Mechanical Properties of Spark Plasma Sintered Aluminium-Carbon Nanotubes Composites (Full dissertation)

by

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Dedication

I am dedicating this work to myself; I know I need it.

Declaration

I **Zwivhuya Lucia Madala** hereby declare that this master's research dissertation is wholly my own work and has not been submitted anywhere else for academic credit either by myself for another person. I understand what plagiarism implies and declare that this research work is my own ideas, words, phrase, arguments, graphics, figures, results and organisation except where reference is explicitly made to another's work. I understand further that any unethical academic behaviour, which includes plagiarism, is seen in a serious light by the University of Johannesburg and is punishable by disciplinary action.

Signed___________ Date 25th February 2020

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List of journal articles and conference presentations

Conference Presentation

[1] Z.L. Madala, M.A. Awotunde, O.O. Ayodele, S Aribo and P.A. Olubambi (2018) "Effect of Ball Milling Parameters on the Dispersion of Carbon Nanotubes Within Aluminium Powders" COSAAMI 2018 Conference.

Abstract

A single material cannot meet the demand of advanced materials; this has contributed in production of composites. Pure aluminium (Al) is soft with moderate strength and young's modulus, however properties such as low density and corrosion resistance has attributed to intense interest it has attracted. For pure aluminium to comply with mechanical properties that are required in different engineering applications, its mechanical properties have to be enhanced. Alloying elements, Solid solution strengthening, strain hardening and precipitation hardening have been used to enhance mechanical properties of Al alloys. This work presents the preparation, characterisation, spark plasma sintering (SPS) and evaluation of aluminium-multi walled carbon nanotubes (Al-MWCNTs) composites' mechanical properties. Low energy ball millings (LEBM) were used to disperse up to 1.5 wt. % MWCNTs into Al matrix (0.5wt. % MWCNTs, 1wt. % MWCNTs and 1.5 wt. % MWCNTs were dispersed into Al matrix). Milled Al-MWCNTs powders composites and sintered Al-MWCNTs composites were characterised using optical microscopy (OP), scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), x-ray diffraction (XRD), Raman spectroscopy and transmission electron microscopy (TEM). OP was used to investigate the effect of MWCNTs on the microstructure of Al-MWCNTs composites, SEM and TEM were used to study morphology of MWCNTs, XRD was used for phase identification and Raman spectroscopy was used for structural integrity investigation. Microstructural characterizations of Al-MWCNTs composites reveal that the homogeneous dispersion of MWCNTs was achieved, MWCNTs were well embedded in the Al matrix, no agglomeration and small amount of aluminium carbide were observed. The effects of MWCNTs on the mechanical properties were studied using ultra nanoindenter tester. It is concluded that the incorporation of MWCNTs into Al matrix results in the increase in elasticity, plasticity, hardness, yield strength, modulus of elasticity, stiffness and strain rate sensitivity of aluminium composites. The enhancements of 55% in hardness, 55% in yield strength, 81% in modulus of elasticity, 89% stiffness and 20% in strain rate sensitivity compared to pure Al were observed.

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List of abbreviations

%	- Percentage
◦ c	- Degree Celsius
Al_4C_3	- Aluminium carbide
Al	- Aluminium
Al_2O_3	- Aluminium oxide
AMC	- Aluminium matrix composites
CNFs	- Carbon nanofibers
CNTs	- Carbon nanotubes
DM	- Dual matrix
g	- Grams
HEBM	- High Energy Ball Milling
K	- Kelvin
LEBM	- Low Energy Ball Milling
Min	- Minutes
mm	- Millimetre
MMCs	- Metal Matrix Composites
Mpa	- Mega Pascal
MWCNTs	- Multiwalled carbon nanotubes
Nm	- nanometre
PCA	- Process Control Agents
p/m	- Powder metallurgy
SEM	- Scanning Electron Microscope
SM	- Single matrix
SPS	- Spark Plasma Sintering
SWCNTs	- Single Walled Carbon Nanotubes
TEM	- Transition Electron Microscope
UTS	- Ultimate Tensile Strength
Vol.%	- Volume fraction percentage
Wt.%	- Weight fraction percentage
XRD	- X ray diffraction

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Chapter 1

1. Introduction

Aluminium alloys are produced by alloying pure aluminium with elements such as magnesium, copper, silicon, manganese, zinc and lithium. The major alloying element in 2000 series is copper, manganese in 3000 series, silicon in 4000 series, magnesium in 5000 series, magnesium and silicon in 6000 series, zinc and magnesium in 7000 series and lithium in 8000 series. Four digits designate aluminium alloys; the first number represents the major alloying element.1000 series are unalloyed aluminium (99% Al). Aluminium Association and International Alloy Designation System use wrought and cast to categorised aluminium alloys. Other way to classified aluminium alloys is through non-heat-treatable and heat-treatable categories (Campbell, 2006). Pure aluminium is ductile, soft, lightweight, malleable and has good corrosion resistance except where chloride is present in significant quantities; its production from bauxite is quite expensive. Its applications include being used as tin, foil, wire pigment, paint cookware etc. Pure aluminium application limitations are yield strength of 11 MPa and tensile strength of 83 MPa. Applications of pure aluminium pose high conductivity, excellent formability and very good corrosion resistance, are preferred where high strength is not essential (Megson, 2014).

Precipitation hardening, strain hardening and solid solution strengthening have be used as individually or in combination to enhance the strength of aluminium alloys. These strengthening mechanisms can be used to achieve wide range of mechanical properties of pure aluminium (Polmear, 2005b). Low mechanical strength of aluminium alloys has also contributed to the development of aluminium composites and aluminium nanocomposites. The developed aluminium composite showed improved mechanical strength (Park et al., 2015), hardness (Ogawa et al., 2017), yield stress (Shin et al., 2016) and ultimate tensile strength (Alekseev et al., 2016) but introduced a new challenge of reduced ductility (Zhu et al., 2016; Pillari et al., 2015; Guo et al., 2017 a). Most researchers reported poor ductility with greater strength (Guo et al., 2011; Choi et al., 2011; Hassan et al., 2014; Park et al., 2015; Zhu et al., 2016 and Zhao et al., 2017). Guo et al. (2017) synthesized pure aluminium with 0.75 and 1 vol.% CNTs using Spark Plasma Sintering (SPS) and hot rolling, sintered at two different temperatures which are 590 and 630°C.

Results has shown that mechanical properties expect ductility increase with increase with CNTs content and also that ductility is influenced by sintering temperature (Guo et al., 2017). Choi et al. (2015) used A2024 and multi walled carbon nanotubes to consolidate Al-MWCNTs composites using ball milling and hot rolling respectively. To prevent cold welding, control agent was used. The composite containing 3 vol. % MWCNTs had great yield strength of 780 Mpa with 2% plastic elongation to failure (Choi et al., 2015). On the research work done by Zhao et al. (2017), Al – CNT composites were consolidated through ball milling, hot pressing and hot extrusion respectively. The results showed ultimate tensile strength of base metal (BM) as 630 Mpa; however, the elongation of BM was only 4% (Zhao et al., 2017). Hassan et al. (2014) synthesized pure aluminium with 2 wt. % CNT using ball milling and extrusion respectively. Milled pure aluminium had 10.2 % elongation and 168.7 MPa tensile strength (Hassan et al., 2014). Zhu et al. (2016) experimental results of 2014 Al – 0.5 wt. % CNTs composites UTS was raised from 530 to 600 and 630 Mpa for treated and untreated CNTs respectively. The total elongation of the composite decreases compared to the pure Al, with pure Al having 13.5 %, untreated Al-CNTs having 12.7% and treated Al-CNTs having 12.0 % (Zhu et al., 2016). Park et al. (2017) synthesized Al with CNTs using ball milling, sintering, melt bending, casting and extrusion respectively.

Both yield and tensile strength were improved while ductility decreases from 21% to 8% (Park et al., 2017). Obtaining the balance between ductility and strength of aluminium composites has been quite a challenge until recent research work by Salama. Salama et al. (2017) successfully fabricated Al- 1wt. % CNT and Al - 2wt. % CNT composites with great ductility and strength by introducing the novel Al-CNT microstructural design where by Single Matrix (SM) and Dual Matrix (DM) structures were prepared. The SM composites were fabricated by dispersing CNTs in aluminium powders. The DM composites were synthesized by embedding pre-processed SM Al/CNT powders into a secondary aluminium matrix. The single matrix and dual matrix samples of Al-CNT composites were synthesized by the solid-state powder processing HEBM technique. Enhancement of ductility by 14% were reported on DM Al-CNTs composites (Salama et al., 2017). Carbon nanotubes reinforced Al matrix composites are used in a different engineering applications such as engine components, aerospace structures, propeller blades and electric cables (Park et al., 2015). As ultra-weight reinforcements, CNTs are preferred because of their superior strength and stiffness, high electrical and thermal properties and anti-corrosive properties (Kayode et al., 2016).

Researchers have investigated mechanical properties of AMCs. However, mechanical properties such as elasticity, plasticity, stiffness, young modulus of elasticity and strain rate sensitivity studies of aluminium composites have been given little attention. Different aluminium applications have certain demands of different set of mechanical properties it should posses in order to meet the standards (Khan et al., 2015). The focus of this research is to synthesize Al – MWCNTs composites with great mechanical properties. Nanoindentation load –displacement curves were used to determine mechanical properties of Al – MWCNTs composites.

1.1 Research problems

Despite the impressive mechanical properties of pure aluminium, wide research has shown some of the limitations of their properties. This includes moderate young's modulus, limited yield and tensile strengths. Those limitations have led to approaches such as alloying elements, precipitation hardening, strain hardening and solid solution strengthening to enhance mechanical properties. However, different approaches had limited success (Polmear, 2005b). Recently researches have focused on composites and reinforced aluminium matrix composites have gained lots of attention. Developed Al – MWCNTs composites have been reported with great strength and limited ductility expect of the research work by Salama et al. (2017). Although aluminium matrix composites strengthened by carbon nanotubes tend to offer replacement for unreinforced aluminium alloys in several applications (Esawi et al, 2010). Challenges such as inhomogeneous carbon nanotubes distribution throughout Al matrix, agglomeration of carbon nanotubes, poor interfacial of carbon nanotubes with Al matrix and formation of Al_4C_3 phase should be overcome in order to attain optimal properties in the Al – MWCNTs composite (Aliyu et al., 2015). Aerospace structural areas require aluminium alloys with great stiffness, great fatigue performance and good strength (Khan et al., 2011). However applications of pure aluminium are limited to those that pose high conductivity, excellent formability and very good corrosion resistance, are preferred where high strength is not essential (Megson, 2014).

In summary, the key research problems are:

- Limited pure aluminium applications due to their mechanical properties.
- Challenges associated with incorporating CNTs into Al matrix.
- Acquiring balance between mechanical properties of sintered Al – MWCNTs composite.

1.2 Aim and objectives

The aim of this work is to investigate the mechanical properties of sintered multi walled carbon nanotubes reinforced aluminum matrix.

The aim will be achieved through the following objectives:

1. Characterise the staring powders and admixed powders (MWCNTs & Aluminium);
2. Dispersion of MWCNTs into Aluminium using ball milling;
3. Sintering of admixed powders using spark plasma sintering;
4. Characterisation of sintered Al-MWCNTs nano composite:
5. Evaluation of the mechanical properties of sintered Al-MWCNTs nano composites using ultra nanoindentation tester.

1.3 Significance and justification of research

More work need to be done to improve dispersion of MWCNTs into Al Matrix and also to explore mechanical properties such as elasticity, plasticity, stiffness, young modulus of elasticity, yield strength and strain rate sensitivity of Al-MWCNTs composite in order to broaden pure Al applications. Acquiring stiffness and plasticity will be of benefit for structural applications in different sectors worldwide. Some potential applications of particles reinforced AMMCs involved being used for production of fan exit guide van in gas turbine engine, being used in producing rotating blades sleeves in helicopters, used for brake system of the trains, valves, crank shafts, drive shafts and microwave (Mosia et al., 2016). If this research is of success potential application Al – CNT composites can be beyond those, which are limited by aluminium mechanical properties. It is taken into consideration that to improve mechanical properties of Al – CNT composite, work still needs to be done to improve dispersion of CNTs.

This study will contribute with knowledge on mechanical properties of Al-MWCNTs composites. Results of this study will be useful for the design of the CNT – Al composites with enhanced mechanical properties.

1.4 Research hypothesis

Carbon nanotubes have been reported to demonstrate excellent mechanical properties that can be explored in strengthening metal matrix composites in order to produce high performance composites. Utilization of carbon nanotubes as a reinforcement material in metal matrices such as aluminium alloy can offer tremendous benefits. Although, carbon nanotubes have advantages and disadvantages, there incorporation can improve the properties of aluminium. The effective reinforcement of CNT will create a synergistic effect in the aluminium matrix that in turn yields great properties of composite material. Developed Al – MWCNTs composites have successfully improved mechanical properties such as hardness (Pillari et al., 2017; Sharma et al., 2016), ultimate tensile strength (Alekseev et al., 2016, Girisha et al., 2014), yield strength (Park et al., 2015, Xiang et al., 2017) and ductility (Salama et al., 2017).

1.5 Scope of the study

The current study of the mechanical properties of spark plasma sintered Al-MWCNTs composites were carried out in University of Johannesburg (UJ) with support University of Witwatersrand (Wits) and Tshwane University of Technology (TUT) laboratories. Characterisation of starting powders, admixed powders and sintered Al-MWCNTs nano composites were carried out using Scanning electron microscope (SEM), Energy dispersive spectroscopy (EDS), Transmission Electron Microscopy (TEM), X- ray diffraction (XRD) and Raman spectroscopy. Experiment test that were conducted using ultra nanoindentation tester and micro hardness test on sintered pure Al and Al-MWCNTs composites.

1.6 Overview of the dissertation

This dissertation consists of five distinct chapters and references.

Chapter 1: Introduction

Gives a brief introduction about the work and explains the motivation and background of the research. It also describes the aim and objectives of the research.

Chapter 2: Literature Review

Consist of the literature review on aluminium alloy, metal matrix composites; carbon nanotubes reinforced aluminium matrix composites, different types of dispersion techniques, various fabrication techniques and mechanical properties of Al-CNTs composites.

Chapter 3: Materials and Methods

The discussion of the as-received materials and the experimental procedures utilized in this work was presented.

Chapter 4: Results and Discussions

Results and discussion chapter entails the findings of all the work conducted during this research. The dispersion characteristics of carbon nanotubes within Al matrix using ball mixing were explained in detail. Furthermore, characterization results from SEM, TEM, EDS, XRD and Raman spectroscopy were investigated and reported to reveal the phases, microstructural morphology and structural integrity of CNT in the composites. The mechanical properties of the Al-MWCNTs samples as well as the test work were explained succinctly.

Chapter 5: Conclusions and Recommendations

Inferences based on the observations from work are reported.

References

All literatures cited in this dissertation are listed.

Chapter 2

2. Literature Review

Pure aluminium with 99% aluminium is of little structural values and its properties includes lightweight, malleable, ductile and being soft. Pure aluminium possesses high conductivity, excellent formability and great corrosion resistance. It is used where high strength is not important; however, solid solution strengthening, strain hardening and precipitation hardening can be used to enhance strength of pure Al (Polmear, 2005b). The demand for advanced materials is ongoing worldwide. This has contributed to production of Al composites since single materials cannot meet requirements in different environments and industries (Kayode et al., 2015; Saheb, 2015). Mechanical properties of aluminium composites are research area that is still being studied even those great works has been done. Enhancement of mechanical properties of aluminium is dated back where it was done through alloying approach (Park et al., 2015). Because of aluminium great properties, it is an ideal alloy for the development of metal matrix composite. MMC has allowed wide applications in different sectors such as aircraft, building materials, automotive and desalination machined components (Kayode et al., 2015). This chapter consists of literature reviewed for this study to be a success.

2.1 Aluminium alloy

The production of pure aluminium is through the electrolytic cell process. Pure aluminium melts at 660℃ and contains less than 1% of impurities. Properties of pure aluminium may be tailor by adding alloying elements so that it meets industries demand. Alloying elements of aluminium will be discussed in broad in the next section. Process such as annealing and work hardening maybe used also to changed aluminium’s properties for example annealed aluminium is soft and ductile while work hardened aluminium is harder and less ductile. Table 2.0.1 shows comparison between annealed and work hardened pure Al.

Table 2.0.1. Mechanical properties of pure aluminium

Mechanical properties	Annealed pure aluminium	Cold worked pure Al
UTS (MPa)	50	100
Elongation (%)	50	50
0.2 % Yield strength (MPa)	15	50
Hardness (Hv)	130	230

2.1.1 Atomic and Crystal structure of aluminium alloy

Thirteen is the atomic number of aluminium atom; this means it has fourteen neutrons and thirteen protons in its nucleus. The vacancy shell contains three electrons, which attribute to the free electron gas of aluminium crystals and excellent electrical conductivity of aluminium atomic crystals. Different lattices are classified as face-centred cubic (FCC), close-packed hexagonal and body-centred cubic (BCC). Aluminium alloys atoms packed together in a good order and assembled into an array to form a crystal lattice. The crystal lattice of aluminium has a face-centred cubic structure (Mondolfo, 1976).

2.1.2 Alloying elements of aluminium alloy

Elements such as copper, magnesium and manganese to mention few, are added into aluminium alloys to improve pure aluminium properties especially its strength. The added elements are referred as alloying elements.

Copper

Aluminium-copper alloys contain 2 to 10% Cu. The strength, hardness expect elongation of both cast and wrought aluminium-copper alloys may be improved by Solution heat treatment and aging.

Manganese

Impurity level in aluminium range from 5 to 50 ppm. The addition of Manganese is preferred for the strength of aluminium alloy but its solubility in aluminium is small.

Magnesium

It has solid solubility in aluminium of about 17 %. The addition of magnesium benefits aluminium with strength and ductility.

Zinc

Zinc presence attributes to great tensile properties of wrought aluminium alloys.

Arsenic

Lower limits of Arsenic are preferred since it is very toxic. Precautions are required where aluminium is used as foil.

Antimony

Solid solubility of Antimony in aluminium is <0.01%.Antimonyis added to restrain hot cracking in aluminium-magnesium alloys.

Beryllium

The maximum of 0.1 %Be is used to restrict the formation of the deleterious iron-aluminium complex. The present of Beryllium reduce oxidation of Al-magnesium alloys at higher temperature on

Bismuth

Bismuth is added to aluminium to achieve free-machining alloys and to aluminium-magnesium alloys to prevent the detrimental effect of sodium on hot cracking.

Boron

Improve conductivity and is great grain finer of aluminium alloy. Effective when used with Titanium.

Cadmium

A maximum of 0.3% Cd may be added to aluminium-copper alloys to increase strength and corrosion resistance and improve rate of age hardening. At range of 0.005 to 0.5%, Cd it is preferred to reduce the time of aging of aluminium-zinc-magnesium alloys.

Calcium

Calcium has low solubility in aluminium and forms the intermetallic $CaAl_4$.Increase strength and decrease elongation of aluminium-silicon alloys.

Carbon

Its presence in Aluminium may leads formation of $A1_4C_{3,}$ which decomposes in the presence of water and water vapour and this may lead to surface pitting.

Chromium

Content of Chromium range from 5 to 50 pp min commercial-purity aluminium.

Prevent recrystallization, control grain structure and prevent grain growth in aluminium-magnesium-silicon alloys during heat treatment.

Cobalt

This alloying element is added to improving strength and elongation of aluminium-silicon alloys. Powder metallurgy has produced Aluminium-zinc-magnesium-copper alloys with Co content of 0.2 to 1.9%.

Gallium

Present at levels of 0.001 to 0.02% in aluminium. Limited effect on mechanical properties.

Indium

Influence the age hardening of aluminium-copper alloys. Present at levels of 0.05 to 0.2% in aluminium alloys.

Lead

Present only as a trace element in commercial-purity aluminium. Improve machinability on other alloys.

Lithium

Increase the oxidation rate of molten aluminium. Promote the discoloration of aluminium foil

Nickel

Solid solubility of nickel in aluminium does not exceed 0.04%.Increases the strength of high-purity aluminium but reduces ductility.

Phosphorus

Its solubility in molten aluminium is ~0.01% at 660^{o}C. Present in a level of 1 to 10 ppm in commercial-grade aluminium.

Vanadium

10 to 200 ppm V is added in commercial-grade aluminium. Precipitated from electrical conductor alloys with boron.

Zirconium

Range from 0.1 to 0.3% in aluminium alloys. Aluminium-zinc-magnesium alloys use zirconium additions to increase the recrystallization temperature and to control the grain structure in wrought products.

Iron

The highest impurity in aluminium is Iron followed by Silicon, preferred because of its solubility in molten aluminium.

Silicon

The range of Si in electrolytic commercial aluminium is from 0.01 to 0.15%.

2.1.3 Aluminium alloy grade

1xxx series

Pure aluminium alloy comprised of 99 % Al and is categorised under 1xxx series of aluminium grades. This series is preferred for properties such as excellent corrosion resistance, excellent workability, high thermal and electrical conductivity hence its application includes transmission or power grid, lines that connect the national grids (Saheb, 2015)..

2.2 Metal matrix composites

Metal matrix composite is the constitute of a matrix to which reinforcement is added to obtain the desired properties. It has three important features that determine its characteristic namely the matrix, the reinforcement and the matrix-reinforcement interface (Mosisa, 2016). The size of reinforcement may be used to categorise metal matrix composites hence metal matrix composite reinforced with nano particles are referred as metal matrix nano composites (MMNCs).The need to enhance mechanical properties of metals has contributed to the development of MMC wherein various reinforcements such as particles, whiskers or fibres has been used (Saheb, 2015). High tensile strength (Zhu et al., 2015), great hardness (Travessa et al., 2015), yield strength (Shin et al., 2016), Wear resistance (Meenakshi & Mahamani, 2016) and better corrosion resistance (Duarte et al., 2017) have been achieved in MMCs. Developed composites materials are aimed to limit challenges if not eliminate problems in different applications in automotive components, sports goods, aerospace parts, consumer goods and marine sectors (Anirrhuda, 2015). Metal matrix composites with nano particles are suitable for functional and structural applications due to promising properties they are being studies worldwide recent years. Metal matrix composites have been widely studied and are preferred over convectional material owing to their improved properties.(Murthy et al., 2015).

2.2.1 Strengthening mechanisms of Al-CNTs composites

Four different mechanisms that can be used to describe the reinforcement strengthening effect in a metal matrix composite are as follows:

i. Load transfer

It is the most common strengthening mechanisms. The strengthening in composites occurs by transferring load between the matrix and reinforcement via interface interactions. Chen et al.(2017) showed that to attain excellent strengthening result in the composite, high aspect ratio of the nano materials is necessary for the load transfer. Therefore, better reinforcement depicts that applied load on the composite must be effectively distributed.

ii. Orowan mechanism

It is much related to the movement of dislocation. It preferred for aluminium alloys that are strengthened by fine precipitates since carbon nanotubes attributes to fine particles. This mechanism requires small spacing between particles of the reinforcements. It has also been concluded that reinforcement with rod-like structures offers better strengthening in comparison to reinforcements with spherical shapes (Park et al, 2015).

iii. Thermal mismatch

This strengthening mechanism requires a significant coefficient of thermal expansion (CTE) between matrix and reinforcements to produce a higher dislocation density, In order to achieve increased strengthening. Park et al. (2015) used load transfer, Orowan and thermal mismatch strengthening mechanisms to study the strengthening efficiency of CNT/Al composites.

iv. Shear lag model

This strengthening mechanism involves transfer of load by interfacial stress.

