed distinct phases comprising alternating layers (fully lamellar) of α and β phases (Da Silva et al., 2007). Nalla and co-workers (2003) also confirmed that lamellar microstructure is associated with high strength due to the size of α phase which results in low ductility. Figure 4.1b-4.1e show optical images of Ti–6Al–4V with an addition of 1-4 vol% TiN. Figure 4.1d and 4.1e present Ti–6Al–4V with 3–4 vol % of TiN showing evenly distributed interconnected equiaxed primary α grains (α) with a duplex (bimodal) structure comprising the retained lamellar structure. This indicates that addition of 1 vol % of TiN could promote transformation from lamellar to equiaxed structure. Figure 4.1b shows a disappearing lamellae phase in the bimodal structure. Fan et al. (2016) stated that the combination of lamellar and equiaxed microstructure possess excellent mechanical properties. Further addition of 3–4 vol. % TiN as shown in Figure 4.1d–e produced lamellar free microstructure. However, the globular (equiaxed) structure is completely transformed to bimodal structure (in Figure 4.1e) which consists of lamellar structure (α + β area). In grain triple points, there are equiaxed particles of primary α phase (α) (Lutjering, 2008; Banerjee and Williams, 2013).
Figure 4.1. Optical micrograph of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN.
4.1.2. Scanning Electron Microscope (EDS)

Figure 4.2 compares the SEM micrographs of the sintered sample without TiN and with TiN addition at higher magnification. The sintered matrix shows a lamellar structure of coarse plates of α and β, which is due to the rate of cooling (Amigo et al., 2003). Significant transformations from fully lamellar (Ti–6Al–4V) to an equiaxed (Ti–6Al–4V + TiN) microstructures were observed in the sintered compacts. Note the visual regularity of the parallel lath structure in the sintered Ti–6Al–4V alloy, in contrast to the sintered nanocomposites. As stated by Heo et al. (2014) and Obadele et al. (2015), Ti alloys/composites undergo phase transformations related to nucleation-and-growth and spinodal decomposition, between continuous and discontinuous displacive transformations.

SEM observations of the sintered nanocomposites indicate uniform distribution of TiN along the grain boundary and within the phase indicating that nitrogen is an alpha stabilizer. Precipitates of α-phase were seen in some of the α grain boundaries, which is characterized by straight lines of β that separate α from the rest of the matrix as shown in Figure 4.2b–e. It was observed that the β phases were along the grain boundary while the proportion of α phase was higher than β phase with an increase in TiN addition. The precipitates were formed from the grain boundary and reduce towards the centre of the β phase. Precipitates that are formed are known for inhibiting movement of dislocations or defects in the crystal lattice and further grain growth. Additionally, SPS processed composites also show a homogenous distribution of TiN precipitates which is known for improving the strength of composites by precipitation hardening (Nandwana et al., 2012). Point EDS analyses confirmed the presence of constituent elements. On the matrix, the EDS scans showed elemental presence of Aluminium and Vanadium, Aluminium stabilized the alpha phase while the vanadium stabilized the beta phase and this was confirmed in the EDS analysis (Pederson, 2002; Fan et al., 2016). At the grain boundary, the EDS scans showed trace amount of TiN which stabilize the alpha phase.
Figure 4.2. SEM and point EDS of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN.

Figure 4.3. SEM Micrograph of Ti–6Al–4V + 1vol% TiN (1µm)
Crystal twinning was observed on Figure 4.3 and Figure 4.4 (sample Ti–6Al–4V + 1vol% TiN and Ti–6Al–4V + 2vol% TiN). These twinning deformations may have been caused by the fiber strengthening which refined the grain size. It is suspected that the HCP formed the deformation twin because of insufficient number of slip system (Guo et al., 2013). Twinning caused changes in plane orientation for slip to occur. It occurred when two separate crystals shared the same crystal lattice points, which serve as obstacles to the dislocation motion. This leads to improved strength and ductility of crystal (Wu and Curtin, 2016).

4.1.3. Scanning Electron Microscope (EBSD)
Scanning Electron Microscope (SEM) equipped with Electron backscatter diffraction (EBSD) was used to determine the phase and crystallographic orientation of the sintered samples from the Kikuchi diffraction pattern. These diffraction patterns were used to characterise the crystal structure and orientation.

Table 4.1. Phases and crystal structures of Ti-6Al-4V

<table>
<thead>
<tr>
<th>Phases</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha (α)</td>
<td>Hexagonal Close Packed (HCP)</td>
</tr>
<tr>
<td>Beta (β)</td>
<td>Body Centred Cubic (BCC)</td>
</tr>
</tbody>
</table>

Table 4.1 Presents the phases and crystal structure of Ti-6Al-4V, and it is evident that Ti-6Al-4V is a two phase alloy, which consist of both alpha and beta phase. The crystal structure of titanium at ambient temperatures and pressure is close packed hexagonal (HCP) and at temperatures above 882.5°C, the titanium undergoes an allotropic transformation from a
closed-packed hexagonal crystal structure (α phase) to a body centered cubic (BCC) crystal structure (β phase) which remain stable (Pederson, 2002).

Figure 4.5 EBSD phase maps for of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN.
Table 4.2. Measured phases and unresolved phases of Ti-6Al-4V and Ti-6Al-4V reinforced (1-4vol %) TiN

<table>
<thead>
<tr>
<th>Sample</th>
<th>HCP (α)</th>
<th>BCC (β)</th>
<th>TiN₃</th>
<th>Ti₂N</th>
<th>Unresolved phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>78</td>
<td>10</td>
<td>1.9</td>
<td></td>
<td>9.6</td>
</tr>
<tr>
<td>Ti-6Al-4V + 1% TiN</td>
<td>81</td>
<td>1.5</td>
<td>0.8</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td>Ti-6Al-4V + 2% TiN</td>
<td>75</td>
<td>7.4</td>
<td>2.5</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>Ti-6Al-4V + 3% TiN</td>
<td>79</td>
<td>0.2</td>
<td>0.9</td>
<td>2.9</td>
<td>16</td>
</tr>
<tr>
<td>Ti-6Al-4V + 4% TiN</td>
<td>92</td>
<td>1.9</td>
<td>1.3</td>
<td></td>
<td>4.4</td>
</tr>
</tbody>
</table>

Figure 4.5 and table 4.2 shows the EBSD maps of measured phases present in Ti-6Al-4V with and without TiN. Hexagonal close packed (HCP) and body centred cubic structure (BCC) were observed because titanium alloys undergoes allotropic transformation at temperatures above 890°C (Lutjering et al., 2003). TiN phase was also observed in all the samples. The TiN help exhibit a strong crystallographic orientation. It is evident that an increase in vol% TiN stabilises α phase at the expense of the β phase (Donachie, 2000). The α phase increased from 78% to 92%, while the β phase decreased from 10% to 1.9% as a result of increased vol% TiN. The interstitial element have strong stabilizing effect on the α phase, which ultimately raises the transus temperature (Pederson, 2002). The high percentage of the unresolved phases could be due to the orientation of the crystals.

**Grain size**

The crystallographic information was used to determine the location and size of the grain boundary. Figure 4.6 present grain size distribution of Ti–6Al–4V without and with TiN addition. Grain size of titanium alloys is important as it determines variety of mechanical properties. For Ti-6Al-4V, the diameter of the grains range from 23.9 to 72.9 μm, Ti-6Al-4V + 1 Vol% TiN, ranges from 4.7 to 21.2 μm, Ti-6Al-4V + 2 Vol% TiN, range from 9.5 to 86.1 μm, Ti-6Al-4V + 3 Vol% TiN, range from 0.7 to 7.3 μm, and Ti-6Al-4V + 4 Vol% TiN ranges from 1.73 to 10.7 μm. It is evident that the grain size decrease with an increase in Vol% of TiN, except for Ti-6Al-4V + 2 Vol% TiN. The significant decrease in grain size could be due to the presence of nitrogen at the grain boundaries which is α stabilizer that acts as solid solution strengthener (Chong et al., 2017). The nitrogen in Ti-6Al-4V is interstitial.
solute that restrict grain growth and promote grain refinement (Moorhouse, 2013). The grain growth is restricted as the grain boundary interfacial energy per unit volume decrease. Falodun et al. (2018) mentioned that alloying Ti–6Al–4V with titanium nitride result in a fine dispersion of titanium alloy. Kutz (2002) stated that there is no data defining the effect of grain size on titanium but smaller particle size and grain size in titanium alloys are always associated with improved mechanical properties. The grain size increased in Ti-6Al-4V + 2 Vol% TiN could be due to the Widmanstätten microstructure which nucleates at the grain boundary and the twinning present in the microstructure.
Figure 4.6. Grain size distribution of Ti–6Al–4V without and with TiN addition. (a) Ti–6Al–4V (b) Ti–6Al–4V + 1TiN (c) Ti–6Al–4V + 2TiN (d) Ti–6Al–4V + 3TiN (e) Ti–6Al–4V + 4TiN

Figure 4.7: Average grain size as a function of vol% TiN

Figure 4.7 shows average grain size as a function of vol% TiN. As shown in Figure 4.7, TiN has an effect of refining the grain size of Ti-6Al-4V. The average grain size was observed to decrease from 20 µm, 6.7 µm, 2.8 µm, 2.6 µm to 3.7 µm, with an increase in vol% TiN respectively. The increase in Vol% of TiN enables a decrease in grain size due to solute mechanism which results in an increase in grain density. Refining grain size, increase dislocation density and hardening precipitates, needed to increase the strength and hardness of different materials (Lutjering and William, 2003; Kao et al., 2005). The grain size for Ti-6Al-4V + 4vol% TiN had a slight increase from 2.55 to 3.65 which could be due to saturation of TiN on the grain boundary and colonies of TiN at the grain boundary and is clearly outlined on Figure 4.7, which ultimately increases grain size. TiN refines the grains of Ti-
6Al-4V up to 3vol%, reinforcement higher than 3vol % clots the grain boundary which is why 4vol% TiN had a slight increase from 2.55 to 3.65.