Esawi et al.(2010) used shear lag model on Al-CNT composite to explain the observed elastic modulus of the composites. This was represented mathematically by:

$$E_c = K_1 V_{CNT} E_{CNT} + (1 - V_{CNT})\, Em \ldots\ldots\ldots\ldots\ldots \quad 2.1$$

Where E_c, E_{CNT} and E_m are the elastic modulus of composite, elastic modulus of CNT and elastic modulus of matrix respectively. V_{CNT} is the volume fraction of CNTs and K_1 is the efficiency parameter of CNT that depends on the length and diameter.

2.3 Aluminium matrix composites

Aluminium matrix composite is the constituent of aluminium alloy, which is termed as matrix phase, and other constituent that serves as reinforcement is embedded in aluminium matrix. The nature of constituents and content plays the crucial role in tailoring properties of AMCs to suits different industrial applications (Selvakumar et al., 2017). AMCs have superior properties and can be taken as replacement of aluminium alloy.

They are viewed as potential composites that can have good economic effect by using selective reinforcement techniques and near–net shape forming to produce different commercial applications. The innovative change made in component design has led to successful development of commercial and military AMCs applications. For the period, AMCs have used in various structural, non-structural and functional applications in different sectors. AMCs were intended to replace materials such as aluminium alloys, ferrous alloys, titanium alloys and polymer based composites in several applications (Sukappa, 2003).

2.3.1 Classification of Aluminium matrix composites

AMC are categorised based on the form of the reinforcement as Particle-reinforced AMCs (PAMCs), Short fibre-reinforced AMCs (SFAMCs), fibre-reinforced AMCs (FAMCs) and Mono filament-reinforced AMCs (MFAMCs). AMCs forms of reinforcement could be continuous or discontinuous (Sukappa, 2003).

2.3.2 Properties of Aluminium matrix composites

Gao et al. (2013) and Ozkan (2016) have reported that aluminium matrix composites properties have been improved and are of reduced density. Properties such as strength, hardness, ductility, ultimate tensile strength, yield strength, wear resistance, great processing performances and corrosion resistance.

2.3.3 Application of Aluminium matrix composites

Potential applications of particles reinforced AMMCs includes being used for production of fan exit guide van in gas turbine engine, rotating blades sleeve in helicopters, brake system of the trains, valves, brake system, crank shafts, drive shafts carrier plates and microwave (Mosisa et al., 2016). Three specific areas in which aluminium base MMCs potential applications concentrate on automotive industry, aerospace sector and leisure market (Bharath et al., 2012). Performance, economic and environmental benefits are the driving force for the use of AMCs in different sectors. The great benefits are in transport sector because it has lower fuel consumption, lower noise and airborne emission.

Currently, aluminium matrix composites are been used in high technology structural applications in aircraft, defence and automotive (Liu et al., 2016). It has been concluded that aluminium is an ideal alloy for production of metal matrix composites since it has expanded its applications in different industries (Kayode et al., 2015).

2.4 Carbon nanotubes as reinforcement

The discovery of Carbon nanotubes is dated back in 1991 (Peng et al., 2014). Bernal et al. (2015) dispersed MWCNT, SDWCNT and SWCNT within alumina matrix using convectional mixing for pristine CNT dispersion followed by Spark Plasma Sintering. This was done to evaluate the CNT effect on hardness and fracture toughness of Al_2O_3 composite. MWCNTs compared to SWDCNT and SWCNT had better response as reinforcement of Al_2O_3 composite (Bernal et al., 2015). Chenglin et al. (2017) used double –walled carbon nanotubes reinforced Al composites to study the mechanical strength of interfaces. The results indicate that the shear lag effect on CNT-Al interfacial possess average interfacial shear strength (IFSS) of about 28.7 Mpa (Chenglin et al., 2017). Ogawan et al. (2017) used both carbon nanofibers and carbon nanotubes as reinforcement to Al composites. A variation of reinforcement content of 1,2,3, 4, 0.5 and 1.5 vol. % was used. Comparison between Al-CNF and Al-CNTs shows that yield strength and ultimate strength (mechanical properties) were all higher in CNTs reinforced aluminium composites. It was further suggested that the results might be influenced by higher strengths and higher elastic moduli of CNTs, which surpass than of CNF and to the different microstructure of composites (Ogawan et al., 2017).

2.4.1 Types of carbon nanotubes

Different types of Carbon nanotubes are Single-walled nanotubes (SWNTs), Multi-walled nanotubes (MWNTs) and carbon nanofibers (CNFs).SWNTs have smallest diameter compared to MWCNTs and CNFs and their length is in the micrometre scale. MWCNTs consist of several SWNTs with each individual tube consisting of different chiralities. The MWCNT inner and exterior diameters range from 2 to 10 nm and 20 to 70 nm respectively and their length range from 5–50 mm. Of all CNTs types, CNFs is the one with larger diameter (ranging from 50 to 200 nm) and their length can be anywhere from micrometres to several centimetres.

Production of CNFs is higher than SWCNTs and MWCNTs and its cost is lower. A CNFs disadvantage are that they usually contain much more defects than MWCNTs and its strength compares to other CNTs. Young's modulus of SWCNT is higher than of the best steel. MWCNT shows lower mechanical properties than SWCNT but previous research results have proven that MWCNT is more chemical stable (Peng et al., 2014). Carbon nanotubes are the most effective reinforcement to produce composite material; they have been used to reinforce different matrices, such as metals, polymer and ceramics (Duarte et al., 2015). Figure 2.0.1 shows different type of carbon nanotubes.

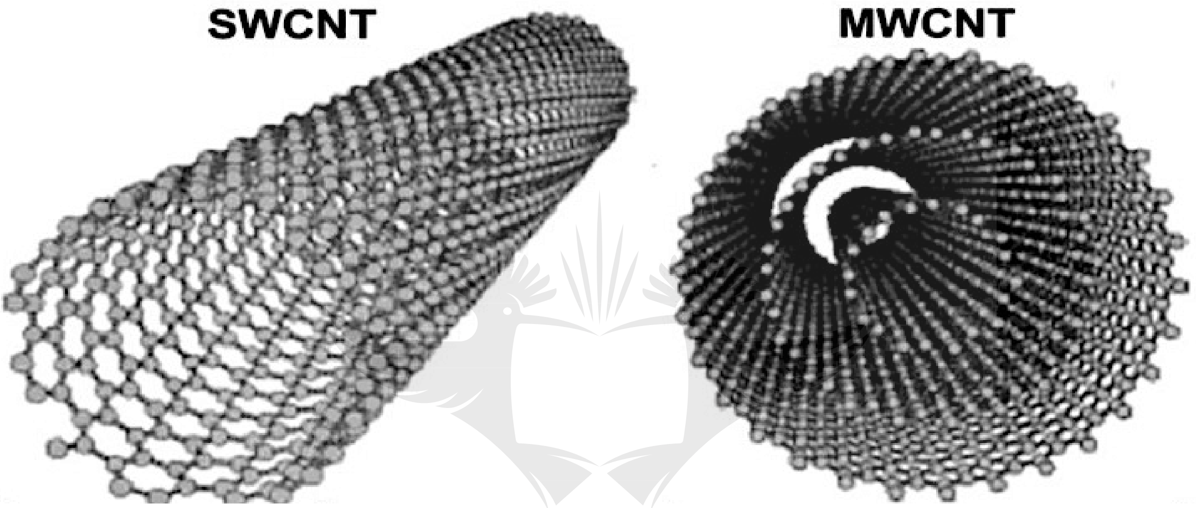

Figure 2.0.1. Carbon nanotubes (Martins et al., 2013)

2.4.2 Properties of carbon nanotubes

As ideal ultra-weight reinforcement, CNTs are preferred due to their properties (superior strength and stiffness, high electrical and thermal conductive, high flexibility, low density, high aspect ratio and anti-corrosive properties). The nanotubes have gain attention as reinforcement in metal matrix because of polymer-matrix composites of high performance in which nanotubes were used as reinforcement (Duarte et al., 2015). The aluminium matrix composites reinforced with CNTs are valuable because of their outstanding properties which includes lightweight, high strength and anti-corrosive properties that make them ideal composites in aerospace and automobile industries. The potential application prospects in aerospace and automotive industries have influenced the use of CNTs as reinforcement of aluminium based composites (Guo et al., 2017). Table 2.0.2. show different types of carbon nanotubes and their mechanical properties.

Table 2.0.3. Mechanical properties of CNTs (Loos, 2015)

Types of CNTs	Density (g/cm ^{3})	Young's modulus (GPa)	Maximum Resistance (GPa)	Elongation (%)
Carbon Fibers	1.93	588	3.82	0.7
SWCNTs	1.33	1054	150	12
MWCNTs	2.6	1200	150	2

2.4.3 Structures of carbon nanotubes

The structure of Carbon nanotubes are one-dimensional structure. SWCNTs have a single graphene sheet enfolded to form cylindrical shape while MWCNTs is a group of SWCNTs. The individual nanotubes are bonded by strong van der waals force. The C–C bonding in CNTs is consisting of honeycomb lattices with each atom joined to three neighbours, as in graphite (Peng et al., 2014).

2.5 Problems associated with incorporating CNTs in metal matrix

The development of MMCs leads to several challenges such as agglomeration of the reinforcement in matrix, grain growth of the matrix, poor wettability, poor dispersion and poor interfacial of the reinforcement with the matrix (Aliyu et al., 2015). The agglomeration of CNT in metal matrix as one of the major challenges for CNT reinforced composites is associated with premature crack initiation and fracture in tension (Guo et al., 2017). CNT tends to hold together and entangle with each other due to strong intrinsic Van der waals forces. To reduce the agglomeration of CNTs, mechanical alloying is recommended by many researchers to disperse CNTs within aluminium matrix. Liu et al. (2015) fabricated aluminium-CNT composites, ball milling were used to admixed aluminium and carbon nanotubes powders. The effect of ball milling time was studied and results showed that 6 hours' of ball milling achieved uniform dispersion of CNTs in aluminium matrix. Esawi and Morsi study of the effect of ball milling time on Al-CNT composite powders and obtain homogeneous dispersion of CNT in aluminium matrix after 48 h of ball milling. Ball milling parameters should be careful selected to avoid damage on MWCNTs and also to obtained homogeneous dispersion (pillars et al., 2017).

The brought together of liquid and solid is influence by intermolecular interaction, the ability of a liquid to maintain contact with a solid surface is known as wettability. Carbon experience poor wettability in molten metal as result of the large surface tension difference. Different types of materials such as Nickel (Ni), Copper (Cu) and Silicon Carbide (SiC) has been used to coat CNTs to enhance its wettability yin molten Al. The coated CNTs are then used as precursor for the incorporation in molten Al, this involves the following stages: mechanical milling of Al powder and CNTs to produce powder precursor followed by electroplating coating material that attribute to better wetting of CNTs with molten Al during the process (Muhammad & Muhammad, 2016). Muhammad & Muhammad, (2016) researched 10 and 20 wt. % of Multi wall carbon nanotubes, the results exhibit good wetting of CNT within matrix with some segregation was also observed (Muhammad& Muhammad, 2016). Homogeneity and final mechanical properties of the composites depends on the quality of dispersion.

Different techniques have been used to solve poor dispersion ability in metal matrix with limited success. Duarte et al. (2016) disclosed an innovation way to uniformly disperse COOH functionalised MWCNT within Al alloy foams by using the powder metallurgy method (Duarte et al., 2016). Through the innovation approach, Isabel et al. (2015a) achieved homogenous dispersion of powder. Isabel et al. (2015a) experiment results show that better dispersion of CNTs reinforcement within metal powder by using high energy mixing process; however limitation of this success were structural damages and loss of CNTs structural –integrity. This is particular major concern for single-walled CNTs since their tubular integrity will be lost but not issue for MWCNTS since the results will be damage in outer walls (Isabel et al., 2015a).Homogeneous dispersion of CNT in molten matrix were achieved by mechanical stirring of the melt. Ball-milled aluminium powder-CNTs melt were mechanical stir first.

Followed by preparing green billet of the milled that is incorporated in molten Al during mechanical stirring. Homogeneous dispersion and good interfacial bonding were achieved which attributed to enhanced mechanical strength (Mohammad & Mohammad, 2016). Functionalized treatment has showed its potential in obtaining homogeneous dispersion of CNT whereby Carboxyl or hydroxyl groups is introduced on the CNTs. Calculations shows that about 0.2 is added to the graphite layer toughness through carboxyl or hydroxyl group. Higher roughness reduced Van der Waal’s force by reducing the proximity of interacting surfaces and by increasing the distance between their atoms.

The disadvantages of carboxyl treatment are the potential to introduce defects on the surface of CNTs and to remove carbon impurities (Zhu et al., 2016). Zhu et al. (2016) studied both treated and untreated carbon nanotubes. The treated carbon nanotubes were treated by Carboxyl. Results shows that treated carbon nanotubes were easier to disperse compared to the untreated carbon nanotubes (Zhu et al., 2016). Zhou et al. (2016) used functionalised treatment of purifying MWCNTs with concentrated HNO_3 for 12 h. Acid treatment were done using H_2 SO_4 / HNO_3 mixture (3: 1, v/v) in the ultrasonic bath for 4h at 323k. The acid – treated MWCNTs were completely dried in an oven at 323k for 12h. The MWCNTs and Al were prepared using Ultrasonification by individually dispersed Al and MWCNTs powders in ethanol for 1 hour. The MWCNT suspension was added by drop into Al suspension. The admixed solution of 0 to 5.0 vol. %. MWCNTs were mechanically stirred for 30 minutes, followed by drying in the oven at 343 K for 24h. Acid treatment attributed to remove amorphous carbon layer and to functionalize the surface of MWCNTs that results in promoting the uniform dispersion of MWCNTs (Zhou et al., 2016).

It is understood that the presence of a large amount of aluminium carbide decreases the mechanical properties of an Al-CNT composite. It is preferable to minimise Al_4C_3 formation during the composite manufacturing process so that produced material with have better mechanical properties. The existence of a minute amount of Al_4C_3 can increase the ad hence between CNT and the metal matrix (Alekseev & Predchenskly, 2016). Since Al_4C_3 can appear not only during high energy mixing but also during the hot pressing of powder mixtures. It is necessary to control its quantity at each step of composite manufacturing process. Formation of Al_4C_3 phase in the Al-CNT system has been observed on different fabricated composites. (Chen et al., 2016).Bradbury et al.(2013) supported that during hot pressing CNTs are partially converted into aluminium carbide through the use of TEM and XRD characterisation analysis. The key to Aluminium carbide problem is to control its amount and size (Bradbury et al., 2013).

The present of impurity phase (Al_4C_3) at the interface of Al-MWCNTs composites and inhomogeneous dispersion of CNTs limits the effectiveness of the CNTs as reinforcing material of Al matrix (Sharma et al. 2016). Using micro–sized SiCp as a vehicle. Li et al. (2016) achieved well dispersion in the Al matrix. Micro sized hybrid reinforcement with CNT growing on the surface of SiC particles were synthesized by a chemical vapour deposition method.

Admixed powders of Al and CNTs were achieved through powders blending. Prone to crack during mechanical loading, premature failure and low ductility of the composites are limitations of micro–sized particles (Li et al., 2016). A lot has been done to overcome inhomogeneous dispersion of CNTs within aluminium matrix in research work. Different fabrication techniques such as HEBM, LEBM and Ultrasonification showed potential in achieving uniform dispersion of CNT with some limitations.

2.6 Dispersion techniques

Dispersion of carbon nanotubes within aluminium matrix is still a challenge for Al-MWCNTs composites. Dispersion techniques such as LEBM (Bradbury et al., 2016), HEBM (Shin et al., 2016) and Ultrasonification (Park et al., 2015) has been explored with limited success. Researchers are fond of combining two dispersion techniques to obtained better dispersion. Xu et al., 2017 used both high and low energy ball milling technique to dispersed CNTs into Al matrix while Zhu et al. (2015) used ball milling and Ultrasonification.

2.6.1 Ball milling

Ball milling is a process in which grinding balls crush and disintegrate the materials into small sizes. Factors that are being controlled during ball milling are speed of rotation, amount of the sample, size and grinding balls and grinding time. During ball milling, material undergo three stages i.e. getting flattened into flakes, getting cold welded into lamellar-structured particles and then getting fragmented into smaller particles. In case of current study, CNTs were firstly dispersed on the surface of Al matrix and then occluded by Al and trapped in the cold welded particles. Different type of ball milling are High Energy Ball milling and Low Energy Ball Milling (Murthy et al., 2015).

2.6.1.1High energy ball milling

High-energy ball milling produces high-energy impacts and high frequency from balls to material. It is divided as wet and dry high-energy ball milling due to the state of mixture involved.

Different materials react differently during HEBM i.e. ductile components particles are initially flattened while in brittle component particles undergo size reduction by fragmentation. The advantage of High-energy ball milling is that it is easy to use. In this process powder particles are trapped between highly kinetic colliding balls and inner surface of the vial (Murthy et al., 2015). Shin et al. (2016) used high energy ball milling (HEBM) to disperse 5 vol.% multi walled carbon nanotubes (MWCNTs) and 0.5 vol.% graphene (FLG) into 2024Al powders respectively. The milled powders were consolidated by hot pressing. 2024Al powder had diameter of < 120um, MWCNT had diameter of 8- 5 um and FLG had diameter of 6-8 nm. HEBM was carried out at 500 rpm for 6 hours. A process control agent of 1 wt.% stearic acid was applied to minimise cold welding and weight ratio of ball to powder was 15: 1 was used and also the chamber was stirred by horizontal impellers. The ball milled powder was consolidated by hot pressing. Al_4c_3 occupied small area on both MWCNT-Al and FLG-Al composites. Morphology of MWCNT-Al composite showed several deformed regions.

Pillari et al. (2017) fabricated AA2219 reinforced with graphene and MWCNT nano composites, by using high-energy ball milling followed by vacuum hot pressing. HEBM were carried out with balls of 10mm diameter, ball to powder ratio of 4: 1 at a rotating speed of 200rpm for 6h. Toluene was used as a PCA during ball milling to prevent powders sticking on milling media and walls of stainless steel container. The study revealed that Graphene is better reinforcement compared to MWCNTs.

Disadvantages of HEBM

Limited production

Maintance is difficult

Time consuming (Murthy et al., 2015)

2.6.1.2 Low Energy Ball Milling

Ogawa et al. (2017) used two types of CNTs, which are vapour grown carbon fibers (VGCFs) and MWCNTs as reinforcement of pure Al matrix. The dimensions of used materials are as follows: VGCFs with a diameter of 150nm, MWCNTs with a diameter of 65nm and pure Al with30 µm average diameter. Aluminium matrix composites were consolidated using ball milling followed by hot extrusion.

The VGCFs and Al powder were mixed in planetary ball mill. Stainless jars containing VGCFs, Al powder, stainless steel balls and stearic acid were rotated at 200 rpm for 3 h. the weight fraction of 20: 1 was applied. Rotation for 20 min was followed by suspension for 40 min was repeated nine times to prevent excessive cold welding of the powder. Scanning electron microscope (SEM) showed that both reinforcements were well dispersed in Al matrix. Presence of CNTs agglomeration appear in both Al composites of 4 vol.% reinforcements. Kwon et al. (2015) mixed Al powder and 1 volume fraction (%) of the nanoparticles in planetary ball mill for 3 hours at 300 rpm using 10mm diameter balls. Ball to powder ratio of 10: 1 and 20 wt.% heptane as a process control agent. Nanoparticles were well dispersed in the composite powders. Zhu et al. (2015) used treated and untreated carbon nanotubes (average diameter of 25 nm and length of 1. 25 µm) as reinforcement of 2014 Al alloy powder with average powder size of about 10um. The experiment process used involved dispersing CNTs in the 250 ml ethanol, sonicate for 1 hour and pour into 250ml ethanol solution into 49.75g 2014 Al alloy powders respectively.

Followed by stirring for 30 min using magnetic stirring then drying at 333k for 24 hours in an oven. Ball milling were carried out in planetary ball mill at a constant speed of 300rpm for 6 h with ball to powder ratio of 8:1 and 0.5 g stearic addition into dried mixture. Ball milled powder were packed and cold compacted. The untreated CNTs had poor dispersion and its CNT were largely agglomerated within 2014Al powders. The treated CNTs were well dispersed in 2014Al powders compared to the untreated CNTs, with some slightly agglomerated treated CNTs in mixed powders (Zhu et al., 2015).Bradbury et al. (2016) mixed Al (Particle size of less than 65 µm) and MWCNT by a laboratory milling, which was conducted using 10 mm steel balls with ball to powder ratio of 10: 1 at a speed of 360 rpm. 20 wt. % heptane was added as PCA. Milling was conducted for a total milling time of 20 h with a repeated sequence of 20 min milling followed by 10 min pause interval. The milled powders were consolidated by hot pressing.

Up to at least 6 wt. % MWCNT uniformly dispersed in Al matrix. No large agglomerates were identified (Bradbury et al., 2016). Hildagon et al. (2017) used pure Al powder with an average particle size of 48 µm as well as grapheme oxide and carbon nanotubes to fabricate AMCs using ball milling followed by hot extrusion. Ball milling was carried for 20min at 70 rpm with ratio of ball to material of 10: 1. Dispersion was poor. Cluster of reinforcements are observed in both Al-CNTs and Al-GO materials.

Extend of clustering was found to be higher in the Al-CNT composite than in the Al-GO composite (Hildagon et al., 2017). Table 2.0.4 show the Dispersity of CNTs using two different mixing techniques.

Table 2.0.5. Dispersion of CNTs based on different techniques (Shadakshari et al., 2015)

Mixing techniques	Al powder morphology	CNT morphology	Dispersion effect
LEBM	Round shape	Medium damage	Dispersed but agglomerates still exist
HEBM	Round shape	Severe damage	Effectively dispersed but CNTs agglomerates

2.6.2 Ultrasonification

Ultrasonification is a simple method used for liquid dispersion. During Ultrasonification CNTs are pre mixed in Al matrix by a standard stirres and then homogenised by ultra sound, Dispersion procedure during Ultrasonification involves three physical phenomena, which are cavitations, heating and formation of free radical (Park et al., 2015). Ultrasonic is an effective route of nanotubes dispersion in liquids. Guo et al., 2011a; Guo et al., 2011b and Sharma et al., 2017 used Ultrasonification to disperse CNT within Al matrix. Guo et al. (2011a) fabricated Al-MWCNTs composites with Al powder of two different particles size (20 µm and 2 µm). Fabrication process involved ball milling and spark plasma sintering respectively.BPR weight ratio of 10: 1was used. To decrease agglomeration CNTs were ultrasonic in ethanol for an hour. The pre-treated Al and 1 vol. % MWCNT powders were then ball milled for 5 h in planetary ball mill under argon atmosphere using pure ethanol as liquid medium (Guo et al. 2011a).

Guo et al. (2011b) ultrasonically treat CNTs in ethanol for 1 hour, to decrease agglomeration. The admixed powders solution of the CNTs and Al were dried at 80℃ for 5 h to evaporate ethanol in vacuum oven, and then the dried admixed powders were sintered by SPS. Uniform dispersion was achieved for rest of composites expect Al-1.0 vol.% CNTs composites (Guo et al., 2011b).