4.2. Mechanical Properties

4.2.1. Nanoindentation

Table 4.3: Nanoindentation values of Ti-6Al-4V reinforced with 1-4 vol. % of TiN.

<table>
<thead>
<tr>
<th>Sintered Material</th>
<th>Hardness (HIT) MPa</th>
<th>Microhardness (HV)</th>
<th>Mod. of Elasticity (EIT) GPa</th>
<th>Max depth (nm)</th>
<th>Contact depth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>5329</td>
<td>494</td>
<td>139</td>
<td>161</td>
<td>141</td>
</tr>
<tr>
<td>Ti-6Al-4V + 1%TiN</td>
<td>5801</td>
<td>537</td>
<td>142</td>
<td>153</td>
<td>133</td>
</tr>
<tr>
<td>Ti-6Al-4V + 2%TiN</td>
<td>6106</td>
<td>565</td>
<td>147</td>
<td>149</td>
<td>129</td>
</tr>
<tr>
<td>Ti-6Al-4V + 3%TiN</td>
<td>6908</td>
<td>640</td>
<td>152</td>
<td>139</td>
<td>119</td>
</tr>
<tr>
<td>Ti-6Al-4V + 4%TiN</td>
<td>7517</td>
<td>696</td>
<td>156</td>
<td>134</td>
<td>114</td>
</tr>
</tbody>
</table>

Table 4.3, presents results obtained from the load-displacement curve which was measured using Oliver and Pharr method (Oliver and Pharr, 2004). The main advantage of the nanoindentation technique is its ability to measure most mechanical properties in small scale. Hardness and modulus of elasticity of Ti–6Al–4V alloy were greatly improved upon the addition of different volume percent of nano-TiN, while the maximum depth and contact depth decrease with increasing volume percent of TiN.

![Figure 4.8: Load displacement curve of Ti–6Al–4V with reinforced 1–4 vol% TiN.](image-url)
Figure 4.8 shows the load–displacement curve of Ti–6Al–4V without and with TiN obtained during nanoindentation tests. The loading curve was observed to be smooth for all the tests and there was an appreciable decrease in depth upon addition of TiN (Wang et al., 2004). The variation of indentation depth shows the difference in the material’s hardness (resistance to deformation). The decrease indicates an increase in hardness value of the sintered nanocomposites. The load displacement curve is a function of the type of material being tested, the force applied and conditions (environments) of the test. Global shape of load-displacement curve differs from one material to the other and in this study; the shape indicates that the material behaves in an elastic-plastic manner (Charitidis et al., 2013). The fact exists that a shift in the curves towards the left generally indicates that TiN effectively reduced the displacement due to the strengthening and load sharing of the nanocomposite.

From the graphical representation in Figure 4.8 Ti–6Al–4V with 4 vol% TiN shows the least displacement and lowest maximum depth (134 nm) while Ti–6Al–4V gave the highest maximum depth of 161 nm and the least modulus of elasticity of 139 GPa. For the sintered nanocomposites, the maximum depth decreased with increasing TiN contents and subsequently increasing the slope of the loading and unloading. The slope of unloading and modulus are closely related to the stiffness which results in increased modulus. The loading part of the curve includes material response to strain including elastic, while the unloading part of the curve consists mainly of plastic recovery (Wheeler, 2009).
Figure 4.9 shows the depth as a function of time for Ti–6Al–4V reinforced with 1, 2, 3 and 4 vol% TiN. On one hand, it was observed that the depth decreased with increasing time and volume fraction of the reinforcement. This behaviour is expected as TiN increases, thus increase in hardness of the material and longer time for indentation (Gong et al., 2005). On the other hand, Ti–6Al–4V has the highest depth compared to the reinforced composites and this is could be attributed to its low indentation hardness value as presented in Table 4.4. The nanohardness value was found to increase with the increase in the volume fraction of the TiN. The hardness was determined at the maximum load in the load–displacement curve using nanoindentation tests (Zeng and Chiu, 2001).

Figure 4.10: Effect of vol. % TiN volume on: (a). Hardness, (b). Modulus of elasticity, (c). Contact depth and (d). Maximum depth.