Sharma et al. (2017) consolidate Al-CNTs composites using Ultrasonification (physical mixing method) and cold pressing respectively. Diameters of the nanotubes were 20-30 nm, the length of 5- 15nm, the average particle size of nano Al was 100 nm. The CNTs were soaked in 200ml of ethanol and sonicate with the help of an ultrasonic probe sonicator (Frequency = 20KHz, power = 100w) for 1 h. The weighed amount of Al nano powder was then added to the solution of dispersed CNTs, which was again sonicate for 1 h. subsequently the mixture was dried at 50ºc on a hot plate to obtain desired nano composites powder, the powder was then compacted. CNTs were homogeneously dispersed in the Al matrix. The agglomerations of CNTs were rare (Sharma et al., 2017). Limitation of Ultrasonification process is agglomeration of CNTs (Guo et al., 2011b). Figure 4 shows mechanism of Ultrasonification.

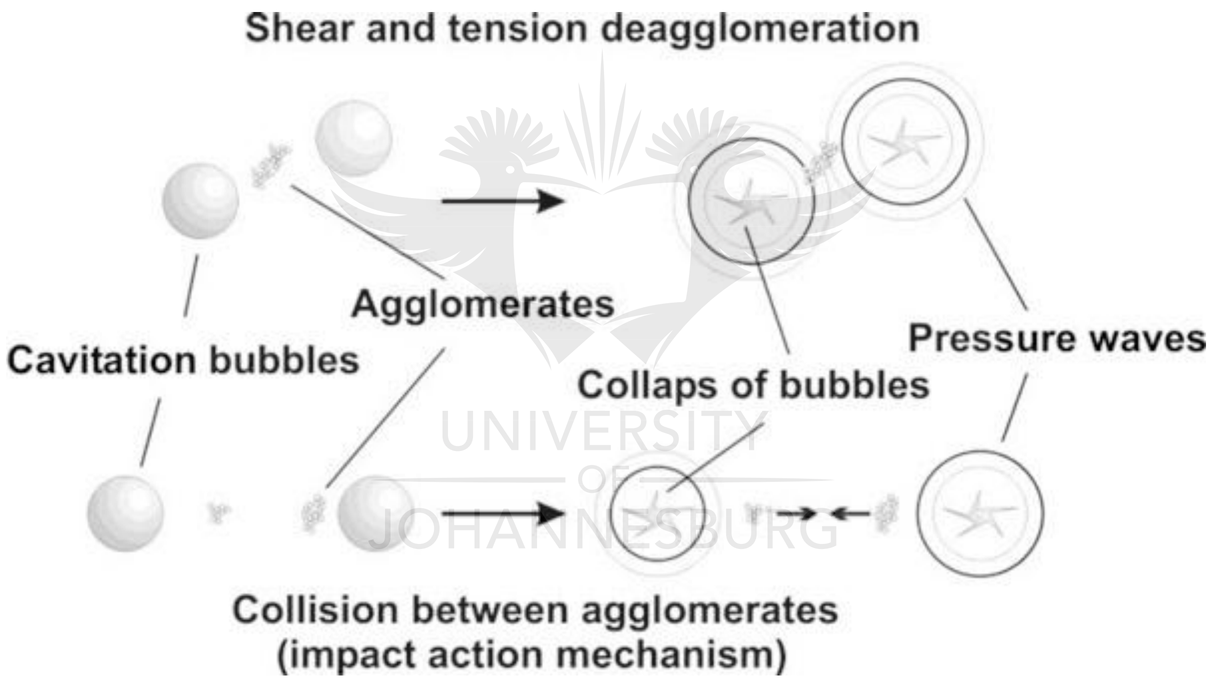

Figure 2.0.2. Main action mechanisms of Ultrasonification (Park et al., 2015)

2.7 Fabrication techniques

There are different methods of fabricating Al-MWCNTs composites such as liquid state, solid state and deposition process. Liquid state process includes stir casting, compo casting and squeeze casting. Solid-state process includes powder blending, ball milling, spray deposition etc. in situ involves ultrasonic assisted casting.

Various researchers have explored methods such as powder metallurgy (Chen et al., 2017); stir casting (Samuel Ratna Kuma et al., 2017), mechanical alloying (Pillari et al., 2017), spark plasma sintering (Guo et al., 2017) etc. Each method has its advantages and disadvantages; the use of the fabrication techniques depends on different factors such as level of reinforcement loading and the degree of structural integrity (Chen et al., 2017). For this study, powder metallurgy route was used.

2.7.1 Powder metallurgy

Powder metallurgy involves producing metal powders and manufacturing powder objects from individual or admixed powders. Powders may be alloyed with different of elements. Three steps involve during production of P/M parts are powders mixing with additives and lubricants, compacting of the admixed powders and heating the green compacts in a furnace in order to bond the particles. In general, powder metallurgy involves four basis steps i.e. powder manufacturing, blending of powder, compacting of powders in a die and sintering. The advantage of powder metallurgy developed parts is properties, which includes sufficient strength and good density. As one of the major fabrication method for production of AMCs, it may results in better interface between the reinforcement and matrix alloy and enhances mechanical properties of the composite. Among all the fabrication methods researchers are very fond of powder metallurgy technique for consolidation of Al- CNT composites (Peng et al., 2014, Shin et al., 2016, Chen et al., 2017&Guo et al.,2017, Zhu et al., 2016).

Powder metallurgy through high energy ball milling has gained much attention on various research work as fabrication technique for Al-CNTs composites. Initial use of powder metallurgy involved short milling times of between 5-10 minutes so that CNTs are not destroyed. Bradbury et al. (2013) reported that longer milling time attributes to enhancement of properties (Bradbury et al., 2013). Esawi et al. (2015) observed that longer ball milling results in disentanglement of CNTs, damaged of CNTs structures and achieve dispersion of CNTs. The damaged CNTs are reported to be easily to react with Al to form Al_4C_3 (Esawi et al.,2015). Figure 2.0.3 Shows powder metallurgy processing.

Advantages of powder metallurgy

- Powder metallurgy can produce MMC in the wide range (Peng et al., 2014; Ravichandra et al., 2015).
- Powder metallurgy prevents formation of cluster (Murthy et al., 2015).
- Powder metallurgy such as HEBM and SPS has effectiveness of consolidate Al-CNT composites with much higher CNT loadings, high controllability of the process parameter and low formation of Aluminium carbide (Salama et al., 2017).
- Powder metallurgy produces quality and close tolerances products in a fair price (Chen et al., 2015).
- Powder metallurgy is low processing temperature in comparison with other techniques (Ravichandra et al., 2013).
- Powder metallurgy assists in achieving high production rates (Sivara et al.; 2016).

Disadvantages

- During powder metallurgy methods, most of the challenges faced are present of aluminium carbide and poor CNTs disperse in the Al matrix.
- The need of expensive powders and its involvement of complicated process during material fabrication (Murthy et al., 2015).

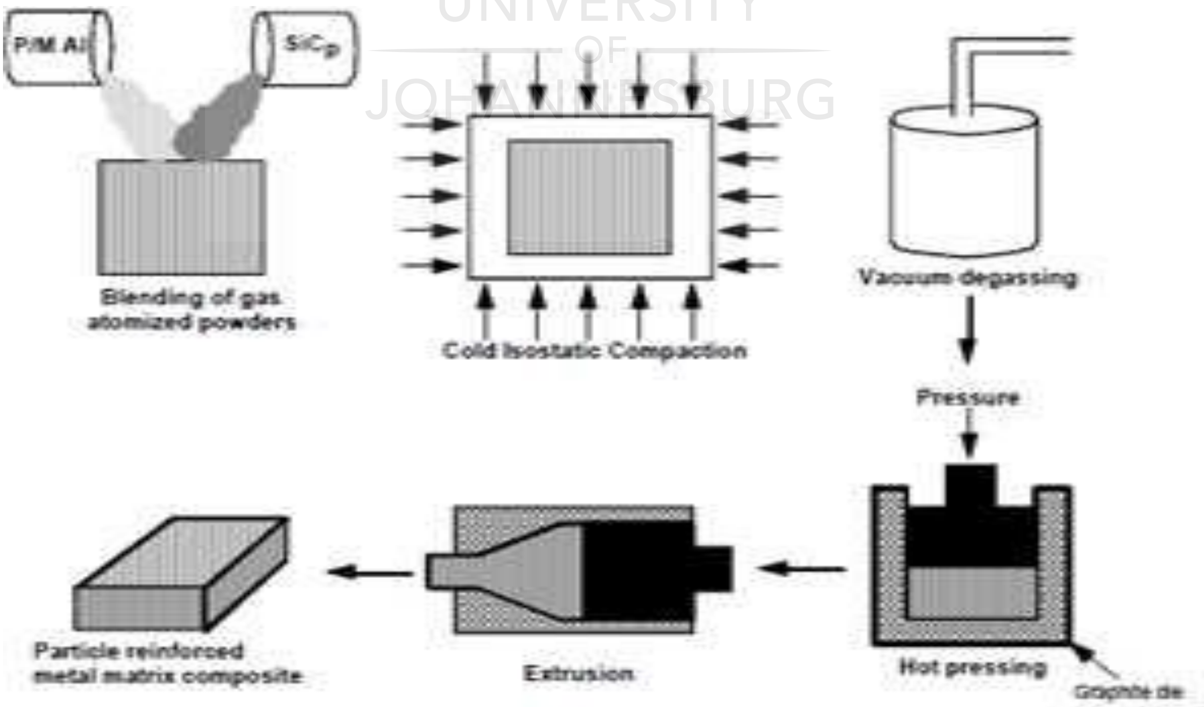

Figure 2.0.4. Processing of Powder Metallurgy (Rana& Dan)

2.7.2 Spark plasma sintering

Spark plasma sintering is powder consolidation process used for processing conductive and non-conductive materials. SPS is great methods for manufacturing fully dense material and has been used for nanocomposite powder consolidation. Advantages of SPS usage are enhancement of materials properties, effective interface formation and cleaner grain boundaries, which contributes to its attention. Nie et al. (2017) fabricated Al - Mo-CNT composites using powder mixing and SPS respectively. A graphitic die with an inner diameter of30 mm were used to load the admixed powders which were consolidated at 580ºC with a holding time of 5 min, heating rate of 100ºC/min and pressure 40 MPa. The addition of Mo during fabrication of Al - Mo-CNT composites prevented the direct contact of Al with CNTs; which attributed to no Al carbide but Mo-CNTs agglomerated in higher CNT content. Cluster of Mo-CNT on Al matrix reduced mechanical properties of Al composites (Murthy et al., 2015).

Nie et al. (2017) research had showed that SPS is limited to agglomeration of CNTs (Nie et al., 2017). Zhu et al. (2015) effectively used SPS to consolidate treated and untreated carbon nanotubes - 2014 aluminium composites with sintering temperature of 793 k and pressure of 50 MPa for 10 minutes and reported enhanced mechanical properties of 2014Al-CNTs composites excluding ductility (Zhu et al.,2015). Guo et al. (2017) studies showed that sintering temperature plays a crucial role in mechanical properties of Al composites. At a constant concentration of 0.75 CNTs, mechanical properties of the composite were significantly improved by increasing sintering temperatures from 590 to 630 ℃ (Guo et al., 2017). Figure 2.0.5 show Spark plasma sintering.

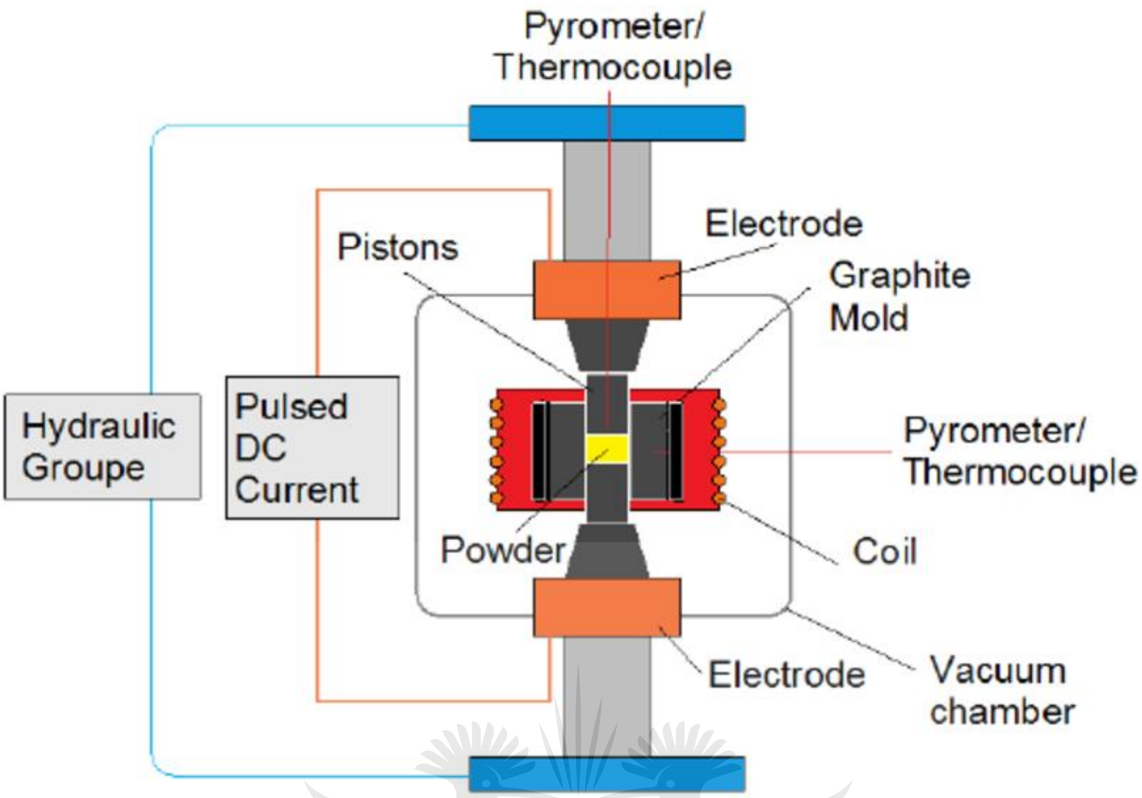

Figure 2.0.6. Spark plasma sintering (Denis et al., 2015)

Three main mechanisms of SPS are plasma heating, joule heating and plastic deformation (Tokita,1999).

i. **Plasma heating**

This involves the creation of electrical discharge in the particles of the powder. This generally leads to incipient heating of the surfaces to form necks. Afterwards, the heat generated is uniformly distributed to produce a solid sample.

ii. **Joule heating**

During this stage, electric current flows through the particles by virtue of the necks connecting them. The flow of electrical current produces joule heat and it main function is to initiate increase in the diffusion of atoms or molecules in the necks. This enhances the increase in size or growth of the atoms or molecules.

iii. **Plastic deformation**

In this stage, the material that has been subjected to heating tends to be softer. The applied uniaxial load created by the equipment also exerts plastic deformation on the material. Plastic deformation combined with diffusion yields densification of the sintered powder to a range of 99% of its theoretical density (www.substech.com).

2.7.3 Stir casting

Stir casting is a liquid state process in which mechanical stirring is used to mixed molten metal and reinforcement. Then the liquid material is cast by casting methods. It is one of the simplest fabrication technique for production of aluminium matrix composites (Prasad Reddy et al.,2017). Samuel Ratna Kuma et al. (2017); Girisha et al. (2014) and Meenakshi & Mahamani (2013) fabricated Al-MWCNTs composites using stir-casting method. Stir casted Al-MWCNTs composites had improve hardness (Girisha et al., 2014), strength (Girisha et al., 2014) and corrosion properties (Meenakshi & Mahamani, 2013.;Samuel Ratna Kuma et al., 2017). Figure 2.0.7 show Set up of stir Casting Design.

Advantages of stir casting

- Ability to manufacture composites with higher volume fraction of reinforcement
- Flexibility
- Good matrix reinforcement bonding
- Great production for near net shaped composites (Murthy et al., 2015).

Disadvantage of stir casting

- Greater agglomeration
- Poor wettability
- Poor incorporation of reinforcement (Murthy et al., 2015).

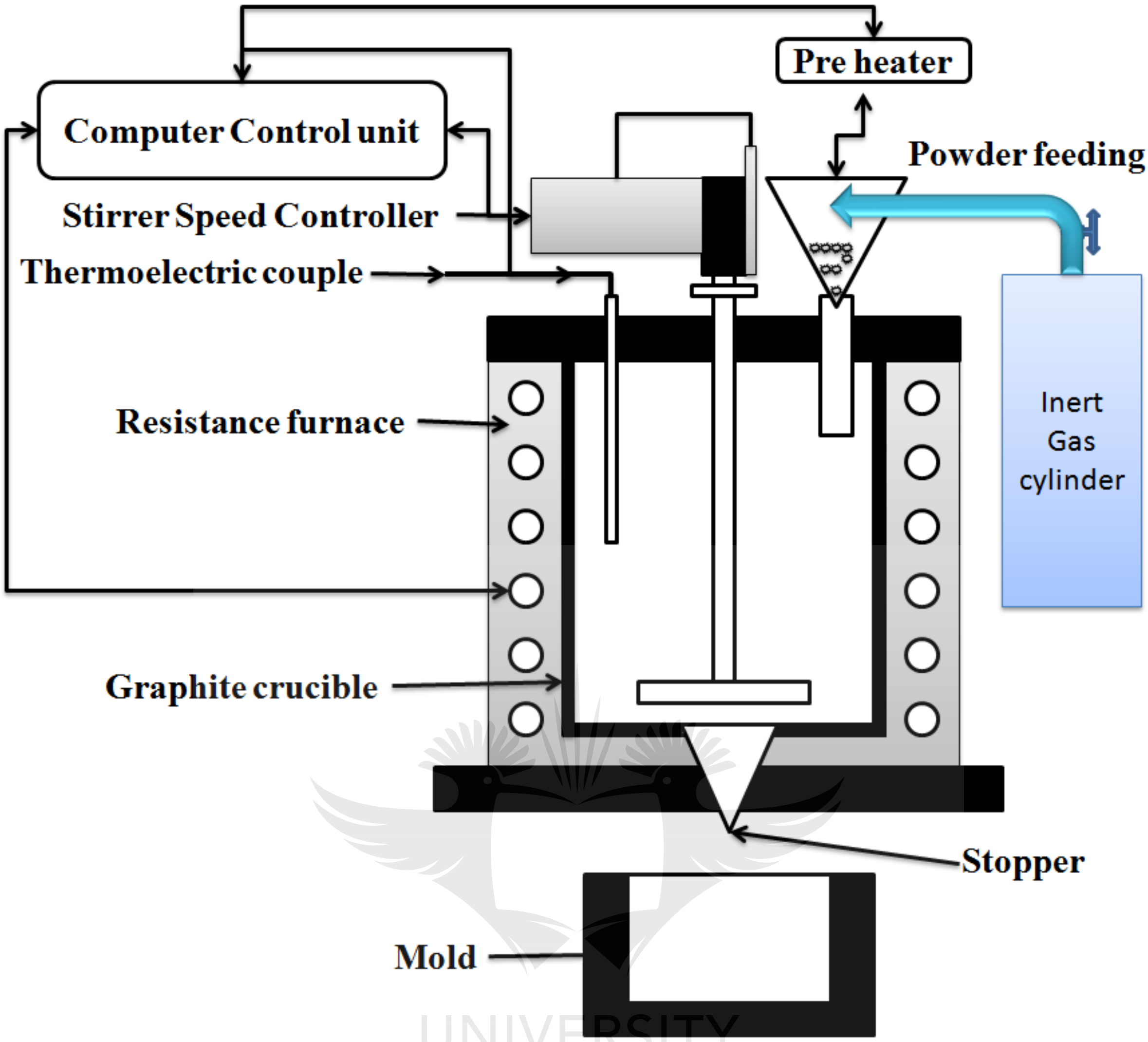

Figure 2.0.8. Stir Casting Design Setup

2.8 Mechanical properties of Al-CNTs composites

Materials are exposed to different forces while in used, which may led to deformation or fracture as results of the applied load, time, temperature and other conditions. Properties of material that involve a reaction to an applied load are known as mechanical properties. Figure 2.0.9 show different mechanical properties. To explore mechanical properties such as strength, ductility, hardness and fracture toughness different tests such as tensile and nanoindentation are conducted. Those tests are governed by standards due to various factors (size and shape of material to be tested, how it is held, and the way test is performed) that may influence the results (Nie et al., 2013).

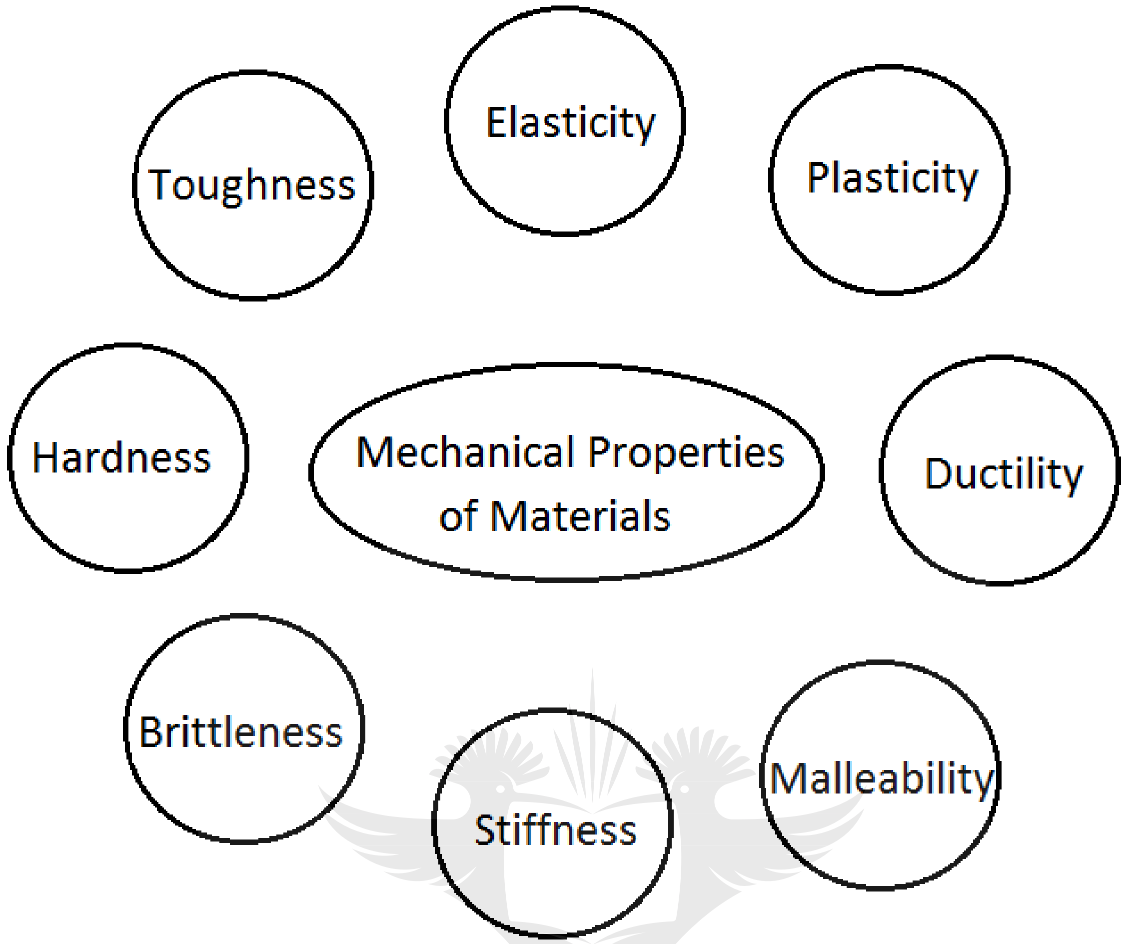

Figure 2.0.10. Mechanical properties (Dannana, 2017)

Choi et al. (2015) produce A2024-MWCNTs composites using ball milling and hot rolling. The tensile ductility of A2024 matrix decreases as MWCNTs are added. 2% plastic elongation to failure was reported as ductility.A2024-MWCNTs composites showed much enhanced yield strength with poor ductility and work hardening capacity(Choi et al., 2015).Guo et al. (2017a) fabricated pure Al-CNTs composites using spark plasma sintering and hot rolling, sintering was done using two sintering temperature which are 590 and 630 °C. Three composites were produced. Figure 2.0.11 show the stress and strain results of Guo et al. (2017a) research work. It is shown that improving temperature from 590 °C to 630 ° attributed to the improved mechanical properties of pure Al-CNTs composites. It also interesting to note that varying content of reinforcement also had effect on ductility with sintering temperature is kept 630 °C (Guo et al., 2017a).

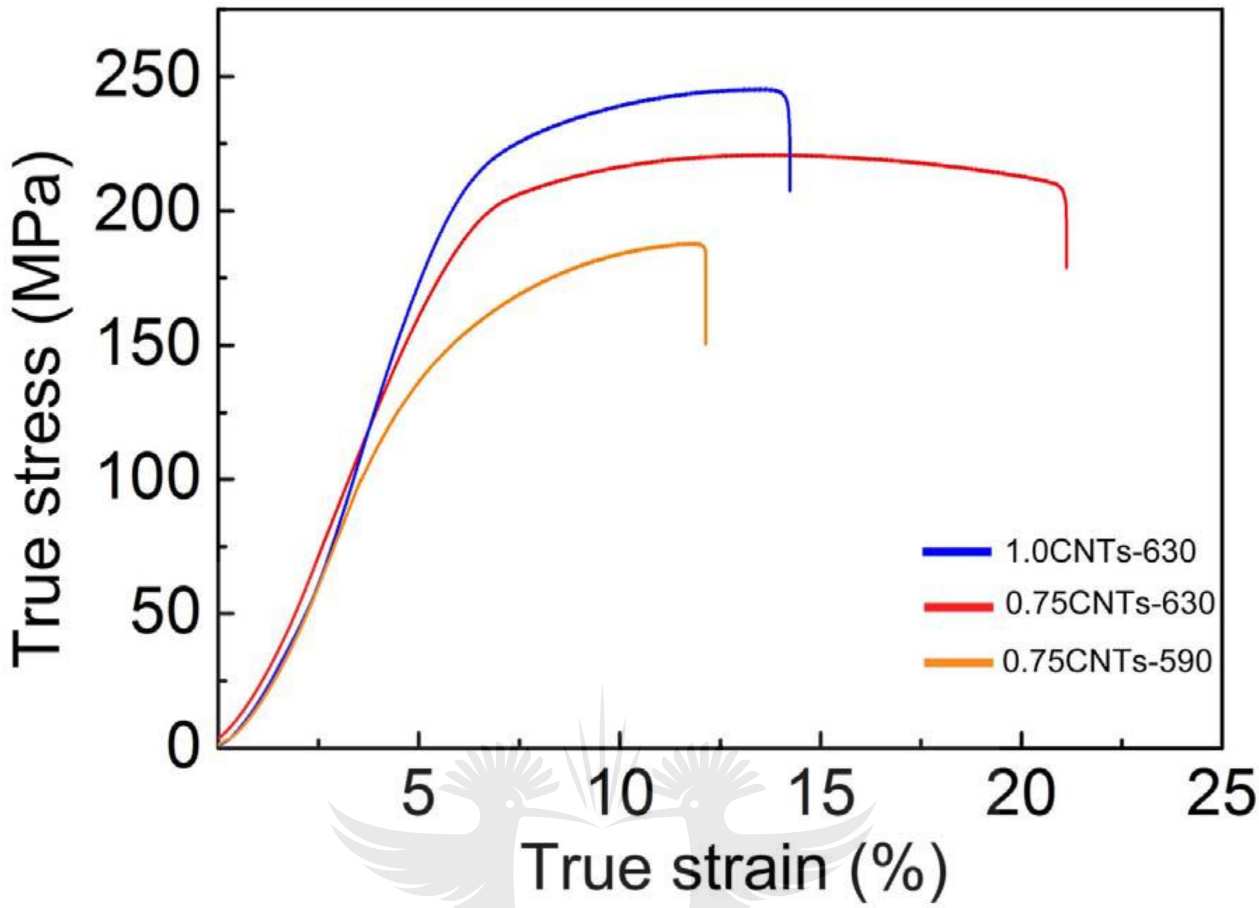

Figure 2.0.12. The tensile stress-strain curves of the rolled Al-CNT composites.

Zhao et al. (2017) consolidated 2017 Al –CNT composites through the use ball milling, hot pressing and hot extrusion respectively. The results show 1% elongation of the (base metal) BM. The obtained 1%elongation is suggested to be attributed to the anisotropy of CNT/Al composites. Other reported mechanical property is ultimate tensile strength of 630 Mpa for the base metal, the improved UTS is associated with CNT strengthening and refined grain (Zhao et al., 2017).

Table 2.0.6 . Pure aluminium with 2 wt.% CNT

Sample	**Elongation**	**young's modulus**	**Tensile strength**
PureAlmilled	10.2±0	56.7±3.0	168.7±1.3
CNTsAl–2wt%mildly	7.17±0.76	66.7±6.7	330.6 ±14.9
Al–2wt%as-received	5.2±2.1	63.8±4.0	333.3±9

Hassan et al. (2014) synthesized pure aluminium with 2 wt.% CNT using balling and extrusion. Results are on table3, whereby the obtained ductility of the Al-CNTs composites is smaller than that of pure Al (Hassan et al., 2014). Zhu et al. (2016) used sintering and hot extrusion respectively to fabricated 2014 aluminium matrix composites reinforced with untreated and treated CNTs. The total elongation of the 2014Al-CNTs composites decreases compared to the Al matrix (pure Al with 13.5, untreated CNTs-Al with 12.7 and treated CNTs-Al with 12.0 %) (Zhu et al., 2016). Park et al. (2015) synthesised Al-CNTs composites using ball milling, sintering, melt blending, casting and extrusion respectively. Elongation decreases dramatically from 20% to almost 2% as CNTs are added as reinforcement. The yield and tensile strength were improved. See figure 2.0.13 (Park et al., 2015). Guo et al. (2017b) studied the effect of Al particle size on Al-CNT composites by using both fine and coarse Al powders. Mechanical properties showed that fine Al powders had better tensile strength while Coarse Al powders had better ductility. This results are shown in figure 2.0.14 (Guo et al. (2017b).

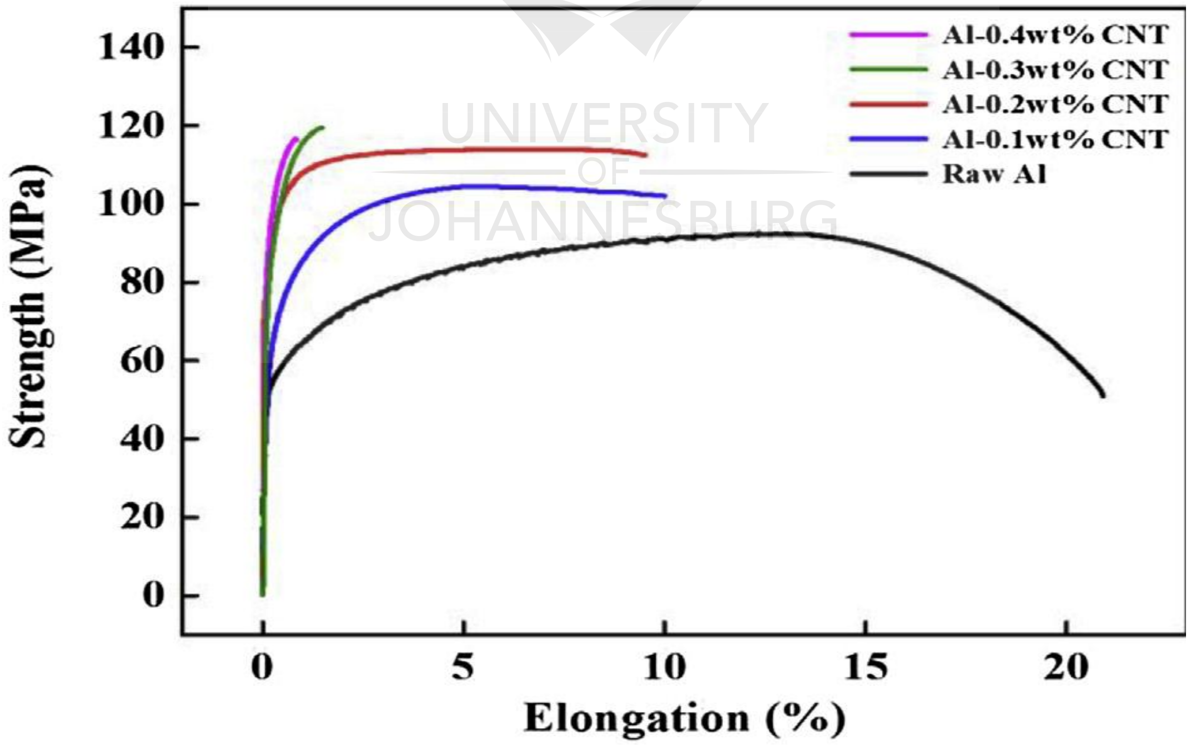

Figure 2.0.15. Tensile test curves from extruded raw Al and Al-CNT composites.

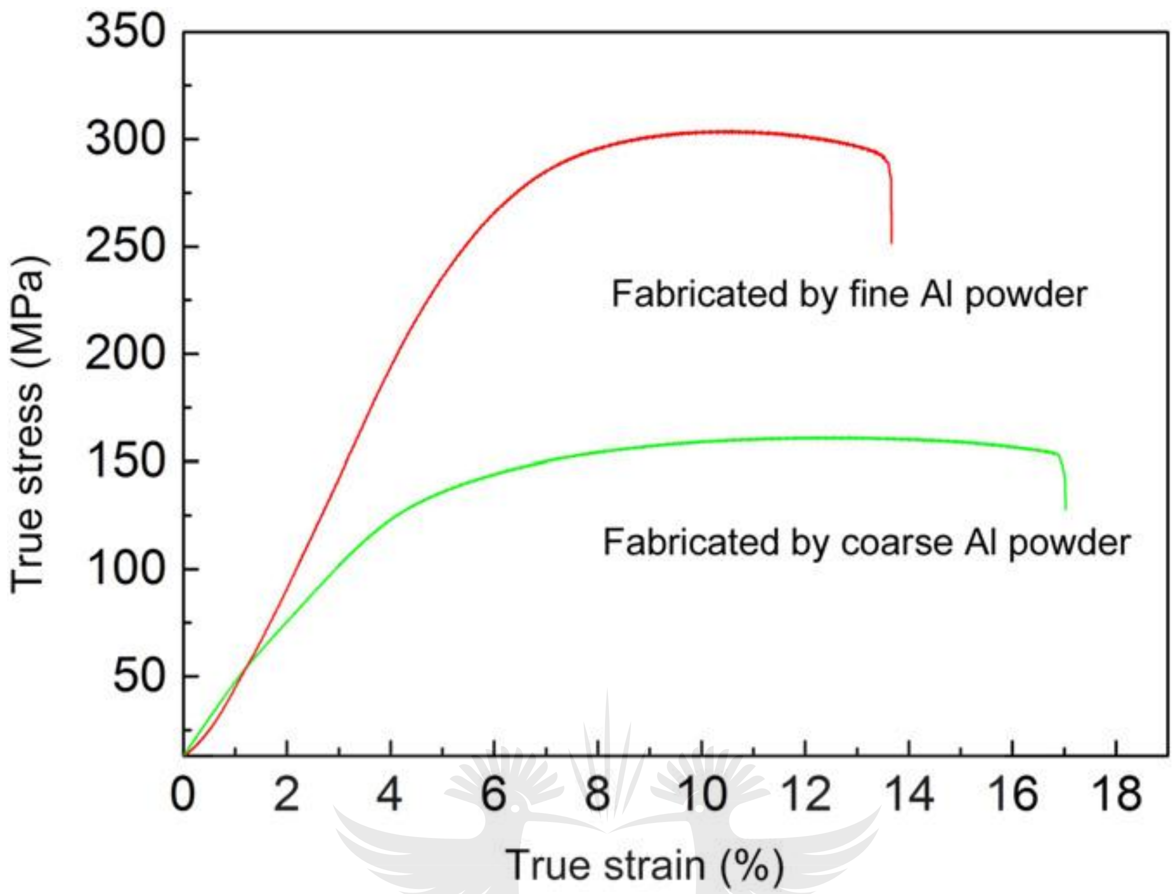

Figure 2.0.16. Tensile curves of the two types of the composites

2.8.1 Elasticity

Aluminium composites may deform when exposed to external load. However, there is a certain load in which pure aluminium can recovery its deformation when the load is remove is known as elastic deformation. The load in which aluminium composites no longer behaves elastically is called elastic limit. When elastic limit is exceeded Aluminium composites, experience permanent deformation when load is removed (Khan et al., 2017).

2.8.2 Plasticity

Also known as permanent deformation. Plasticity is the permanent strain that occurs after elastic limit and before onset of localised. Advantages of knowing plasticity of material are providing a degree of safety in use and permit forming of parts. Plasticity is practically independent of the applied pressure but is due to dislocation and vacancies (Khan et al., 2017).

2.8.3 Stiffness

Aerospace structural areas require aluminium application with good stiffness, fatigue strength and good strength (Khan et al., 2015).Xiang et al. (2017) reported great enhancement of stiffness and strength through dispersion of a small fraction of CNTs into Al matrix. The initial slope of the unloading load-displacement curve at a maximum depth of penetration is known as Unloading stiffness (Koumoulus et al., 2014).

2.8.4 Hardness

This is the resistance of a material to indentation. Hardness of aluminium reinforced carbon nanotubes composites increases with increase weight content of carbon nanotubes (Kwo et al., 2015; Samuel Ratna Kumar et al., 2017; Pillari et al., 2017; Sharma et al., 2016). Bradbury et al. (2016) study show that there is a limit where CNTs content as reinforcement is not effective on enhancing hardness, peak hardness were exhibit and further additions led to decrease (Bradbury et al., 2016). The micro hardness of Al-CNT composites increased with increasing volume fraction of CNTs (Ogawa et al., 2017, Girisha et al., 2014, Travessa et al., 2015). Grain refinement and strain hardening of powder particle during ball milling attribute to enhancement of Al-CNT composites hardness. Clustering or agglomeration of Nano particles and presence participate attribute to decrease in hardness (Pillari et al., 2017). Anirruddha et al. (2013) carried out nanoindentation studies on 6061Al- CNTs composites and reported an increase in 6061Al (Aniruddha et al., 2013). Ferreira et al. (2017) fabricated Al-TiO_2 composites with TiO_2content of 2.5, 5, 7.5 and 10 %.A slight change of hardness of Al-TiO_2 composites were observed (Ferreira, 2017).

2.8.5 Young's modulus

Modulus of elasticity of Al-MWCNTs composites increases as MWCNTs content increases (Anirruddha et al.,2013).

2.8.6 Strain rate sensitivity

Strain rate sensitivity is directly proportional to ductility. Ductility tends to increase with strain rate sensitivity (Jianshe, 2006). Strain rate sensitivity of AA8006-B_4C composites was largely influence by temperature (Khodobakhshi et al., 2019).

2.8.7 Elongation

Elongation is the measure of ductility. It is determine by gauge length of material before and after fracture. Elongation is the gauge length after fracture divided original gauge length before fracture. Ogawa et al. (2016) research results of Al-4.0 CNTs shows that elongation is reduced due to CNTs agglomeration (Ogawa et al., 2017).

2.8.8 Ultimate Tensile Strength

Pure aluminium has tensile strength of around 90 Mpa. The maximum stress that material can withstand without being elongated is known as ultimate tensile strength. Alekseev et al., 2016 used both hot pressing and cold rolling to produce aluminium – carbon nanotubes composites with tensile strength of 441 MPa. Girisha et al., 2014 obtained a UTS of 150 MPa with 2 wt.% MWCNTs. Zhu et al., 2015 used both treated and untreated MWCNTs reinforcing 2014 Al and determine tensile strength of aluminium composites. Treated and untreated multi walled carbon nanotubes reinforcing 2014 Al and determine tensile strength of aluminium composites. Treated carbon nanotubes reinforced aluminium composites had better tensile strength (Zhu et al., 2015). Ogawa et al., 2017 by increasing volume fraction of CNTs on aluminium composites lowered UTS and fracture strain. It was concluded that it was due slight clustering of Nano particles and presence participate in decrease in hardness (Pillari et al., 2017). Tensile strength increases on 0.1 CNT content to 0.4 CNT content as 0.5 CNT content is added tensile strength decreases by a difference of 2 (Park et al., 2015).

2.8.9 Yield strength

The maximum stress applied along the axis that material can withstand before it changes shape is known as Yield strength. The formulated relationship between hardness and yield strength is by Tabor which is H= 3*tensile strength (Khan et al., 2010). Yield strength increases with increasing carbon nanotubes content (Park et al., 2015). The small fraction of CNTs into Al matrix contribute to great the strength enhancement of CNT-Al composite (Xiang et al., 2017).

2.8.10 Fracture strain

Increase on the volume fraction lowered fracture strain. This is suggested to be due to slight clustering at the higher CNT content. UTS and fracture strain of Al- 4.0 CNTs were reduced due to CNTs agglomeration (Ogawa et al., 2017).

2.8.11 Ductility

Salama et al. (2017) novel of improving ductility with adequate strength was of success. The ductility of Al-MWCNT composites were improved up to 14%. Figure 2.0.17 show the stress and strain curves of the developed Al-MWCNTs composites prepared by Single Matrix and Dual Matrix structures. The production of the DM composites involves embedding pre-processed SM Al-MWCNT powders into a secondary matrix of soft aluminium. The SM composites were consolidated by dispersing MWCNTs in aluminium powders using mechanical milling. Dual Matrix Al-MWCNT composites exhibit better ductility with slight reduction of strength compare to Single Matrix Al-MWCNT composites (Salama et al., 2017).

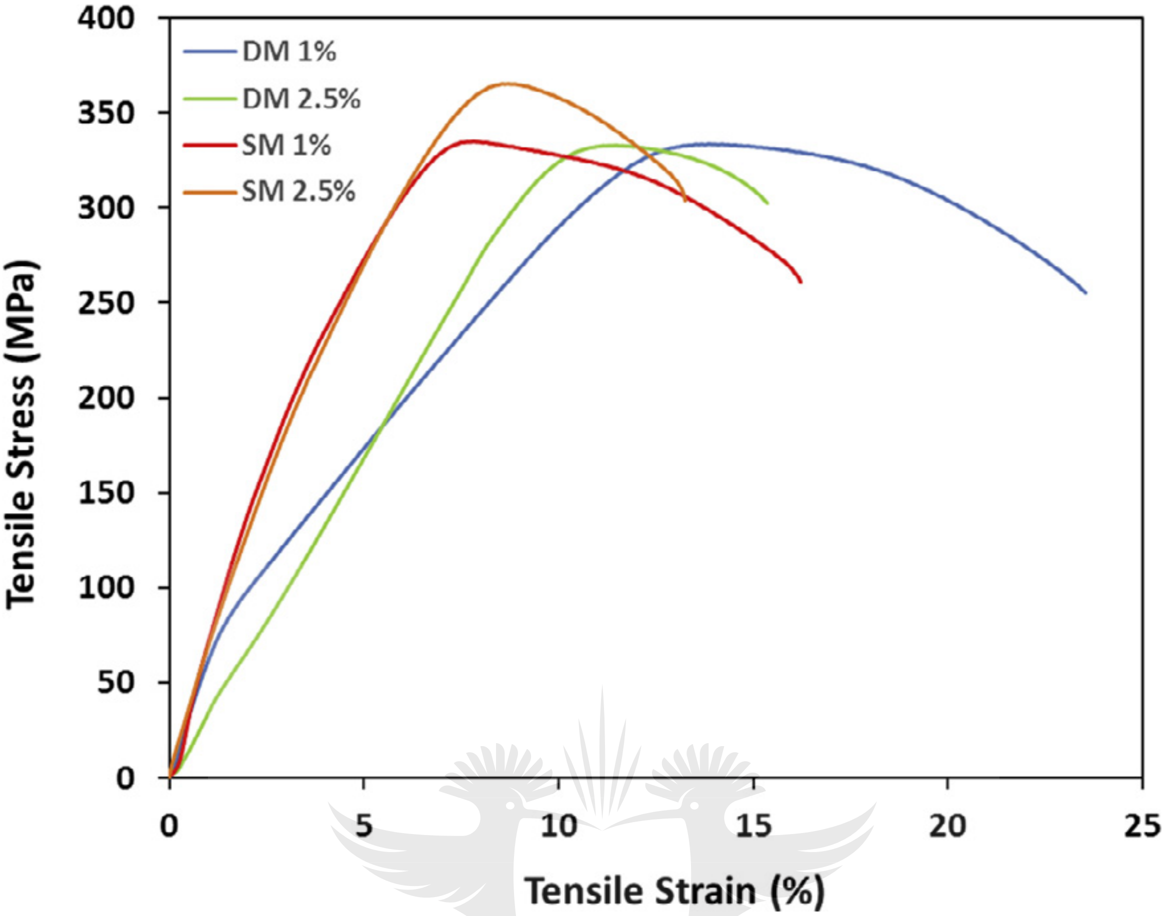

Figure 2.0.18. Plots of (a) tensile strength, and (b) elongation % of DM Al/CNT composite

Table 2.0.7. Properties of Al-CNT composites consolidated through various techniques

Composites	Processing techniques	Properties	References
Al+1wt.% MWCNT	hot pressing Cold rolling	ultimate tensile strength :441Mpa	**Alekseev et al., 2016**
0.5 wt. %MWCNT 1 wt.% MWCNT 1.5 wt.% MWCNT 2 wt.% MWCNT	Stir casting	55 BHN: 147 MPa: 10.575% 59 BHN:151 MPa: 9.1% 66 BHN: 152 MPa: 8.43% 69 BHN: 150 MPa: 7.92%	**Girisha et al., 2014**
0.5 wt.%CNT-2014Al 0.5wt.%CNT – 2014Al	Ball milling Hot extrusion Sintering	600 UTS 12.7% 630 UTS 12%	**Zhu et al., 2015**
1 wt.% MWCNT 2 wt.% MWCNT	High energy ball milling Extrusion	Hardness significantly increased after addition of MWCNT to the alloy.	**Travessa et al., 2015**
Al+1Vol.% MWCNT	Mechanical ball milling Hot pressing	Hardness 92 HV	**Kwo et al., 2015**
Al + 0.1 wt.% CNT Al + 0.2 wt.% CNT Al + 0.3 wt.% CNT Al + 0.4 wt.% CNT	Mechanically pulverizing Sintering	71 YS & 103 TS 90 YS & 114 TS 102 YS & 119 TS 111 YS & 117 TS	**Park et al., 2015**
Al+5Vol.% MWCNT	High energy ball milling	The yield stress of both the composites is two times higher than that of Al2024-T6.	**Shin et al., 2016**
1 wt.% CNT 2 wt.% CNT 3 wt.% CNT 4 wt.% CNT 5 wt.% CNT	Ultra sonication Cold pressing	3.62 GPa HV93.33 GPa 3.63 GPa HV 104.79 3.82 GPa HV 86.45 3.67 GPa HV 41.75 3.08 GPa HV35.78	**Sharma et al., 2016**
1, 2, 3, 4, 0.5 & 1.5 Al-CNT (MWCNT & CNFs)	Ball milling Hot extrusion: 550 Ext ratio : 9	Micro hardness exceeds 100 Hv tensile strength 457.9 MPa	**Ogawa et al., 2017**
1 wt.% CNT 2.5wt.% CNT	Ball milling	14.8% ductility	**Salama et al. (2017)**
0.5 wt.% CNT	Ball milling Hot extrusion	Perpendicular: 42 HV Parallel: 40 HV	**Hildalgo –Manrique et al., 2017**
1 wt.% CNT 2 wt.% CNT	Powder Metallurgy	Hardness increases with CNTs content	**Anirruddha et al., 2013**

Table 2.0.8. Properties of Al-CNT composites consolidated through various techniques

Composites	Processing techniques	Properties	References
0.5 wt.% MWCNT 1 wt.% MWCNT 2 wt.% MWCNT	High energy ball milling Hot pressing	Exhibit peak hardness & further additions led to a decrease in hardness	**Pillari et al., 2017**
1 wt.% CNT 3 wt.% CNT 6 wt.% CNT 9 wt.% CNT	Ball milling Hot compression	The hardness increased with increasing fraction of MWCNT up to 6 wt.% then remain constant.	**Bradburg et al., 2016**
0.75-590 0.75CNTs-630 1.0 CNTs-630	Spark plasma sintering Hot rolling	12.5% 90 HV 22% 120 HV 13% 110 HV	**Guo et al., 2017a**
1 vol.% CNT 1 Vol.% CNT	Ball milling Ultrasonication Spark Plasma Sintering	12% 306MPa 17% 153MPa	**Guo et al., 2011b**
2 wt.% as received 2 wt.% mildly D 2 wt.% severely D	Ball milling	7.17% 330.6 MPa 5.2% 333.3MPa 4.4% 288.1MPa	**Hassan et al., 2015**
2 wt.% CNT	Ball milling Powder metallurgy	UTS: 253 MPa EL: 16 %	**Liu et al., 2017**
0.5 Mo-CNTs	Powder mixing Spark Plasma Sintering	Electrical conductive of composites decrease with increase CNTs content. Hardness increase with increase in CNTs content.	**Nie et al., 2017**
0.5 Vol.% CNT 0.5 Vol.% CNT	Ball milling Hot extrusion	Increase of CNTs content increases Vickersmicro hardness	**Ogawa et al., 2017**

Chapter 3

3. Research Methodology

This chapter consists of various materials, equipments and experimental procedures used towards fulfilling the research objectives of this study. The use of ball milling to dispersed multi walled carbon nanotubes within aluminium matrix, the use of various characterisation techniques on powders and sintered composites, the use of SPS to consolidate Al-MWCNTs composites and the use of ultra nanoindenter tester to evaluate mechanical properties of Al-MWCNTs composites were explained in details.