Figure 4.10a shows the hardness values with respect to varying TiN additions. Hardness is defined as a measure of how resistant a solid matter is to different kinds of permanent shape changes when force is applied (Mott, 2007). Hardness was determined at the maximum load in the load–displacement curve. Addition of nano- TiN showed an increase in hardness...
values. Increase in hardness values is due to the presence of TiN within Ti–6Al–4V matrix (Pederson, 2002; Saravanan et al., 2015). Hardness values were found to increase by 9%, 15%, 30% and 41% for 1, 2, 3 and 4 vol% TiN respectively. Figure 4.11b shows an increase in modulus of elasticity for the different volume fraction of TiN reinforced Ti–6Al–4V. The modulus of elasticity increased with increasing volume fraction of TiN reinforcement which could be related to the higher elastic modulus of TiN and contributing strengthening of the matrix (Meenashisundaram et al., 2016). For samples sintered with 1–4 vol% TiN, the young modulus values were found to increase by 3%, 6%, 9% and 12% respectively.

Figure 4.10c–d shows the relationship between the contact depth and maximum depth versus volume% TiN. In comparison with increase in volume fraction of TiN, there is a decrease in maximum and contact depth. The contact depth values were found to decrease by 6% for 1 vol % TiN, 9% for 2 vol% TiN, 16% for 3 vol% TiN and 19% for 4 vol% TiN. Furthermore, the maximum depth decreased by 5% for 1 vol% TiN, 7.5% for 2 vol% TiN, 14% for 3 vol% TiN and 17% for 4 vol% TiN. Again, it is evident that the sintered composite are stiffer than the sintered Ti–6Al–4V alloy, which explains the shallow indent depth recorded for Ti–6Al–4V + 4 vol% TiN (Chawla and Shen, 2001).

Figure 4.11c–d shows the relationship between the contact depth and maximum depth versus volume% TiN. In comparison with increase in volume fraction of TiN, there is a decrease in maximum and contact depth. The contact depth values were found to decrease by 6% for 1 vol % TiN, 9% for 2 vol% TiN, 16% for 3 vol% TiN and 19% for 4 vol% TiN. Furthermore, the maximum depth decreased by 5% for 1 vol% TiN, 7.5% for 2 vol% TiN, 14% for 3 vol% TiN and 17% for 4 vol% TiN. Again, it is evident that the sintered composite are stiffer than the sintered Ti–6Al–4V alloy, which explains the shallow indent depth recorded for Ti–6Al–4V + 4 vol% TiN (Chawla and Shen, 2001).

Figure 4.11: Hardness and elastic modulus (H/Er) and H³/Er² ratios of Ti–6Al–4V with volume fraction of TiN.

Figure 4.11 shows the result of H/Er and H³/Er² which was calculated from the hardness (H) and reduced elastic modulus (Er) values of Ti–6Al–4V with the different volume fraction of TiN. The elastic behaviour is described as the ratio between hardness (H) and elastic modulus (E), ‘elastic strain to failure’, which is used to determine the limit of elastic behaviour in a
surface contact, and also influence the wear behaviour (Rebholz et al., 1999; Leyland and Mathews, 2000; Da Silva et al., 2007; Xu et al., 2014). Also, yield pressure \( (H^3/Er^2) \) proven to be another important way of describing the ability of a material to resist plastic deformation in loaded contact (Ehtemam-Haghighi, 2017).

Furthermore, the higher value of indentation hardness (HIT) and reduced elastic modulus \( (Er^2) \) gives the sintered nanocomposites better wear and resistance to plastic deformation (Musil et al., 2002). Consequently, this parameter was estimated to determine the anti-wear ability of the sintered Ti–6Al–4V with nanocomposite which is caused by the gradual removal of the material with respect to plastic deformation (Xu et al., 2014). The average values of hardness (H) and reduced elastic modulus (Er) of the sintered composite were determined by nanoindenter which is presented in Figure 4.11. The incorporation of 1–4 vol\% nano-sized TiN improves the hardness of Ti–6Al–4V and could possibly enhance the sliding wear resistance of the material. Zhang et al. (2011) reported that the hardness of a material is directly proportional to the strength of a material. A harder material will exhibit higher strength. Moreover, the presence of higher 4 vol\% TiN in the alloys contributes to the observed increased.