3.1 Materials

In this study, pure aluminium is used as a matrix material and multi walled carbon nanotubes as reinforcement. Aluminium and MWCNTs powders (NX7100-A-Ultra purified CNT) were supplied by Nanocyl Belgium. The characteristics of the as received powders are given in table 3.0.1 and the compositions of Al powder obtained from EDS analysis are summarized in table 3.0.2.

Table 3.0.1 Specification of Al and MWCNTs powders

Specification	**Al**	**MWCNTs**
Outer diameters	-	20 – 30mm
Inner diameter	-	9.5 nm
Length	-	1.5µm
Purity	99.8%	>95%
True density	~2.6 g/cm^3	~2.1 g/cm^3
Bulk density	-	0.28 g/cm^3
Specific surface area	-	110m^2/g
Ash	-	1.5 Wt. %
Particle size	25 µm	-

Table 3.0.2. Compositions of the as-received Al powder (wt.%)

Elements	**Ti**	**Al**
Composition	0.75	99.25

3.1.1 Pure Aluminium

Pure Aluminium is normally used for applications that pose high conductivity, excellent formability and very good corrosion resistance due to its limited mechanical properties (Megson, 2014).

3.1.2 MWCNTs

MWCNTs are ideal ultra-weight reinforcement. Due to superior strength and stiffness, high electrical and thermal conductive, high flexibility, low density, high aspect ratio and anti-corrosive properties are preferred (Duarte et al., 2015).

3.2 Experimental procedures

3.2.1 Ball milling

Pure aluminium powders and pure aluminium-MWCNTs powders with composition of 0.5, 1 and 1.5 wt. % MWCNTs were prepared under similar conditions (procedure and parameters). Ball milling was chosen as the method for grinding and mixing Al and MWCNTs powders. Admixed powders were placed into 250 ml stainless steel mixing jar, which had milling balls of 10 mm and 5 mm diameters. The jar was filled with argon and agitated using planetary ball mill at 100 rpm for 6 hours and also for at 300 rpm for 1 hour, for dispersion of 0.5, 1 and 1.5 wt. % MWCNTs into aluminium matrix. Rule of mixture was employed to calculate the proper amount of individual powders for efficient dispersion. The weight ratio of ball to powder of 10: 1 was used. Ball milling is shown in figures 3.1.

Figure 3.0.1 Ball milling

3.2.2 Characterization of as received powders and admixed powders

The as received powders of aluminium and multi walled carbon nanotubes were characterised using SEM. Al-MWCNTs admixed powders were characterised using SEM, EDS, TEM, XRD and Raman spectroscopy. SEM and TEM were used to characterise the morphology of Al-MWCNTs powders. EDS were used to identify the chemical composition of Al-MWCNTs powders. X - ray diffraction was used for confirmation of phases present in the Al-MWCNTs powders. Raman spectroscopy was used to ascertain structural integrity of MWCNTs powders. Figures 3.0.2 – 3.0.4 show pictures of some of the equipments used for characterization.

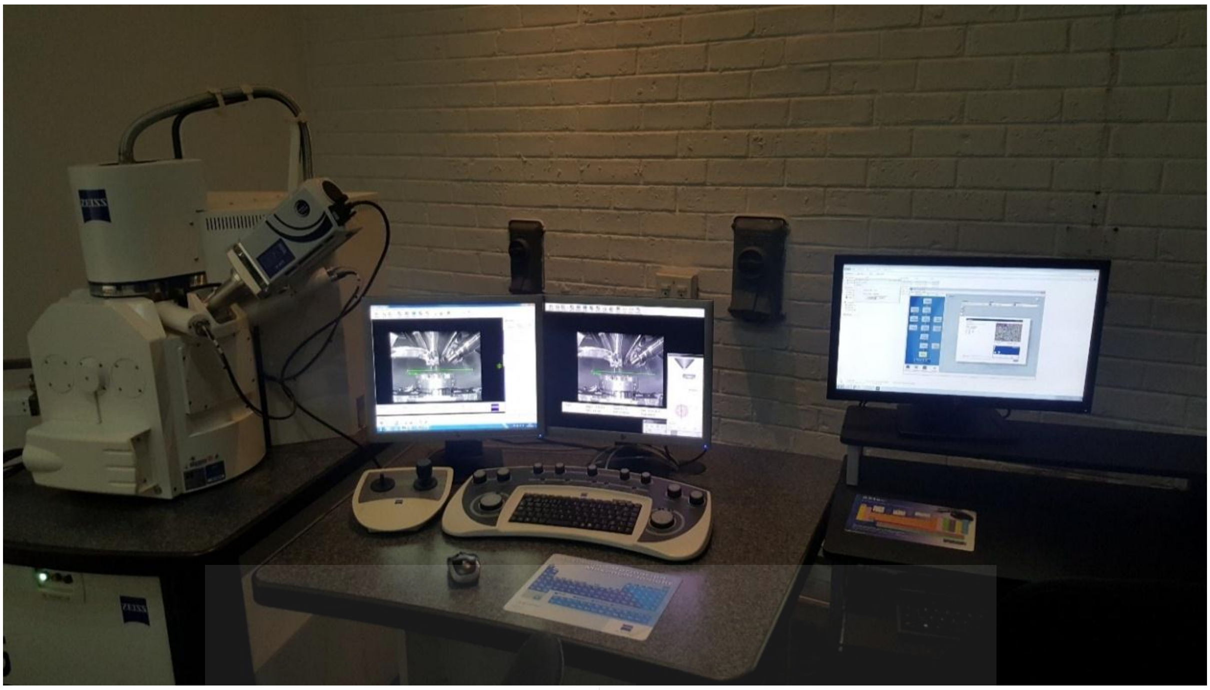

Figure 3.0.2 Scanning Electron Microscope Equipped with EDS

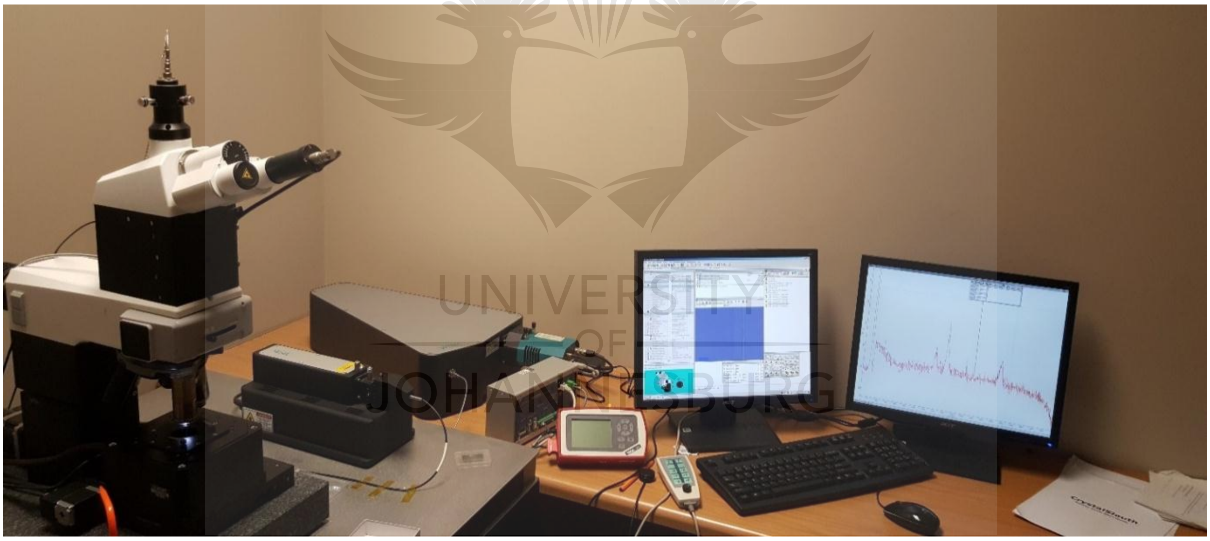

Figure 3.0.3 Raman Spectroscope

Figure 3.0.4 X ray diffraction

3.2.3 Spark Plasma Sintering of powders

Various amounts of admixed powders were sintered to produce four composites (Pure Al, Al-0.5 wt.% MWCNTs, Al-1wt. % MWCNTs andAl-1.5 wt. % MWCNTs). A graphite die punch (20 mm inner diameter) with graphite foil inserted in between the punch and the powders were used to consolidate these powders. Sintering were performed in vacuum at 590℃ for 7 min with 100℃/min heating rate under a pressure of 50 MPa. Sintered Al-MWCNTs composites were cleaned using sand blasting machine to remove the graphite foils. Figure 3.0.5 shows the SPS facility.

Figure 3.0.5 Spark Plasma Sintering

3.2.4 Characterization and testing of Al-MWCNTs Sintered Samples

3.2.4.1 Density Measurement

The sintered Al-MWCNTs composites were subjected to Archimedes' principle for density measurement. The samples were carefully weighed in air and de-ionized water using an electronic balance. The weights recorded in the two environments were recorded and used to compute the density of the material. Rule of mixture was used to obtain the theoretical densities of the composite. The equation 3.1 was used to calculate the density of the samples.

$$\rho_s = \frac{Ma}{Ma - Mw} \quad \text{..........} \quad 3.1$$

Where ρ_s is the density of the sample while M_a and M_w are the weight in air and water respectively.

3.2.4.2 Metallography of Sintered Al-MWCNTs composites

Sintered composites of 20 mm by 5 mm were cut into two pieces using cutting equipment shown in figure 3.0.6. One piece of sintered sample was placed horizontal, the second piece was placed vertical during mounting, and the same mounting conditions were used for all the samples.

Figure 3.0.6 Cutting machine

Mount samples were prepared using automatic grinding and polishing equipment. Figure 3.0.7 show the automatic grinding and polishing equipment used to obtain mirror like surface of sintered samples.

Figure 3.0.7 Automatic grinding and polishing equipment

3.2.4.3 Characterization of sintered Al-MWCNTs composites

Sintered Al-MWCNTs composites were characterised using OP, SEM equipped with EDS, XRD, Raman spectroscopy and TEM. Those equipments were used for the same reason as for the admixed powders to see if there is any change after sintering. Figure 3.0.8 show the Optical microscopy used on this study.

Figure 3.0.8 Optical microscopy

3.2.4.4 Mechanical properties analysis of Al-MWCNTs composites

Metallographic prepared sintered Al-MWCNTs composites were used for micro hardness test(Figure 3.9) and ultra nanoindentation test (Figure 3.10) to evaluate mechanical properties of Al-MWCNTs composites.

Micro hardness

Micro hardness measurements of the sintered Al-MWCNTs composites samples were conducted using digital tester. A profile of three indents were made on the samples on different locations. The applied load was kept at 20kgf for all the tests for a peak-load time of 10s. The indent diagonals were measured optically to give the hardness values of the test samples with an accuracy of ±0.1μm.

Figure 3.0.9 Micro hardness tester

Local mechanical properties at nano-scale were assessed using nanoindentation testing technique by controlling the load and position of indenter during indentation testing. The contact load between the indenter and polished surface is important durimg indentation testing hence the load and indentation depth record continously after producing the contact. Quantities such as the peak load (Pmax), the maximum depth (hmax), the final or residual depth after unloading (hf) and the slope of the upper portion of the unloading curve (S) are importatnt during testing.Creep behavior of Al-MWCNTs composites was evaluated with a nanoindenter at maximum load of 100 mN. The dwell time was set to be 10s and loading rate was set to be 40Mn/min.On each sample, 3 indents were made with a Berkovich indenter, all three indents were performed under similar conditions. Figure 11 shows the indent points with their corresponding hardness and modulus of elasticity values.

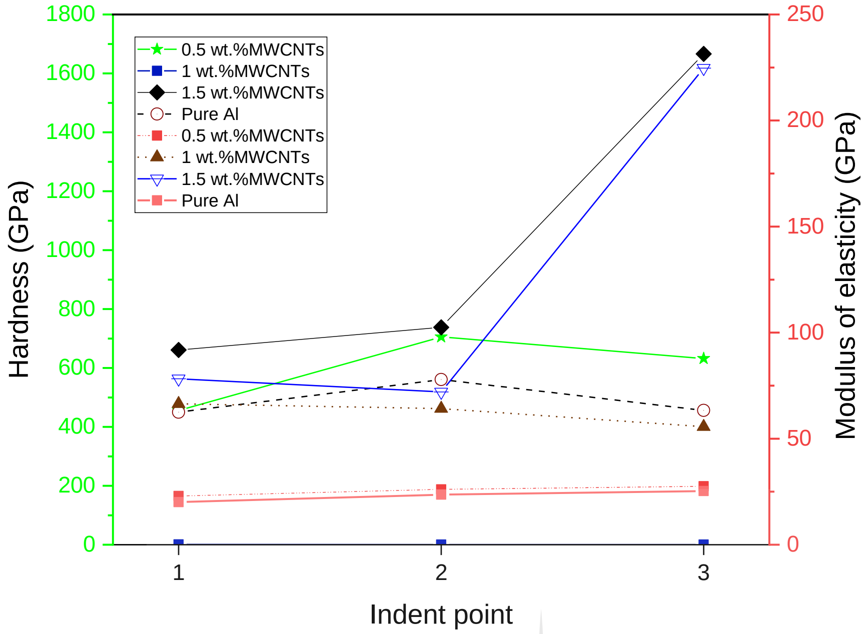

Figure 3.0.10. Modulus of elasticity and hardness of Al composites

Figure 3.0.11 Ultra nanoindentation tester

3.2.4.5 Conversion methods used to obtain mechanical properties

- **Plasticity**

Plasticity= $\frac{\text{Wtotal} - \text{wu}}{\text{Wtotal}}$ 3.3

Where W_{total} is work of total indentation process and W_u is work during unloading

- **Elasticity**

Elasticity = $\frac{\text{Wtotal} - \text{wl}}{\text{Wtotal}}$ ………………………………………………………………….. 3.4

Where W_{total} is work of total indentation process and W_l is work during loading

- **Densification**

Densification= $\frac{Theoretical\ density}{Actual\ density} \times 100$ …………………………………………………….3.5

The total of 3 indents from nanoindentation tests were averaged to determine the following mechanical properties:

- **Hardness (nano)**
- **Modulus of elasticity**
- **Yield strength**
- **Stiffness**
- **Strain rate sensitivity**

Chapter 4

4. Research results and findings discussion

This chapter consists of characterisation and mechanical properties results and discussion of spark plasma sintered Al-MWCNTs composites. Detailed characterisation results and characterisation discussion of the as-received powders (pure Al and MWCNTs), Al-MWCNTs admixed powders and sintered Al-MWCNTs composites (Al-0 wt.% MWCNT, Al-0.5 wt.% MWCNTs, Al-1 wt.% MWCNTs and Al-1.5 wt.% MWCNTs) studied using OP, SEM equipped with EDS, TEM, XRD and Raman spectroscopy are well presented. Further discussion of presented mechanical properties results of plasticity, elasticity, hardness, yield strength, modulus of elasticity, strain rate sensitivity and stiffness of spark plasma sintered Al-MWCNTs composites led to the success of this study.

4.1 Characterization of Al-MWCNTs composites

4.1.1 SEM analysis of admixed Al-MWCNTs powders

Figure 4.0.1 show morphology of as-received pure Al (a) and MWCNTs (b). Morphology of pure Al depicted spherical structure with average particle size of 25µm. MWCNTs agglomerated into clusters as shown due to the presence of strong Van der Waal (VDW) forces(~100 eV/mm), large aspect ratios(~100 to 3000), enormously high specific surface area(~250 m2 /g) and high flexibilities (Munir et al., 2017). To achieve uniform dispersion of MWCNTs within Al powders it requires de-entangling of MWCNTs (Kwon et al., 2015).

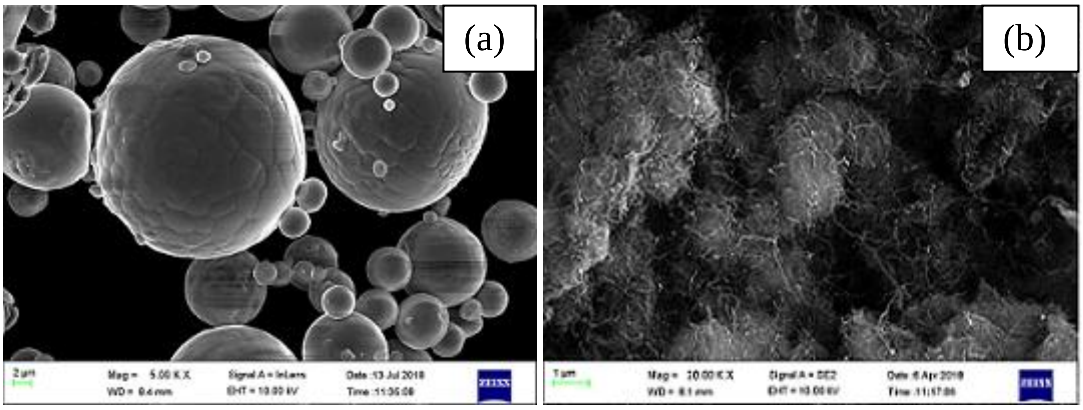

Figure 4.0.1. SEM images of (a) pure Al and (b) MWCNTs powders

Figure 4.0.2 (a), (b) and (c) shows SEM images of Al-0.5wt% MWCNTs, Al-1wt% MWCNTs and Al-1.5wt% MWCNTs admixed powders composites respectively. It is seen from all SEM images that MWCNTs are uniformly distributed within the Al matrix. The attachment of MWCNTs on Al surface is seen to be strong under the mechanical force of milling balls. However in both Al-1wt% MWCNTs and Al-1.5wt% MWCNTs admixed powders composites, MWCNTs are uniformly distributed on large flaky Al surfaces (Figure 4.0.2b and 4.0.2c) while in Al-0.5wt% MWCNTs admixed powders composite, MWCNTs are distributed in small flaky Al surfaces (Figure 4.0.2a). This dispersion is as results of combing milling parameters, which are prolonged milling time with lower speed and shorter milling time with higher speed. The obtained dispersion is associated with sufficient impact energy extended on powders when long and short milling time where combined. Therefore, it is suggested to have sufficient impact energy so that MWCNTs will dispersed well in Al powders, since the main aim of incorporating MWCNT into Al powders is to improve the properties of the aluminium matrix (Kwon et al., 2015). Enough Impact energy (Impact energy is of milling a function method and milling parameters) is required to deagglomerate the clustered MWCNTs. Beside impact energy, poor compatibility between powders also plays crucial role in homogeneity of MWCNTs within Al matrix because it leads to segregation of powders (Zhu et al., 2015, Ogawa et al., 2017).

In order to prevent poor compatibility of MWCNTs and Al powders, ball milling was used to disperse MWCNTs within Al matrix. Even those it has been showed in previous research work that ball milling is one of the effective technique to disperse MWCNTs, milling parameters plays a major role in morphology and structure of MWCNTs (Bradbury et al., 2016, Guo et al., 2011). Esawi et al. (2016) reported that CNTs are homogeneous distributed on Al matrix surface after milling for 30 minutes while Wu et al. (2015) reported uniform dispersion of CNTs after initial 2 hours of milling with no dispersion improvement during further milling times (Esawi et al. 2016, ,Wu et al., 2015). According to the literature, CNTs clusters break and CNTs are uniformly distributed during early stages of ball milling. Prolonged ball milling is associated with the following:

- Cold welding, which lead to the formation of large particle size.
- Work hardening, which decreased the ductility of final composite.
- Damaged to CNTs, which can degrade the mechanical properties of the composites.

Hence in the present work, prolonged milling time with lower speed and shorter milling time with higher speed has been chosen for effective grinding and mixing of Al and MWCNTs powders. MWCNTs uniform dispersion quality was maintained throughout different MWCNTs contents (0.5wt% MWCNTs, 1wt% MWCNTs and 1.5wt% MWCNTs). Agglomeration of CNTs was not found in all Al-MWCNTs admixed powders composites. Homogeneous dispersion of MWCNTs within Al matrix prepared by ball milling was achieved by selecting suitable milling parameters to overcome strong van der waals forces between MWCNTs. Therefore, it is assumed that transfer of MWCNTs properties into Al matrix during composite production will be effective since MWCNTs are uniformly dispersed within Al matrix (Shin & Bae, 2013).

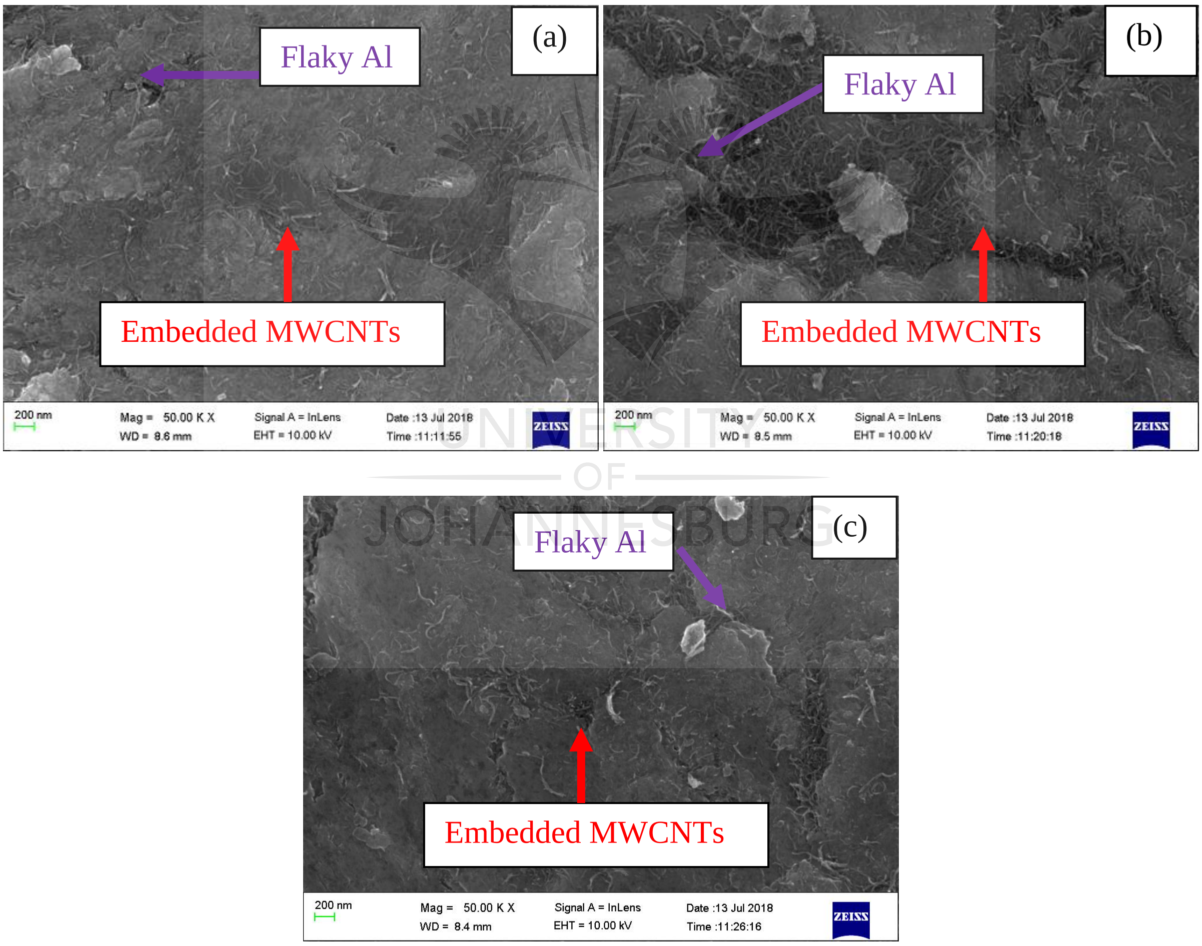

Figure 4.0.2. SEM images of (a)Al-0.5wt.%MWCNTs, (b)Al-1wt.%MWCNTs and (c)Al-1.5wt.% MWCNTs admixed powders

4.1.2 SEM equipped with EDS analysis of admixed Al-MWCNTs powders

Figure 4.0.3 show SEM and corresponding EDS analysis of Al-MWCNTs admixed powders composites. In this research work, MWCNTs content of 0.5 wt.% MWCNTs, 1 wt.% MWCNTs and 1.5 wt.% MWCNTs was dispersed within Al matrix using low energy ball milling. During ball milling, two stages milling was introduce i.e. 100 rpm for 6 hours and 300 rpm for 1 hour. Figure 4.0.3 shows SEM and corresponding EDS analysis of (a) pure Al, (b) Al-0.5 wt. % MWCNTs, (c) Al-1 wt. % MWCNTs and (d) Al-1.5 wt. % MWCNTs admixed powders respectively. The presents of Al, carbon and oxygen were confirmed. It is observed from EDS that C is present in Al powders after ball milling with the amount that range from 8.41 wt. % to 19.33 wt. %. MWCNTs were well embedded in flake-like shape Al powder matrix. Well embedded MWCNTs are associated with reducing the damage of CNTs while flake-like shape Al powder is associated with largely increasing Al specific surface (Liu et al., 2017).

Liu et al. (2017) also reported such flake like-shaped CNT- Al composite powders and further explained that the flake-like shaped Al sheets is of advantage because it provide sufficient surface area for the separated MWCNTs to achieve a good contact between Al and MWCNTs. Literature has revel that the flake-like morphology of the composite powder gradually changes as milling time increases to sphere-like multilayer particles due to the cold welding between Al and MWCNTs resulting in a certain degree of compaction. When the ball milling time exceeds a certain value, the particle size eventually reaches an almost steady state due to the dynamic equilibrium between fracturing and agglomeration (Liu et al., 2017).

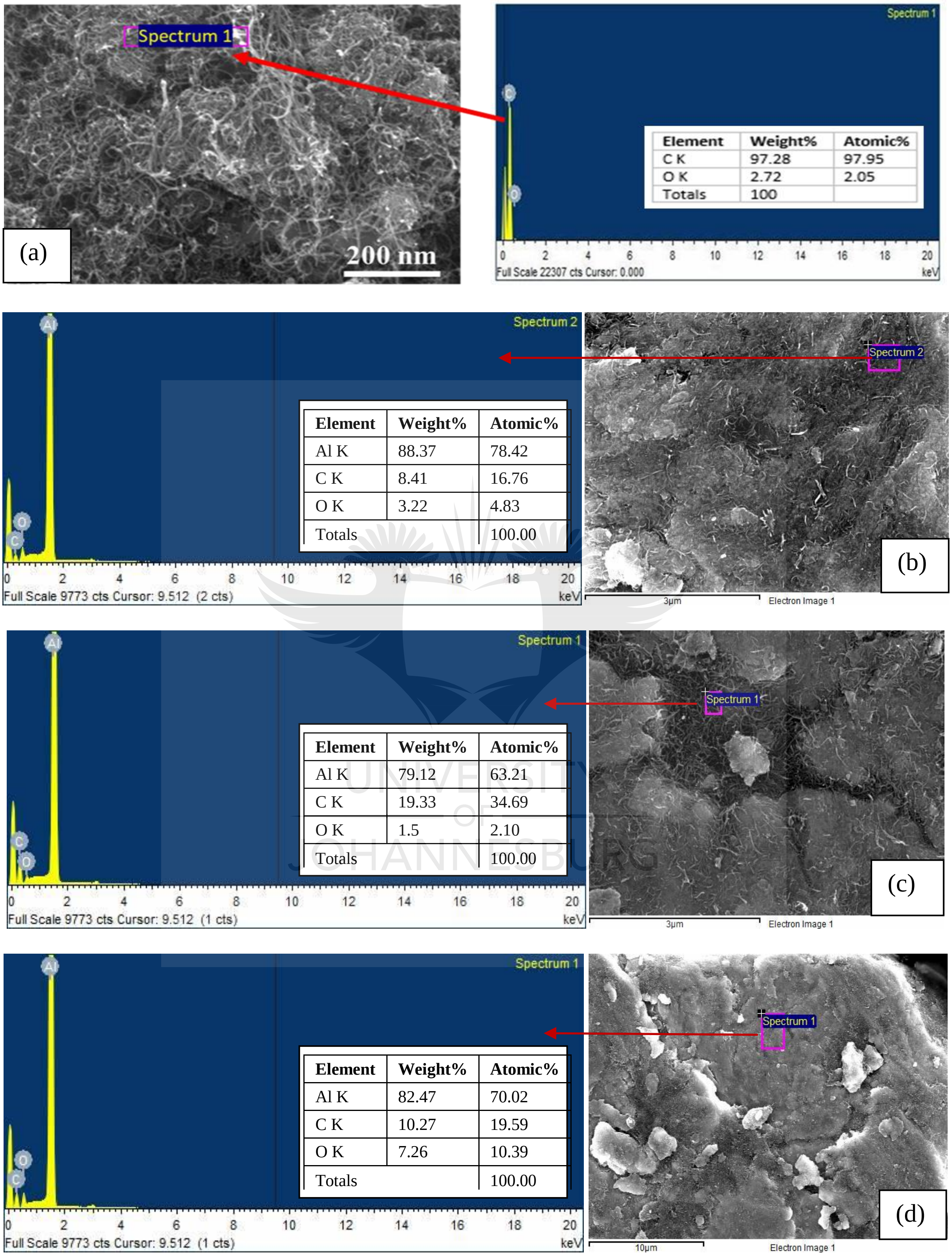

Figure 4.0.3. EDS images of (a)Al-0.5wt.%MWCNTs, (b)Al-1wt.%MWCNTs and (c)Al-1.5wt.% MWCNTs admixed powders

4.1.3 TEM analysis of admixed Al-MWCNTs powders

The microstructural revolution of MWCNTs after dispersion in Al powders are as shown in figures 4.0.4 and 4.0.5.

4.1.3.1 Low Resolution TEM analysis

Low magnification TEM analysis was conducted and revealed the good dispersion of MWCNTs within the aluminium matrix as shown in figure 4.0.4 (b-d). The TEM images confirms SEM images in figure 4.0.2 (b-d) which shows good dispersion of MWCNTs within the aluminium matrix. Based on the literature long milling duration tend to achieved great dispersion but results in damaged CNT and degrade the mechanical properties of the composites due to amorphization. The amorphous carbon tends to react with aluminium to form aluminium carbide. In the case of interfacial bonding, the amorphous carbon generated during the chemical vapour deposition could affect the interfacial bonding status between CNTs and Al matrix to some extent (Zhu et al., 2016). The selected area electron diffraction (SAED) patterns of MWCNTs are shown in figure 4.0.4 (a-d) and they were used to study crystalline and amorphous phase. The SAED pattern of MWCNTs in figure 4.0.4 (b) and (c) had more impurities (indicated by green arrows) compare to that of figure 4.0.4 (d).

From the SAED patterns of MWCNTs figure 4.0.4 (b-d), sharp rings patterns were observed this indicates that MWCNTs have high crystalline nature and had no distortion on its planes. Crystalline natures of MWCNTs features are sharp coaxial rings pattern and identical chiralities of zigzag type (Arababad et al., 2016). Jagannatham et al. (2015) studied the crystalline and amorphous formed after dispersion of MWCNTs within Al matrix using SAED pattern (Jagannatham et al., 2015).

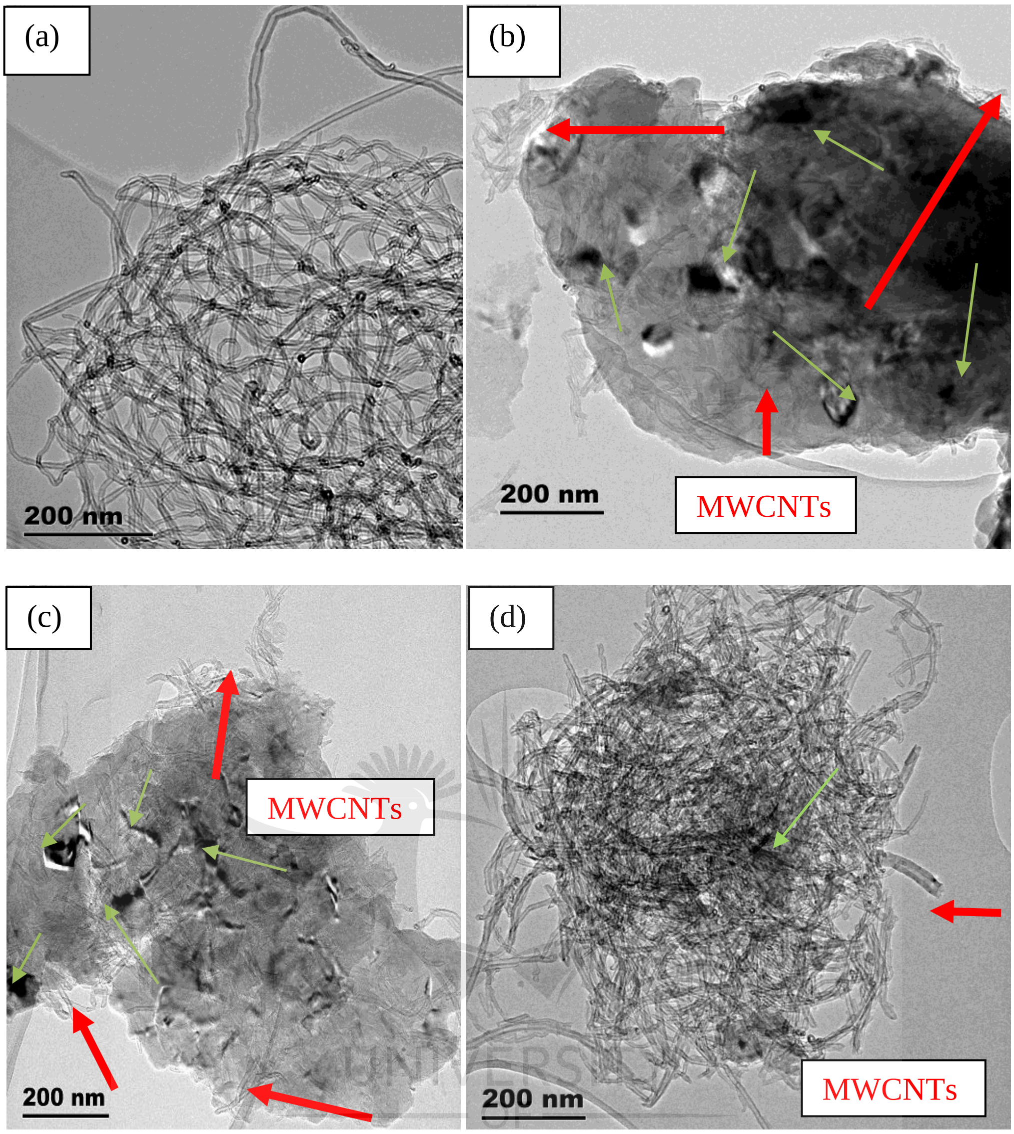

Figure 4.0.4. Low resolution TEM images of (a) MWCNT, (b)Al-0.5wt.%MWCNTs, (c)Al-1wt.%MWCNTs and (d)Al-1.5wt.% MWCNTs admixed powders

4.1.3.1 High Resolution TEM analysis

The HRTEM images in figure 4.0.5 (a – d) show images of MWCNTs and Al-MWCNTs admixed powders composites respectively. TEM images confirm that CNTs are MWCNTs in nature and they experience some level of strain. Arc discharge synthesized MWCNT of all Al-MWCNTs admixed powders composites consist of around 15 walls per tube. Figure 4.0.5 (c) shows the tubular morphology of MWCNTs with more damaged walls compared to MWCNTs walls in figure 4.0.5 (a). The intertubular spacing between walls of Al-0.5 wt.% MWCNTs and Al-1 wt. % MWCNTs is the same with value of 0.345 nm while intertubular spacing between walls of Al-0.5 wt. % MWCNTs is 0.353 nm among stacked nanotube layers. The increase in intertubular spacing of MWCNTs is due to strain on the nanotubes which is as a results of prolong ball milling conditions. The resulted strain was not severe hence crystal defects were not formed, this is supported by SAED results (Okoro et al., 2019).

The surfaces of the MWCNT are partially covered with thick amorphous carbon layers (brown arrows) and defects (blue arrows). Defects increase the roughness of the surface, which is believed to be beneficial for stress transfer from the matrix to the MWCNTs. Zhu et al. analysed Al composite reinforced with treated CNTs (carboxyl-functionalized) and Al composite reinforced with untreated CNTs, the surface of untreated CNT had amorphous carbon layers while the surface of treated CNT had defects but both without noticeable damages on the surface of the MWCNTs. The results show that the treated CNTs had larger effective interfacial contact with aluminium matrix as a results of large amount of -COOH group and defects on the surface interacting with Al by strong chemical and physical interactions.

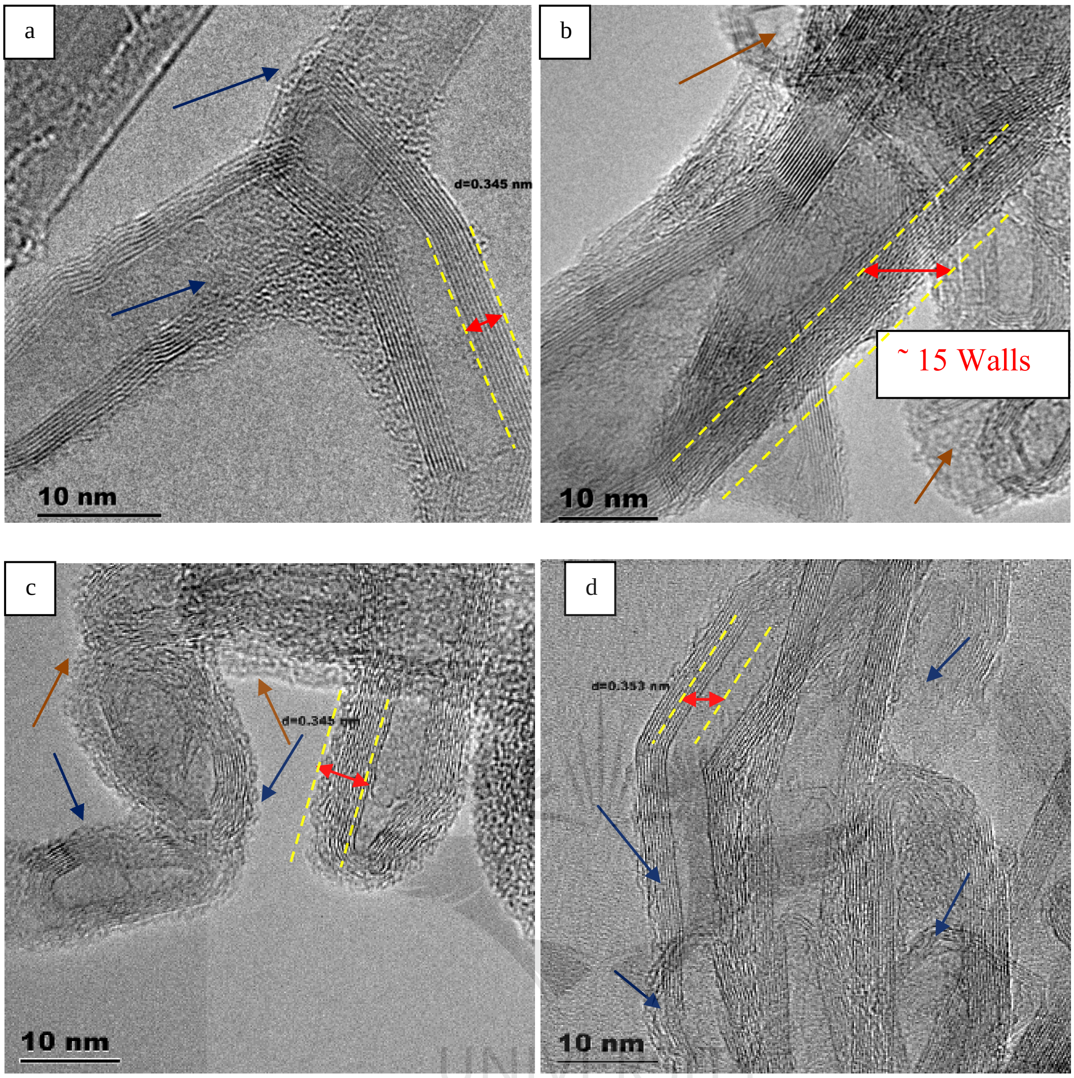

Figure 4.0.5.High resolution TEM images of (a) MWCNT, (b)Al-0.5wt.%MWCNTs, (c)Al-1wt.%MWCNTs and (d)Al-1.5wt.% MWCNTs admixed powders

4.1.4 Densification of Sintered Al-MWCNTs composites

The densification achieved after the sintering were examined using Archimedes principles. The densification values of the Al-MWCNTs composites are given in table 4.0.1 below. Al-MWCNTs composites are fully dense, the measured density of Al-MWCNTs composites range from 94 to 98%. The best densification value were obtained on Al-1.5 wt. % of MWCNT composite. This is attributed to the good dispersion achieved on Al-1.5 wt. % of MWCNT composite. The densification value of pure Al, Al-0.5 wt. % MWCNTs and Al-1 wt. % MWCNTs are the same (94%), this is likely due to small weight of MWCNTs content and also attributed to better distribution of MWCNTs within Al matrix. The following characterisation results support the obtained densification behaviour trend of Sintered Al-MWCNTs composites:

- Raman spectroscopy results of Al-1 wt. % MWCNTs sintered composite has reported structural changes.
- ID/IG ratio of Al-1.5 wt. % MWCNTs sintered composite is the lowest compare to theAl-0.5 wt. % MWCNTs and Al-1 wt. % MWCNTs composites.ID/IG ratio of Al-1.5 wt. % MWCNTs sintered composite is 1.000, which is not much of different to ID/IG ratio of MWCNTs.
- SEM and TEM micrographs of Al-0.5 wt. % MWCNTs admixed and sintered composites

Table 4.0.2. Theoretical Density of admixed Al-MWCNTs powders

Al-MWCNTs powders	Theoretical Density(g/cm^3)
Pure Al	2.6903
Al-0.5 wt.% MWCNTs	2.6863
Al-1 wt.% MWCNTs	2.6826
Al-1.5 wt.% MWCNTs	2.7137

Table 4.0.3. Densification of Sintered Al-MWCNTs composites

Al-MWCNTs composites	Density(g/cm^3)	Densification (%)
Pure Al	2.529	94
Al-0.5 wt.% MWCNTs	2.5251	94
Al-1 wt.% MWCNTs	2.5214	94
Al-1.5 wt.% MWCNTs	2.6611	98

4.1.5 Optical microstructure analysis of Sintered Al-MWCNTs composites

The microstructure of sintered Al-MWCNTs composites were characterised by optical microscope. Figure 20 (a-d) shows optical micrographs of unetched sintered Al-MWCNTs composites. Al-MWCNTs composites had no voids; this is supported by densification results of Al-MWCNTs composites (He et al., 2017). Aluminium oxide formation makes sintering of Al difficult since it prevents direct contact between Al particles. To break oxide, high sintering temperature during Spark plasma sintering must be used. For the current study 590 ℃, sintering temperature was used for all Al-MWCNTs composites. No aluminium oxides were observed (Jagarintham et al., 2015).