4.2.2. Micro-hardness
Vickers hardness measurements were performed randomly on the surface of Ti-6Al-4V and Ti-6Al-4V with the varying volume percentage of TiN samples. A total of 8 indentations per sample were performed on each sample and averaged. The average hardness measurements are presented in Table 4.4, and graphically presented in Figure 4.12. Hardness measurements increased from 356 HV\(_{0.2}\) to 528 HV\(_{0.2}\) with increase in volume percentage of TiN. The increase in hardness of the reinforced samples could be due the present of TiN, which promotes grain boundary strengthening. The strengthening occurs by grain size reduction that restricts dislocations from running into grain boundaries and act as, strong dislocation barriers (Hall-Petch effect). The average increase in average hardness was attributed to grain boundary strengthening. This is partly responsible and there is the contribution from the particles (particle strengthening) and potential dislocation strengthening due to thermal mismatch between the matrix and the TiN particles.
When dislocation and interstitial atom come in contact, they disturb the slip plane which reduces the movement of dislocation (Morris, 1984). Dislocations are regularly main carriers of plasticity, which hardens the material. This strengthening is observed on the transition from a lamellar structure to a fine grained bimodal microstructure. Smaller grain size result in harder material and it makes crack propagation difficult. The Ti-6Al-4V sample shows the lowest hardness as compared to the other samples which is due to plate like lamellae structure.

Table 4.4: Micro-Hardness vs. nano-indentation results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Micro-Hardness (HV)</th>
<th>Nanoindentation (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al-4V</td>
<td>356</td>
<td>494</td>
</tr>
<tr>
<td>Ti-6Al-4V + 1% TiN</td>
<td>382</td>
<td>537</td>
</tr>
<tr>
<td>Ti-6Al-4V + 2% TiN</td>
<td>420</td>
<td>565</td>
</tr>
<tr>
<td>Ti-6Al-4V + 3% TiN</td>
<td>473</td>
<td>640</td>
</tr>
<tr>
<td>Ti-6Al-4V + 4% TiN</td>
<td>528</td>
<td>696</td>
</tr>
</tbody>
</table>

Figure 4.12: Micro-Hardness measurements of Ti-6Al-4V without and with TiN
Comparison of micro-hardness and nanoindentation hardness

Micro-hardness and nanoindentation results were compared because of the tip geometry used in both the Vickers and Berkovich produce the same strain in material. A difference of about 20–30% was observed between the micro-hardness and nanoindentation. Nanoindentation was found to be 20–30% higher than the micro-hardness which could be attributed to analyses methods. The differences in the micro-hardness and nanoindentation hardness values obtained in this study are in agreement with the reported literature. Fizanne-Michael et al. (2014) observed a difference of 10% between nanoindentation and microindentation, while Qian et al. (2005) observed a difference of 10–30% between nanoindentation and microindentation. The two studies reported higher nanoindentation hardness values than that of micro-hardness values.

Qian et al. (2005); Fizanne-Michael et al. (2014) stated that the differences in the micro-hardness and nanoindentation hardness values are attributed to the analyses method. Micro-hardness and nanoindentation techniques use two different methods to calculate the contact area and there are other factors which affects the results. The nanoindentation technique uses the projected contact area at the maximum load, assumes the elastic contact and possibility of pile-up or sink-in during indentation test, while the micro-hardness test uses the residual projected area.

The other reason for the difference in hardness could be the low loads which were used for the nanoindentation test. Micro-hardness covers more volume than the volume measured by a nanoindenter. Meaning the probability of the indent, indenting on more than one phase in micro-hardness test is higher than that in nanoindentation technique. Nanoindentation is more localised and micro-hardness gives average hardness over a larger area.

4.2.3. Nanoindentation mapping (Grid indentation)

Grid indentation was used to map the surface of the two dissimilar phases present in Ti-6Al-4V, which would rather be difficult to mapping using the standard micro-hardness testing techniques (Nohava et al., 2010). The indenter can indent either on α phase, β phase and the grain boundary, and the average hardness of each phase is shown in Figure 4.13. It is evident that the β phase exhibits the highest hardness as compared to α phase and the grain boundary. Highest hardness of the β phase could be due to uniform distribution of TiN along the grain boundary and β phases were found along the grain boundary (Pederson, 2012; Falodun et al.,
The other reason for an increase in hardness for β phase might be the precipitates which were formed from the grain boundary. Precipitates that are formed are known for inhibiting movement of dislocations or defects in the crystal lattice and further grain growth (Brooks, 1982; Nandwana et al., 2012; Li et al., 2016). The dislocations are regarded as carriers of plasticity which ultimately hardens the material. Increasing the TiN, increases the hardness of α phase, β phase and grain boundary from 340 HV to 530 HV, 350 HV to 600 HV, 345 HV to 495 HV respectively. The grain boundary has the lowest hardness which may be a result of pores along the grain boundary and the indent may have indented on a pore.