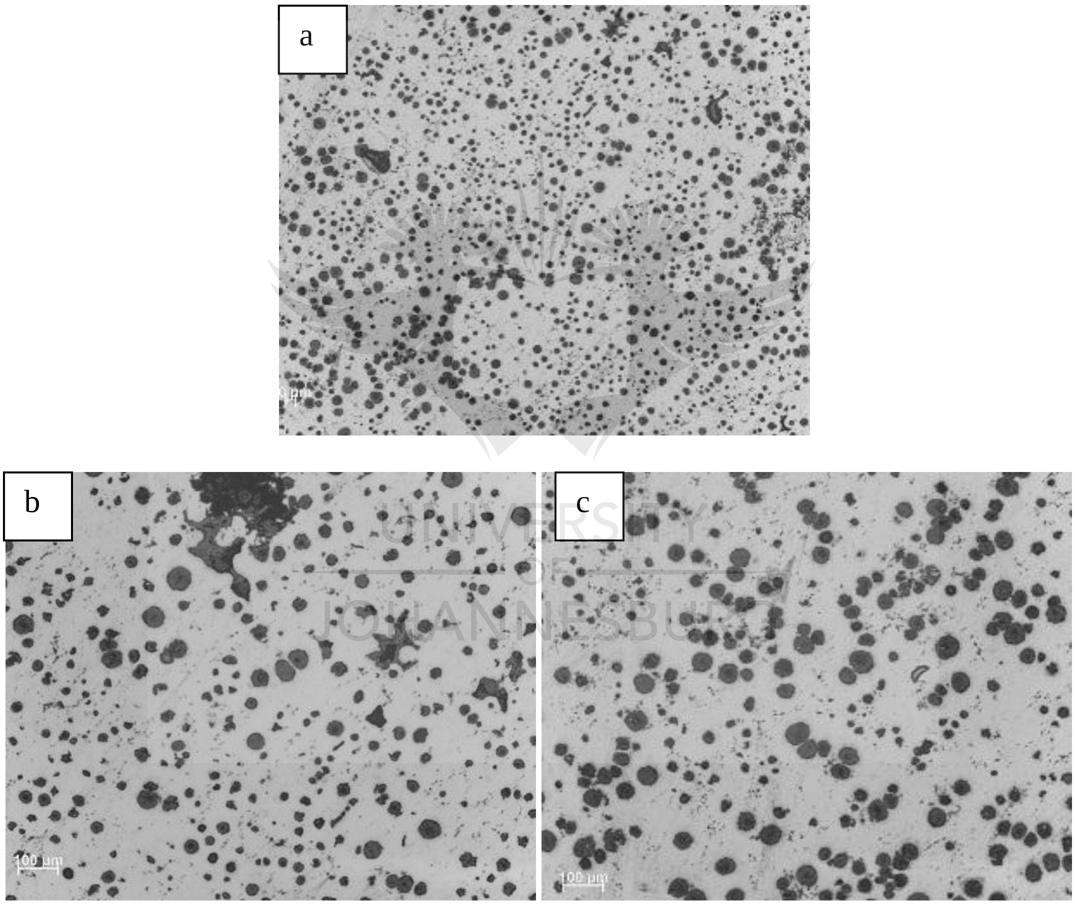

Figure 4.0.6. Microstructure of (a) Al-0.5wt. % MWCNTs, (b) Al-1wt. % MWCNTs and (c) Al-1.5wt. % MWCNTs composites

4.1.6 SEM analysis of Sintered Al-MWCNTs composites

SEM images of sintered pure Al, Al-0.5 wt. % MWCNTs, Al-1 wt. % MWCNTs and Al-1.5 wt. % MWCNTs composites after two stage ball milling followed by spark plasma sintering are shown in figure 4.0.7 (a-d). It is seen from SEM images that in all sintered composites MWCNTs (0.5 wt. % MWCNTs, 1 wt. % MWCNTs and 1.5 wt. % MWCNTs weight content) are homogeneous dispersed within Al matrix. Based on literature review, homogeneous dispersion of MWCNTs within Al matrix plays a crucial role in enhancing mechanical properties of composites (Pillars et al., 2017). Al-0.5 wt. % MWCNTs and Al-1.5wt. % MWCNTs sintered composites have retained MWCNTs after sintering while Al-1wt. % MWCNTs composite does not have the retained MWCNTs. The retained MWCNTs can be associated with MWCNTs content since based on the literature, the retained MWCNTs are the results of agglomerated CNTs (Guo et al., 2017).

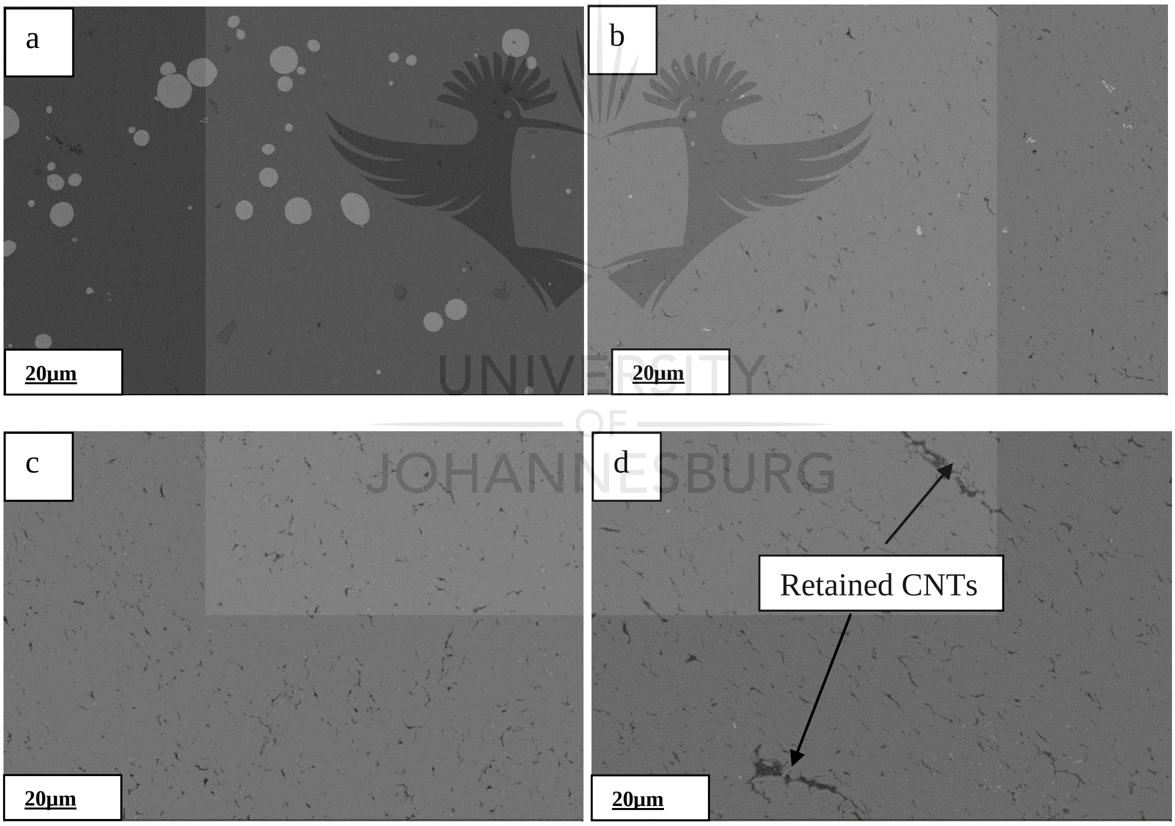

Figure 4.0.8. SEM images of (a) Pure Al, (b) Al-0.5wt. % MWCNTs, (c) Al-1wt. % MWCNTs and (d) Al-1.5wt. % MWCNTs composites

4.1.7 EDS analysis of Sintered Al-MWCNTs composites

Figure 4.0.9 show SEM images and corresponding EDS images of Al-MWCNTs composites. The EDS images confirm the presence of Al, C and O on sintered Al-MWCNTs composites.

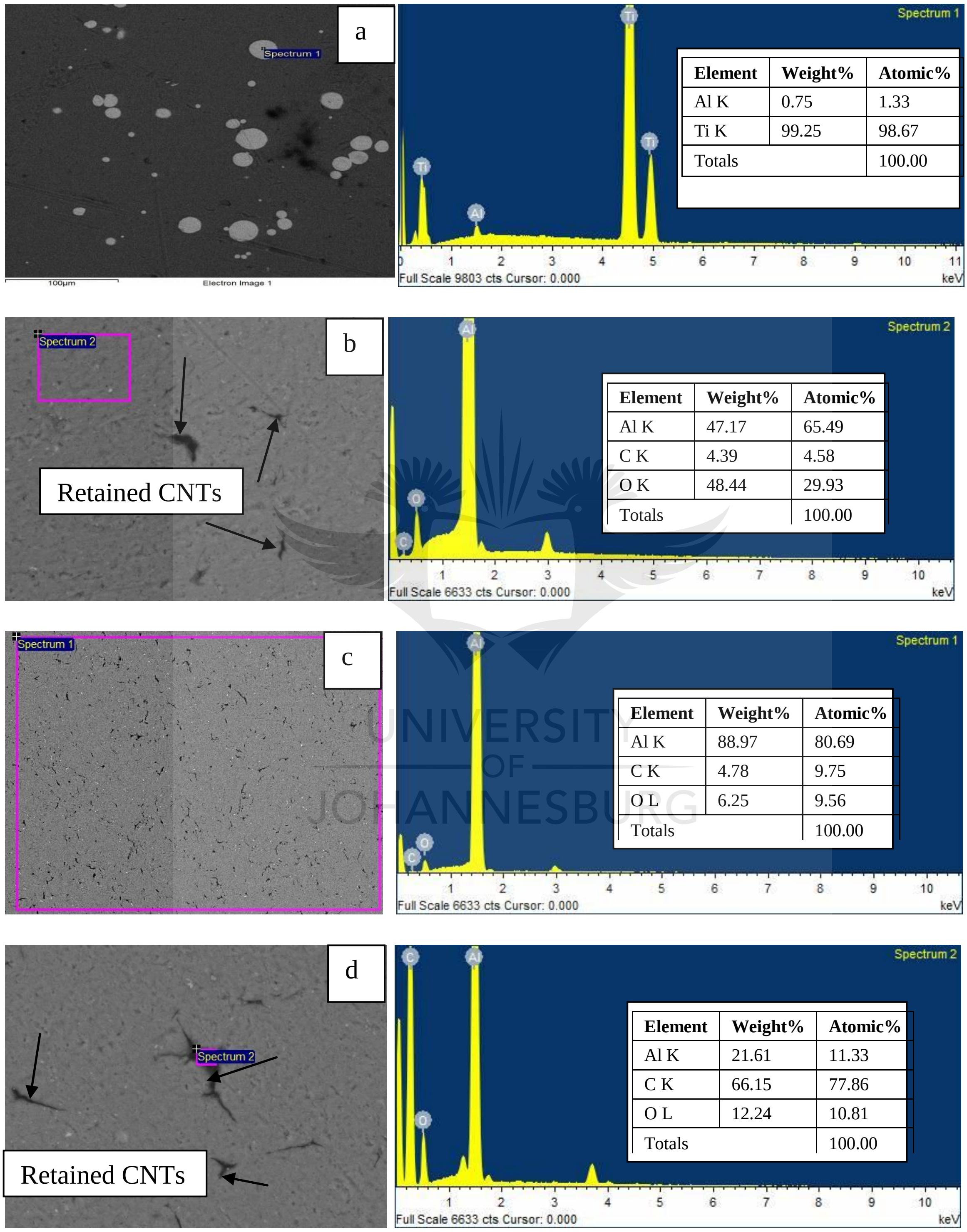

Figure 4.0.10. EDS images of (a) Pure Al, (b) Al-0.5wt. % MWCNTs, (c) Al-1wt. % MWCNTs and (d) Al-1.5wt.% MWCNTs composites

4.1.8 XRD analysis of Al-MWCNTs powders and sintered composites

XRD was used to examine the structural changes and phase present in admixed powders and sintered composites. Figure 4.0.11 indicate the XRD patterns of pure al, admixed powders (a) and sintered Al-MWCNTs composites (b). Various aluminium powders peaks are prominent at 2ϴ = 38.59, 44.89, 65.31, 78.50 and 82.72 which corresponds to the planes (111), (200), (220), (311) and (222) respectively. XRD pattern results show that there were no structural changes on the Al-MWCNTs structure. Ball milled admixed powders XRD patterns revealed peaks corresponding to pure Al. Fig. 4.0.12 (b) shows the XRD pattern of sintered Al-MWCNTs composites with peaks remain on position similar to that of the Al-MWCNTs admixed powders. The identical peaks indicate that MWCNTs maintain highly ordered tube structure and small damage of MWCNTs structure (Zhu et al., 2016). XRD pattern results shows that there is a structural change to the Al- 1 wt. % MWCNTs structure. The incorporation of MWCNT into Al powders via ball milling and spark plasma sintering techniques result in the formation of new phases in the sintered Al-1 wt. % MWCNTs composite.

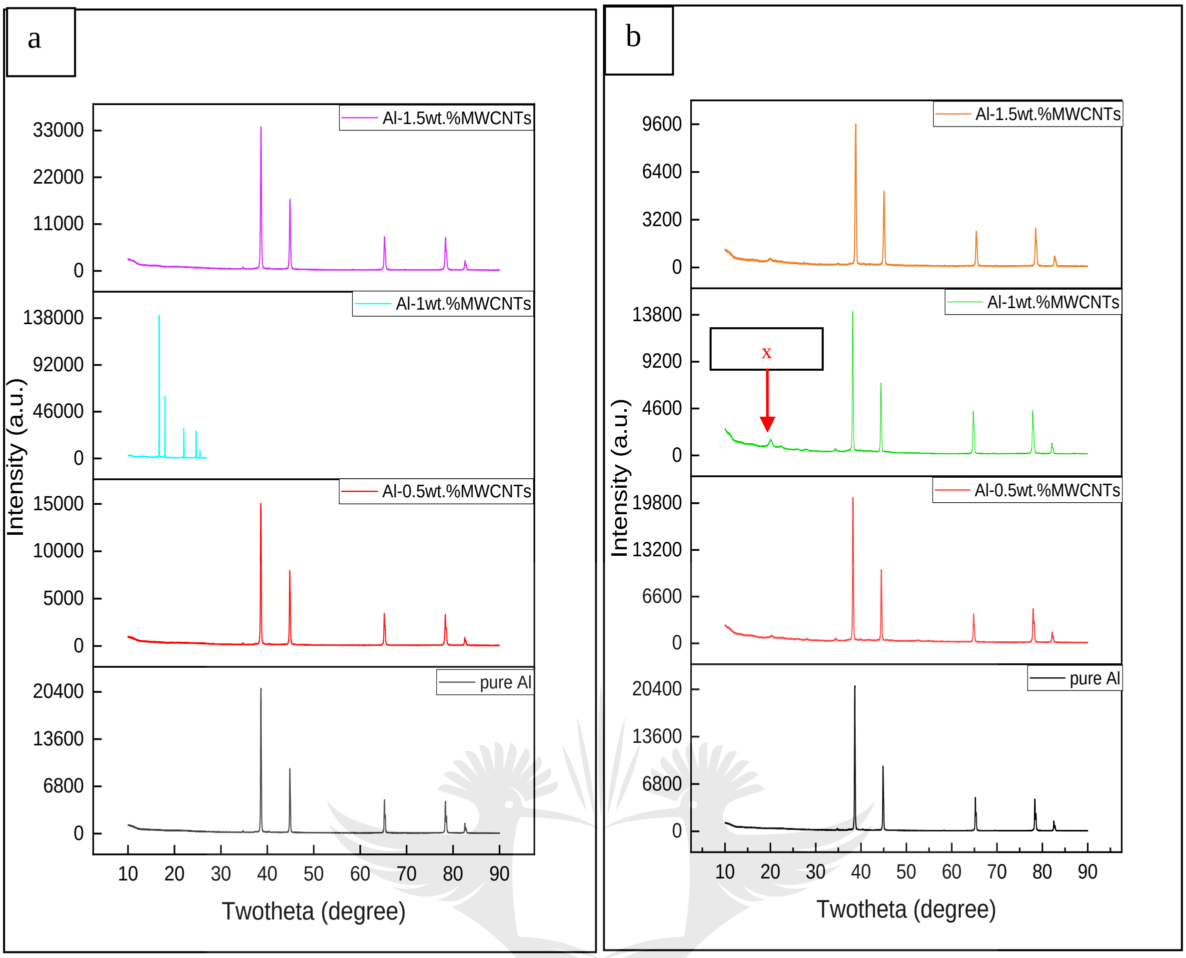

Figure 4.0.13. XRD results of (a) admixed powders and (b) sintered Al-MWCNTs composites

In sintered composites and admixed powders there were no trace of the MWCNT peaks in the XRD pattern of Al-MWCNTs composites because of low weight fraction of the MWCNT (<1.5 wt.% MWCNTs) (Esawi et al., 2009).

4.1.9 Raman analysis of Al-MWCNTs powders and sintered composites

The structural evolution of the MWCNTs within Al powders during ball milling and spark plasma sintering was studied. The study showed the level of the imposed strain on the structural integrity of MWCNTs. Raman spectroscopy was used to characterize MWCNTs, Al-MWCNTs admixed powders and sintered Al-MWCNTs composites.

Table 4.0.4. Intensity ratio of MWCNTs during various composite processing

Sample	% increase in ratio	Ball milled powders	Sintered composites
MWCNTs	0%	0.8913	0.8913
Al-0.5 wt.% MWCNTS	8%	0.9655	1.0499

Al-1 wt.% MWCNTS	13%	0.9957	1.1399
Al-1.5 wt.% MWCNTS	0%	1.0005	1.000

Table 4.0.5 summarize the intensity ratio of MWCNTS during ball milling and spark plasma sintering while figure 4.0.14 shows Raman spectra of MWCNTs powders, Al-MWCNTs admixed powders (a) and sintered Al-MWCNTs composites (b). The main graphitic peaks correspond to D band and G band. The D band shows the non-sp^2structural associated with defects concentration (The disorder in C-C bonds). The G band shows the degree of crystalline in the graphitic materials (Peng & Chang, 2014; Pillar et al., 2017). It was observed that the spectra of Al-MWCNTs depict small intense peaks. Due to the known reason that Raman technique is usually used to ascertain the structural integrity of MWCNTs(when used as reinforcements to enhance materials properties) during composites production to which the content of MWCNTs range as follows: 0.5, 1 and 1.5 wt.% MWCNTs (Okoro et al., 2019). The intensity ratio (ID/IG) of the Raman peaks has proven to be an effective means to study the evolution of MWCNTs as reinforcement of different composites during various processing techniques (Munir et al., 2015). The Raman spectra of MWCNTs in Figure 4.0.15 (a) indicated the D and G bands peaks, which are of different heights in the spectral range of 500-2500/cm at 1250 and 1600/cm.

The corresponding ID/IG ratio of MWCNTs was calculated to be 0.8913. Admixed powders observed ID/IG ratio of Al-0.5 wt. % MWCNTs is 0.9655 indicating 8% increase in ID/IG while the observed ID/IG ratio of Al-1 wt. % MWCNTs is 0.9957 indicating 10 % increase and Al-1.5 wt. % MWCNTs composite is 1.0005 indicating 11 % increase. From figure 4.0.16 (b),observed ID/IG ratio of Al-0.5 wt. % MWCNTs sintered composites is 1.0499 while the observed ID/IG ratio of Al-1 wt. % MWCNTs is 1.1399 and Al-1.5 wt. % MWCNTs composite is 1.000.In both admixed powders and sintered composites there is no shift of G- peaks, this is attributed to normal inter-atomic distance of carbon atoms during the milling and sintering processes. Previous research has reported that an increase in the ID/IG ratio after Al-MWCNTs composite synthesis means an increase in the defect density and implies some sort of damage incurred to CNTs while processing while decrease in the ID/IG ratio may indicate graphitization by annealing effect produced during processing (Okoro et al., 2019). The sintered composite ID/IG ratio of Al-1wt. % MWCNTs is greater than the ID/IG ratio of Al-1.5wt. % MWCNTs indicating that structural strain imposed on 1 wt.% MWCNTs were much severe compare to those of 1.5 wt.% MWCNTs content. Since the level of structural strain imposed on the MWCNT was not severe, and were not capable of forming aluminum carbide phases on the nanotubes, which would have reflected as prominent peaks on the Raman spectra of sintered composites.

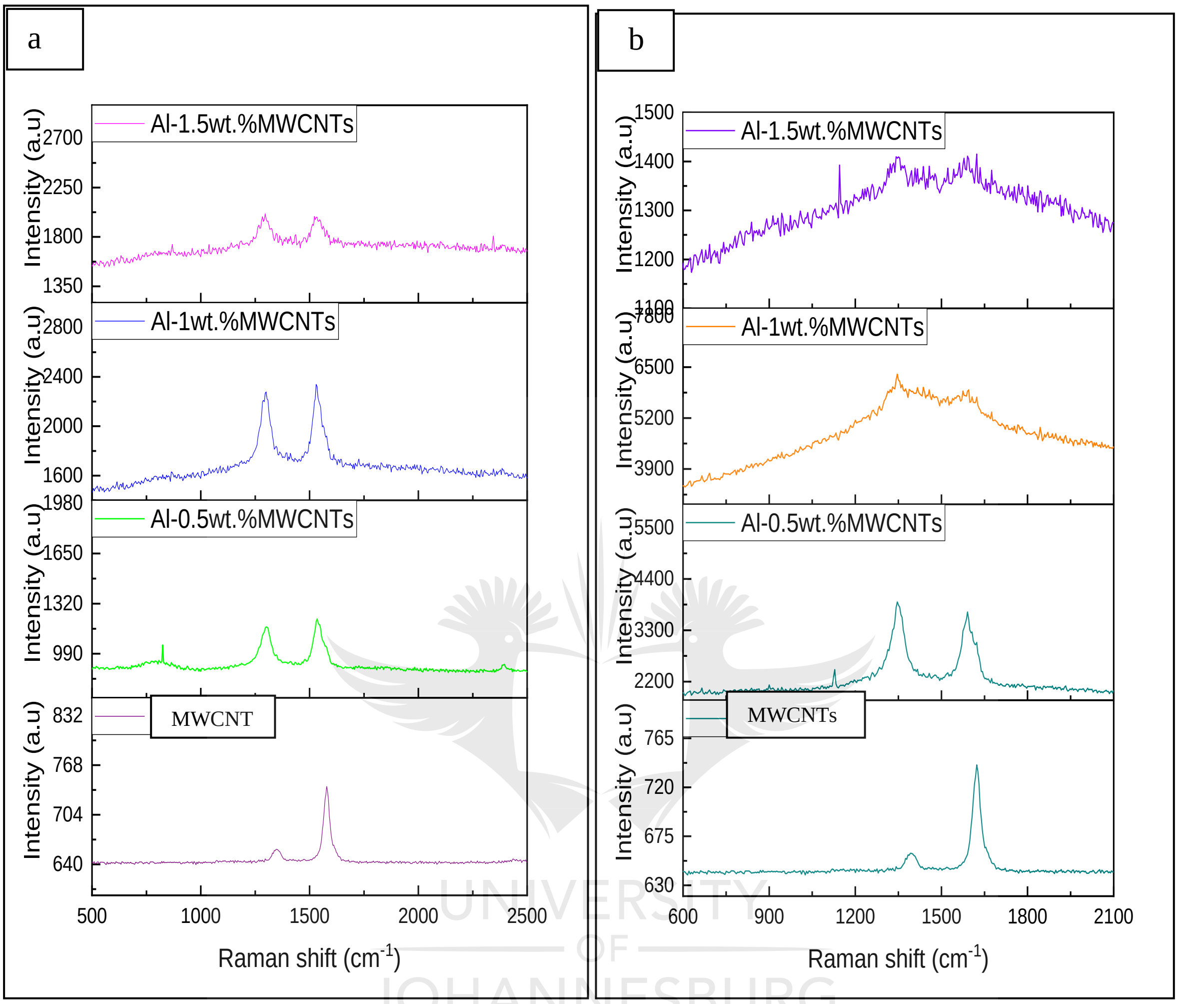

Figure 4.0.17. Raman spectroscopy results of (a) admixed powders and (b) sintered Al-MWCNTs composite

4.2 Nano-indentation response and property

4.2.1 Plasticity and Elasticity of Al-MWCNTs composites

Figure 4.0.18a shows the force-depth curves of Al-MWCNTs composites with loading rate of 40Mn/S, holding time of 10s and unloading rate of 40Mn/S for applied load of 100 µN. The unloading behaviour is in relation with to elastic contact stiffness of material therefore it is important in analysing mechanical properties (hardness and young modulus of elasticity) of Al-MWCNTs composites using the Oliver-Pharr approach (Khodobakhshi et al., 2019). The indentation depth of Al-MWCNTs composites decreases with an increase in MWCNTs content, indicating that Al-MWCNTs composites harden due to the present of MWCNTs in Al composites.