Figure 4.13: Effect of TiN on hardness

![Graph showing the effect of TiN on hardness](https://example.com/graph.png)

Figure 4.13: Effect of TiN on hardness

![Histogram showing frequency distribution of hardness](https://example.com/histogram.png)

Figure 4.13: Histogram showing frequency distribution of hardness
Figure 4.14 shows the hardness distribution of Ti–6Al–4V without and 1-4vol% TiN additions. Ti-6Al-4V without reinforcement shows two distinct peaks with hardness of 276 HV and 396 HV, standard deviation of 110.4 HV and mean of 335. Ti-6Al-4V + 1vol% TiN shows one distinct peak with hardness of 450 HV, standard deviation of 163 HV and mean of 380. Ti-6Al-4V + 2vol% TiN shows one distinct peak with hardness of 663 HV with standard deviation of 148 HV and mean of 617. Ti-6Al-4V + 3vol% TiN shows one distinct peak with hardness of 111 HV with standard deviation of 207 HV and mean of 486. Ti-6Al-4V + 4vol% TiN shows one distinct peak with hardness of 381 HV with standard deviation of 205 HV and mean of 497.

The standard deviation indicates that the hardness measurements in Ti-6Al-4V without reinforcement are tightly clustered around the mean value, while the standard deviation for the reinforced samples is spread out over a wide range. The hardness measurements are widely spread, but most of the measurements are higher than the mean of Ti-6Al-4V without reinforcement. This is due to the presents of hard nanoparticles reinforced in the matrix (Munir, 2006; Suryanarayana, 2011; Saheb, 2012). The hardness increases with increasing vol% of TiN, which is shown by the mean values.
The average modulus of elasticity of each phase is shown in Figure 4.15. The modulus of elasticity does not follow any significant trend, it fluctuates slightly. Cuy et al. (2002) mentioned that modulus of elasticity of similar (same) material does not change much, which may be due to the lack of a trend in the modulus of elasticity. 2vol % TiN exhibited the highest modulus of elasticity than all the samples, while 1vol% TiN had the lowest modulus of elasticity. The α phase, β phase and grain boundary did not have much difference as compared to the hardness. The fluctuation or lack of trend for the modulus of elasticity might be due to bond strength between atoms in the lattice structure and possibly due to pores. (Person et al., 2008), stated that the modulus of elasticity is dependent on the material texture and orientation. In this case, the TiN shifts the lattice structure and results in modulus of elasticity which is not improved. The other reason for reduction in modulus of elasticity may be the influenced of the adjacent grains (Fizanne-Michael et al., 2014). Additions of TiN nano particles are expected to increase the modulus of elasticity due to the fact that it has higher modulus of elasticity than the matrix (TI-6Al-4V) and they impede the movement of dislocations (Munstermann et al., 2013).
The diagrams illustrate the frequency distribution of the Modulus of Elasticity (GPa) for different compositions of Ti-6Al-4V.

**Ti-6Al-4V**

- Frequency distribution for Modulus of Elasticity ranging from 37 GPa to 178 GPa.

**Ti-6Al-4V + 1% TiN**

- Frequency distribution for Modulus of Elasticity ranging from 30 GPa to 175 GPa.

**Ti-6Al-4V + 2% TiN**

- Frequency distribution for Modulus of Elasticity ranging from 46 GPa to 196 GPa.
Figure 4.16 shows the modulus of elasticity distribution of Ti–6Al–4V and Ti–6Al–4V with 1–4vol% TiN additions. Ti-6Al-4V without reinforcement shows two distinct peaks with modulus of elasticity of 108 GPa and 128 GPa, standard deviation of 25.2 GPa and mean of 117 GPa. Ti-6Al-4V + 1vol% TiN shows one distinct peak with modulus of elasticity of 120 GPa, standard deviation of 27.4 GPa and mean of 111 GPa. Ti-6Al-4V + 2vol% TiN shows one distinct peak with modulus of elasticity of 126 GPa with standard deviation of 42.5 GPa and mean of 139 GPa. Ti-6Al-4V + 3vol% TiN shows one distinct peak with modulus of elasticity of 124 GPa with standard deviation of 28.8 GPa and mean of 113 GPa. Ti-6Al-4V + 4vol% TiN shows one distinct peak with modulus of elasticity of 119 GPa with standard
deviation of 25 GPa and mean of 116 GPa. The modulus of elasticity measurements in Ti-6Al-4V without reinforcement, Ti-6Al-4V + 2vol% TiN and Ti-6Al-4V + 4vol% TiN are tightly clustered around the mean value, while that for Ti-6Al-4V + 1vol% TiN and Ti-6Al-4V + 3vol% TiN are spread out over a wide range. The samples with measurements which are tightly clustered around the mean (smallest standard deviation), has higher mean values as compared with samples who’s measurements are widely spread out.

The hardness of the β phase for all the samples was generally higher than that of α phase and the hardness increased with increasing vol% TiN. This is probably due to hard nano particles of TiN, along the grain boundary (Falodun et al., 2018). The modulus of elasticity of the β phase was found to be slightly higher for Ti-6Al-4V and Ti-6Al-4V + 1vol%, which suggested that increase in TiN decrease the modulus of elasticity for the β phase. Increase in TiN, increased the modulus of elasticity for α phase from Ti-6Al-4V + 1vol% to Ti-6Al-4V + 4vol% (Huang and Geng, 2017). The modulus of elasticity may have been influenced by the adjacent grains and saturation of TiN along the grain boundary at higher vol% of TiN.

4.2.4. Nanoindentation Creep
Creep behaviour of Ti–6Al–4V and Ti–6Al–4V with 1-4vol% TiN additions was investigated by applying different loads and holding for 600 s at room temperature. Increase in penetration depth when the load is kept constant was calculated as indentation creep property (Chudoba and Richter, 2001). The load displacement curve at 4mN, 23mN and 80Mn are presented in Figure 4.17, whilst the creep curves (depth-time graph) at varying maximum loads are presented in figure 4.18. The indentation creep stress and strain rates are presented in figure 4.19. The results were compared with the model equations to predict the creep behaviour.
Figure 4.17a-c shows the load-displacement curve for Ti–6Al–4V and Ti–6Al–4V with 1-4 vol% TiN additions. The curves show that titanium behaves in an elastic-plastic manner (Jha et al., 2013). In all three load-displacement curves, Ti-6Al-4V had the highest penetration depth against the samples which were reinforced with TiN. The high penetration depth in Ti-6Al-4V can be explained by the hardness. Jia et al., (2017) mentioned that the relationship between hardness and indentation depth is that, hardness decreases with an increase in indentation depth; this is revealed on the load displacement curve where most of the material is recovered. The harder the material, the more difficult it would be to penetrate the sample. Ti–6Al–4V is softer than the reinforced sample hence the high penetration depth. Furthermore, it was observed that the hardness increase with a decrease in gain size due to
grain refinement which will result in Ti-6Al-4V experience more creep and plasticity than the reinforced samples (described by the hall-patch relation) (Liu et al., 2013).
The creep depth and time curves for Ti–6Al–4V and Ti–6Al–4V with 1-4vol% TiN additions at different loads are shown in Figure 4.18. The curves show high penetration rate at the primary (transient creep) stage and constant creep at the secondary (steady state) stage (Mayo and Nix, 1988; Kumar et al., 2012; Jiangjiang et al., 2017). The orientation of the indentation usually influences the transition in slope from the transient to the steady state. Creep deformation was found to be higher in Ti-6Al-4V (0% TiN) against the other samples. Ti-6Al-4V + 1vol% TiN and Ti-6Al-4V + 3vol% TiN exhibit similar creep deformation. Reinforcing with TiN particles restrict creep flow by arresting the dislocation movement.

Figure 4.19: Logarithmic stress and strain rate graphs
Figure 4.19 shows the indentation strain rate-stress for Ti–6Al–4V and Ti–6Al–4V with 1-4vol% TiN additions. It is assumed that the steady state conditions (secondary creep) were attained during the long hold of 600 s and two creep mechanisms was suggested by the presence of two stress exponent (Nautiyal et al., 2016; Liu et al., 2016). The stress exponents were calculated from the logarithmic stress and strain rate graph, as it is the slope of the graph. Stress exponent regime were obtained for each addition of TiN (sample); 0% TiN had an n (3.4), while 1% TiN had an n (3.2), while 2% TiN had an n (6.3), while 3% TiN had an n (3.4), while 4% TiN had an n (2.1). It was concluded that 2% TiN had the highest stress exponent than all the other samples and 4% TiN had the least stress exponent. The stress exponent of 6.3 in 2% TiN may be due to twinning which was observed on the microstructure. It is worth mentioning that the Twinning is the leading plasticity mechanism in 2% TiN sample. The other reason for the highest stress component in 2% TiN could be the equiaxed microstructure of α and β alloy. The larger value of the stress exponent is associated with greater creep resistance (Liu et al., 2016). According to the stress exponent calculations, the creep mechanism in Ti-6Al-4V (n value higher than 3) is assumed to be dislocation and power rule and in Ti-6Al-4V + 4vol% TiN (n value is 2) it is assumed to be grain boundary sliding. Wang et al. 2009; Somekawa and Mukai 2010; Nautiyal et al. 2016) used stress exponent to predict the creep mechanism. The dislocation glide allows the dislocation to glide through the lattice and obstacles which is why it dominates most conditions at room temperature (Frost and Ashby, 1982).
CHAPTER 5

Conclusion
In this study, nanoindentation studies were carried out on sintered Ti–6Al–4V reinforced without and with 1-4 vol% TiN. The microstructural evolution and mechanical properties of the samples were correlated and assessed using different techniques. The effect of TiN on Ti-6Al-4V matrix under microhardness, nanoindentation hardness, and modulus of elasticity and nanoindentation ambient creep properties has been identified and discussed. The following conclusions were reached:

- The high heating rate and reduced holding time in spark plasma sintering technique helped control the recrystallization and minimized the grain growth.
- Additions of nanosized TiN to Ti–6Al–4V matrix were found along the grain boundary and resulted in grain boundary strengthening, which promotes transformation from lamellae microstructure to bimodal microstructures. The transformation results in grain size reduction from about 20 µm to 3.7 µm.
- Hexagonal close packed (HCP) and body centered cubic crystal structure (BCC) were observed, where an increase in vol% TiN stabilized α phase at the expense of the β phase.
- Bulk nanoindentation test of the metal matrix composites (MMCs) showed an increase in hardness and modulus of elasticity when reinforced with 1–4 vol% TiN, which was found to strengthen and improve the matrix. This material could presentation higher hardness and better wears resistance (i.e. larger H/Er and H3/Er2 ratios) than the Ti–6Al–4V alloy.
- The modulus of elasticity for bulk nanoindentation was found to increase with an increase in vol% TiN, while the modulus of elasticity for grid indentation (mapping) did not have a trend, this could be due to bulk hardness only indenting on a few areas, and mapping indentation covering a wide area.
- Nanohardness and micro-hardness values were compared, the nanohardness values of the MMCs were found to be higher than the microhardness values, but the results obtained are in agreement with the reported literature between nanoindentation and micro-indentation.
- Equiaxed microstructure of α and β alloy in 2% TiN resulted in improved creep properties.
It was observed that the twinning was the most likely dominant creep mechanism in 2 vol% TiN and dislocation glide for Ti-6Al-4V (0% TiN), therefore addition of TiN could enhances creep resistance of Ti-6Al-4V at room temperature.

Microstructure, crystal orientation and grain boundary affects the mechanical properties of Ti. Reinforcing Ti–6Al–4V with TiN restrict movement of dislocations which improves the mechanical properties.

**Contribution to knowledge**

Ti-6Al-4V reinforced with 1-4 vol% TiN is a promising MMC produced by spark plasma sintering process. There are numerous MMC but little is known about the nanoindentation behaviour of Ti-6Al-4V matrix, the particulate fibre being the reinforcement, and the effect of the reinforcement on the microstructure and the morphology of the matrix. The above lead to nanoindentation investigations of Ti-6Al-4V reinforced with 1-4 vol% TiN for applications in the aerospace industry. From the results obtained in this study, the followings contributions to knowledge have been made;

- The maps and grain size of the MMC which has never been reported in literature on Ti-6Al-4V reinforced with 1-4 vol% TiN have been evaluated and discussed, signifying newly developed information.
- Nanoindentation studies (hardness, modulus of elasticity and creep properties), which has never been reported in literature on Ti-6Al-4V reinforced with 1-4 vol% TiN have been generated and discussed. Reinforcing the matrix (Ti-6Al-4V) with vol% TiN reduced the grain size which ultimately improved the hardness, modulus of elasticity and the creep resistance.

**Recommendation**

The metal matrix composite (Ti-6Al-4V reinforced with 2vol% TiN) could be used for structural applications at ambient temperatures. The aircraft industry would benefit as it requires improved or enhanced creep properties and the Ti-6Al-4V reinforced with 2vol% TiN had the highest creep resistance properties. This MMC could be used on fan blades, engine parts, and general structural material such as bolts. For future investigations, creep and fatigue properties of this metal matrix composite at temperatures above 400 °C should be considered.
REFERENCES


Fischer-Cripps, A.C. (2002). Nanoindentation, USA: Springer


Huygens, C. (1912). *Treatise on light: in which are explained the causes of that which occurs in reflexion, & in refraction, and particularly in the strange refraction of Iceland crystal*, 99; London, Macmillan


Kessel, H.V., Henniche, J., Kirchner, R. and Kessels, T. (2009). Rapid sintering of novel material by fast/ SPS- further development to the point of an industrial production process with high cost efficiency, Germany: FCT system GmbH.


Liu, X., Zhang, Q., Zhao, X., Yang, X. and Luo, L. 2016. Ambient-temperature nanoindentation creep in ultrafine-grained titanium processed by ECAP. Materials Science and Engineering, 676, pp. 73-79


Liu, X., Yuan, F. and Wei, Y. (2013). Grain size effect on the hardness of nanocrystal measured by the nanosize indenter. Applied Surface Science, 279, pp.159-166


Nautiyal, P., Jain, J., Agarwal, A., 2016. Influence of loading path and precipitates on indentation induced creep inMg-6 wt. % Al-1wt% Zn magnesium alloy, Material Science Engineering, 650; 183–189.