Therefore, it can be concluded that multi walled carbon nanotubes has contributed to the strengthening of Al-MWCNTs composites. Similar curves showing similar behaviour of Al alloy is show in (Chi tsai et al., 2017) at room temperature. Anirruddha et al. (2013) have found experimental and simulated similar curves for Al alloys (Anirruddha et al., 2013). Al – 1.5 wt. % MWCNTs composite had higher resistance to applied load i.e. higher applied load values are needed for Al – 1.5 wt. % MWCNTs composite to reach same displacement of the pure aluminium composites. Figure 4.0.19b shows the depth-time curves for Al-MWCNTs composites. The depth–time curves provide deeper penetration depth results in larger creep displacement. The end of the curves is generally assumed to be the steady-state creep period, therefore the steady-state creep of pure Al, Al-0.5wt.%MWCNTs, Al-1wt. %MWCNTs and Al-1.5 wt. %MWCNTs composites is assumed to be 950s, 301s, 302 and 303s respectively. The effective shift in the curves toward left indicates the effective reduction in the displacement accounting to the strengthening of the matrix by CNTs.

From all four Al-MWCNTs composites, it can be seen that as depth increases so does the time. Pure Al composite showed a significant creep of 2750 nm over 950s dwell time while Al-0.5 wt. %MWCNTs composite showed a significant creep of 2450 nm over 301s dwell time, Al-1 wt. %MWCNTs composite showed a significant creep of 2250 nm over 302s dwell time and Al-1.5 wt. %MWCNTs composite showed a significant creep of 2200 nm over 920s dwell time. It can be concluded based on MWCNTs content that Al-MWCNTs composites experienced most creep when MWCNTs content is less and least creep when MWCNTs content higher. Previous research studies showed how factors such as nanoindentation temperature (Koch et al., 2015) penetration depth (Zhao et al., 2018) and loading strain rate (Zhao et al., 2018) are dependent of creep deformation of material. Pure Al composite has greater plasticity meaning energy stored at the material after indentation is over (Koumolous et al., 2014). The ratio of plastic to total work of indentation (w_p/ w_t) of pure Al, Al-0.5wt.% MWCNTs, Al-1wt.%MWCNTs and Al-1.5 wt. %MWCNTs composites is 0.8812, 0.8920 0.9299 and 0.9994 respectively. The plasticity of pure Al, Al-0.5wt.% MWCNTs, Al-1wt.% MWCNTs and Al-1.5wt. % MWCNTs composites is0.309, 0.0591, 0.070 and 0.149 respectively. Deformation is likely to be elastic, when plasticity index is much less than unity (Koumolous et al., 2014). Greater plasticity is revealed in Al-1.5wt.%MWCNTs composite, with pure Al composite exhibiting higher elastic recovery.

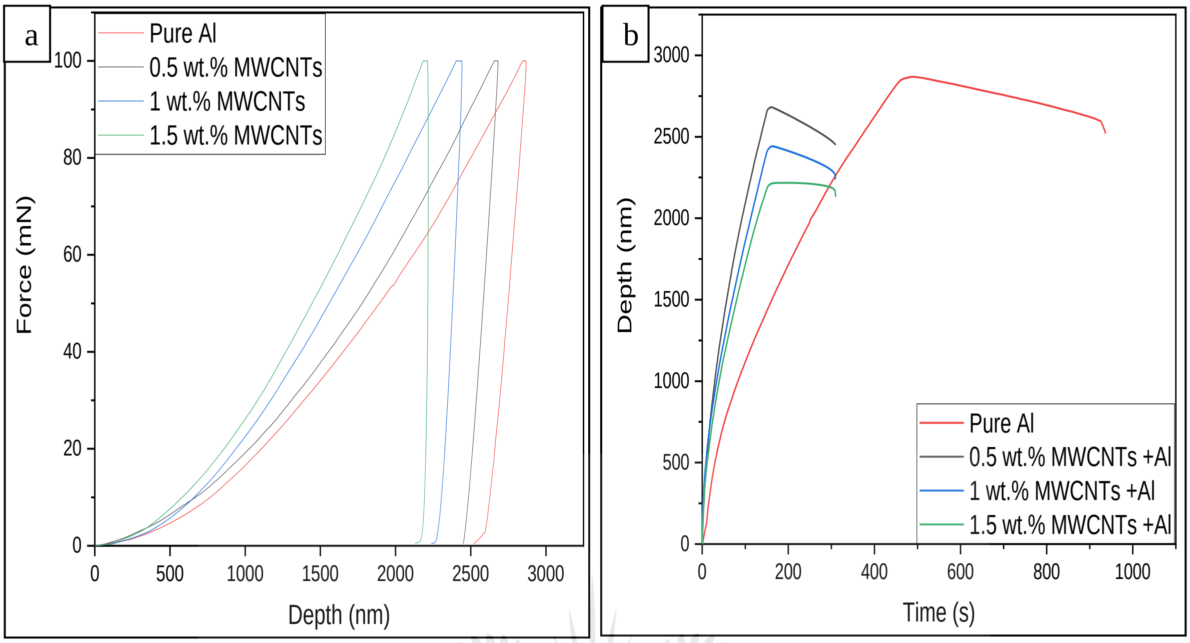

Figure 4.0.20. Creep curves of Al-MWCNTs composites (a-b)

Table 4.0.6 . Plasticity and elasticity of Al-MWCNTs composites

Al-MWCNTs composites samples	**Plasticity**	**Elasticity**	**(w_p/ w_t**
Pure Al	0.1187	99.9691	0.8812
Al-0.5 wt.% MWCNTs	0.1080	99.9409	0.8920
Al-1 wt.% MWCNTs	0.070	99.93	0.9299
Al-1.5 wt.% MWCNTs	0.0006	99.851	0.9994

Plasticity was obtained by substituting the measured values of work during unloading and total work into equation 1 and elasticity was calculated through equation 2.

$$\text{Plasticity}=\frac{\text{Wtotal}-\text{wu}}{\text{Wtotal}} \qquad (1)$$

Where W_{total} is work of total indentation process and W_u is work during unloading

$$W_e = w_t - w_p \qquad (2)$$

Where W_e is elastic work, w_t is total work and w_p is plastic work of indentation.

4.2.2 Hardness of Al-MWCNTs composites

Hardness of spark plasma sintered Al-MWCNTs composites were determined by ultra nanoindentation and micro hardness tester.

Table 4.0.7. Nano hardness and micro hardness of Al-MWCNTs composites

Al-MWCNTs composites samples	Nano indentation hardness		Micro hardness tester Vickers hardness
	Hardness(Mpa)	Vickers hardness	
Pure Al	455,6	42,193	45.55 HV/20
Al-0.5 wt.% MWCNTs	597,6333333	55,347	47.65 HV/20
Al-1 wt.% MWCNTs	771,8233333	62,09966667	59.41 HV/20
Al-1.5 wt.% MWCNTs	1021,676667	94,61866667	93.71 HV/20

Table 4.0.8 Show comparison between nano hardness and micro hardness of Al-MWCNTs composites. Both hardness results shows similar trend of hardness that increases with increase in MWCNTs content. Pure aluminium composite exhibits lowest hardness while Al-1.5 wt.% MWCNTs composite exhibits highest hardness. The improvement in hardness compared to unreinforced pure Al is attributed to the grain refinement and strain hardening of powder particles during ball milling (Pillari et al., 2017). Improvement of hardness can be associated with the good dispersion of MWCNTs within Al matrix as well as the good interfacial bonding strength at MWCNTs interface. The decrease in hardness is associated with presence of MWCNT clusters, which introduces many pores in the matrix (Nie et al., 2013). The obtained results trend aligned with drawn conclusion of Al-MWCNTs composites hardness by various researchers (Girisha et al., 2014; Guo et al., 2017; Sharma & Sharma, 2016). Guo et al. (2017) obtained hardness results of Al-1.5 wt.% MWCNTs composite which is similar to the current study (Guo et al., 2017). Girisha et al. (2014) observed an increase in hardness of Al-MWCNT composites with increasing reinforcement up to 2 wt.% (Girisha et al., 2014). Ogawa et al. (2018) used two type of CNT (MWCNTs and VGFs) and obtained similar trend as obtain in current study and went further in concluding that MWCNTs composite’s hardness values were higher than VGFs composites. Spark plasma sintered Al-MWCNTs composites hardness were further determined using Micro hardness tester. A similar trend is showed i.e. as MWCNTs content increases hardness of Al-MWCNTs composites increases.

Bradbury et al. (2016) obtained maximum hardness of Al-MWCNT composites reinforced with 6 wt.% MWCNTs and further addition did not result in any improvement in hardness (Bradburg et al., 2016).

In another study, Nie et al. (3012) observed that hardness of Mo-CNT/Al composites increase up to 0.5 wt.% Mo-CNT content further increase of Mo-CNT content results in reduction of hardness of Mo-CNT/Al composites, the reduction in hardness has been attributed to poor dispersion and clustering / agglomeration of nanoparticles. Pillari et al. (2017) fabricated AA2219-graphene/MWCNT nanocomposites using high-energy ball milling followed by vacuum hot pressing. Hardness results had a trend which is similar to that of Bradbury et al. (2016) and Nie et al. (2012), further decrease of hardness was associated with agglomeration of reinforcement (Pillari et al. (2017). It has been proven that when MWCNTs content is high, uniform distribution of reinforcement is hard and MWCNTs may get together to form micro-split source which results in reduction of hardness. The large number of fine MWCNTs distributed in composite contributes to fair deformation resistance to the movement of dislocation (Nie et al., 2012). Figure 4.0.21 shows hardness results of the current study. Additions of CNTs into the Al matrix have a negligible effect on microhardness of Al-0.5 wt.% CNTs composites on work done by Hildalgo et al. (2017).

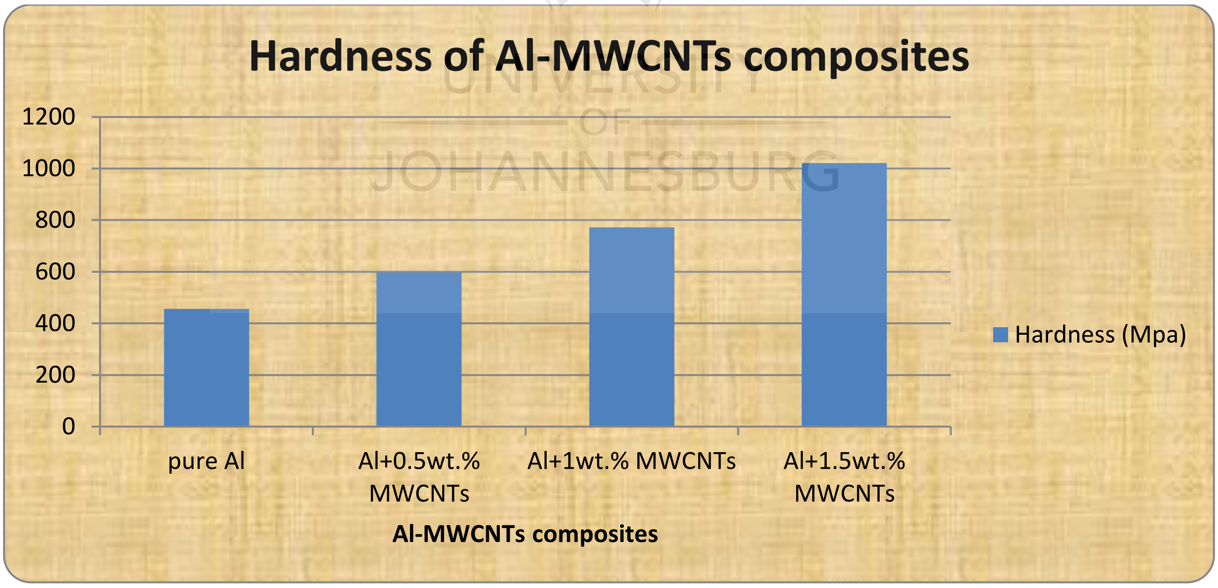

Figure 4.0.22. Hardness of Al-MWCNTs composites

4.2.3 Yield strength of Al-MWCNTs composites

Yield strength of spark plasma sintered Al-MWCNTs composites were determined by Tabor (H= 3 × tensile strength) using the relationship between hardness and yield strength (Khan et al., 2010).

Strengthening effect of MWCNTs is observed by pure aluminium composite exhibiting lowest yield strength while Al-1.5 wt.% MWCNTs composite exhibits highest yield strength. Figure 4.0.23 show that yield strength increases with increase in MWCNTs content. Guo et al. (2017b) obtained similar trend on yield strength of Al-CNTs composites when Al-1 vol.% CNTs composites were fabricated through spark plasma sintering and extrusion respectively. Effect of particle size of Al powders on the yield strength was also showed by 2 µm Al- 1 vol.% CNTs composite with 279 MPa and 20 µm Al- 1 vol.% CNTs composite with 138 MPa (Guo et al. (2017b).

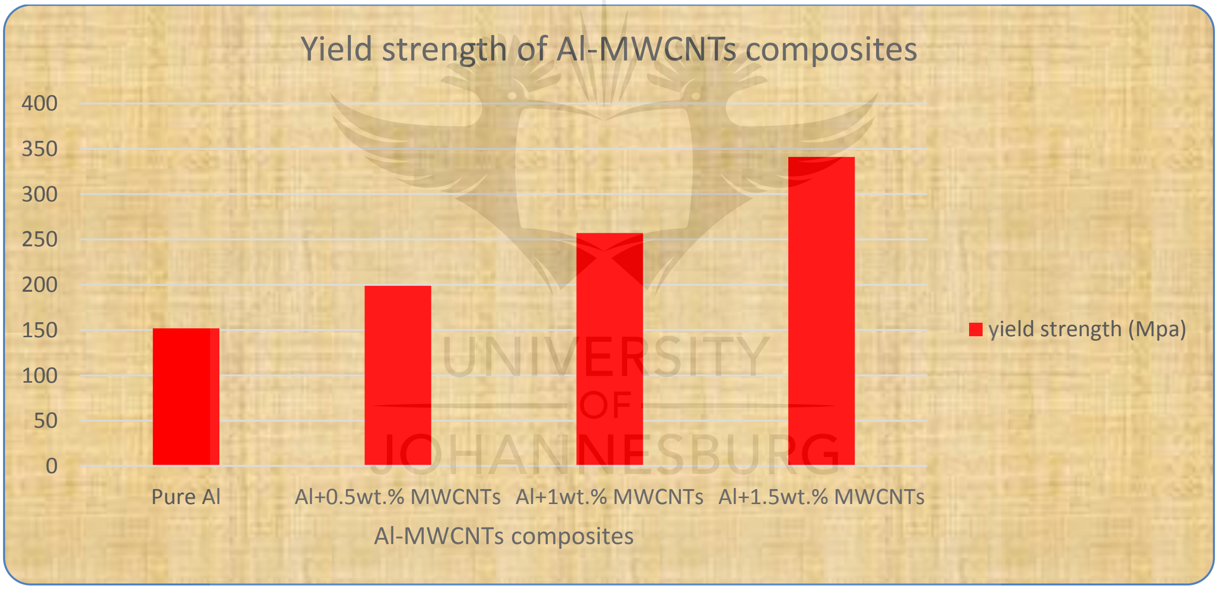

Figure 4.0.24. Yield strength of Al-MWCNTs composites

Girisha et al. (2014) fabricated Al-MWCNTs composites with different MWCNTs weight content of 0.5, 1, 1.5 and 2 wt.% using stir casting. The yield strength results were as follows: pure Al with 86 MPa, Al-0.5 wt.% MWCNTs with 97 MPa,Al-1 wt.% MWCNTs with 95.95 MPa, Al-1.5 wt.% MWCNTs with 98.6 MPa and Al-2 wt.% MWCNTs with 98.2 MPa. The reinforcement effect of MWCNTs were fairly on the yield strength of casted Al-MWCNTs composites. Comparing Girisha et al. (2014) with the current study it is clear that the developed Al-MWCNTs had better yield strength (Figure 4.0.25.), this can be associated homogeneity of carbon nanotubes within Al matrix. Liu et al. (2017) research work showed that longer ball milling results in greater yield strength while short ball milling results in smaller yield strength of extruded Al-2 wt. % CNTs composites. The enhancement of yield strength is associated with fine grains of the Al-CNTs composites (Table 4.0.9).

The two stage ball milling of 100 rpm for 6 hours and 300 rpm for 1 hour employed on the current study is also associated with enhanced yield strength of Al-MWCNTs composites. 56% of yield strength on Al-1.5 wt. % MWCNTs was achieved.

Table 4.0.10. Yield strength of ExtrudedAl-2 wt. % CNTs composites during ball milling

Ball milling time (h)	Yield strength (MPa)
2	98
4	125
6	162
8	173
10	193
12	210

4.2.4 Modulus of elasticity of Al-MWCNTs composites

The load-displacement curve in figure 4.0.26a plotted for Al-MWCNTs composite is useful in determining the modulus of elasticity, which can be calculated from reduced young's of modulus (E_r) obtained from nanoindentation. The shift of the load-displacement curve to the left indicates great reduction of displacement due to the strengthening of Al matrix by MWCNTs therefore smaller displacement is attributed to higher modulus of elasticity value while bigger displacement is attributed to higher modulus of elasticity value (Anirruddha et al., 2013). Figure 4.0.27 show modulus of elasticity of Al-MWCNTs composites. Modulus of elasticity of Al-MWCNTs composites increases as MWCNTs content increases. Modulus of elasticity depends on bonding between MWCNTs and matrix and in interfacial shear stress transfer, therefore lower modulus of elasticity of Al-0.5 wt. % MWCNTs composite is associated with poor interfacial bonding between MWCNTs and Al and poor interfacial shear stress transfer (Anirruddha et al., 2013). MWCNTs strengthening effect influence on modulus of elasticity of Al-MWCNTs composites is observed in all four Al-MWCNTs composites (pure Al, Al-0.5 wt.% MWCNTs, Al-1 wt.% MWCNTs and Al-1.5 wt.% MWCNTs) hence the stiff nature of MWCNTs composites results in increase in modulus of elasticity of those Al-MWCNTs composites (Shen et al., 2019).

On the indentation loading curves, modulus of elasticity can be estimated by determining the contact stiffness form unloading segment (Khodabakhshi et al., 2019) and it can be calculated by different models such as Isostrain, shear and Isostress (Anirruddha et al., 2013). The estimation has suggested that the elastic modulus of composites should be enhanced, if good dispersion is achieved and there is low damage of the CNTs.

From the published papers, some researchers reported significantly enhancement of elastic modulus of between 68–95Gpa (Anirruddha et al., 2013; Musset, 2002, Khodabakhshi et al., 2017) as well as nearly no difference (Shen et al., 2019, Roude et al., 2015). Previous works by Esawi et al. (2009) has reported that addition of 2 wt. % CNT provides the most significant strengthening Young's modulus but saturates at 5 wt. % CNT (Esawi et al., 2009). Modulus values of Al-TiO_2 composites showed big difference on Al-TiO_2 composites, Al-5% TiO_2 and Al- 7.5% TiO_2 composites had least modulus compared to Al-2.5% TiO_2 and Al- 10% TiO_2 composites (Ferreira, 2017). Sharma and Sharma (2015) consolidate nano aluminium composites with CNTs content of 1, 2, 3, 4 and 5 wt. %. Enhancement of modulus of elasticity occurs on nano Al-1 wt. % CNTs and nano Al-2 wt.% CNTs composites the rest of the nano Al composites modulus of elasticity decreases as a results of the re-agglomeration of CNTs at the higher loadings . The nano Al-3 wt. % CNTs composite had elastic modulus, which is approximately equal to that of the nano Al (Sharma and Sharma, 2015).

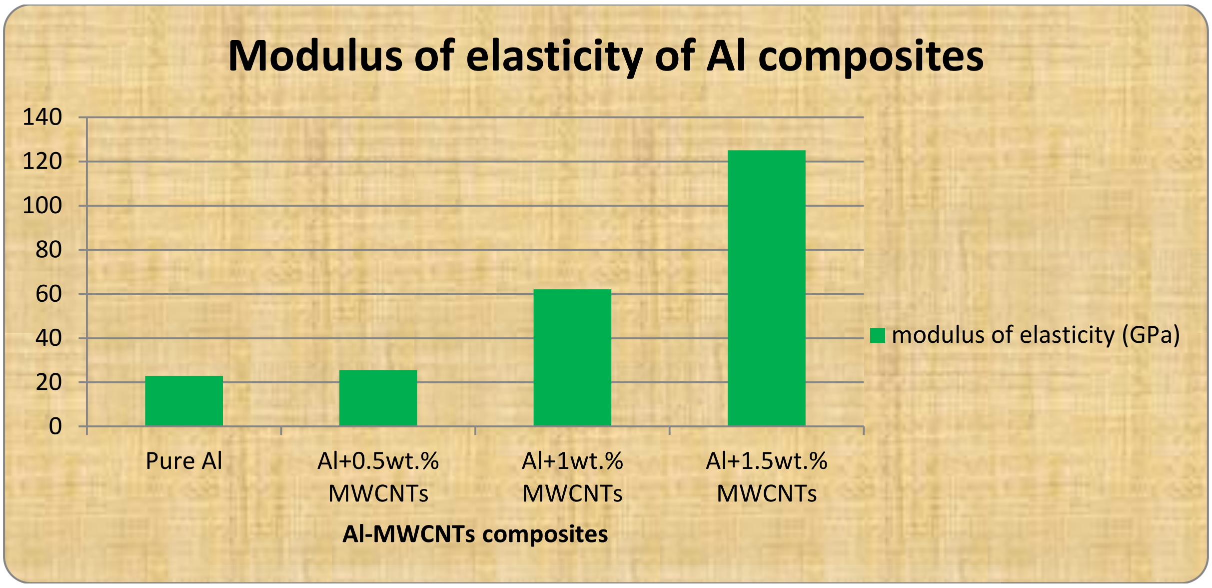

Figure 4.0.28. Modulus of elasticity of Al-MWCNTs composites

4.2.5 Strain rate sensitivity of Al-MWCNTs composites

Strain rate sensitivity (SRS) is one of the factors that are necessary for understanding the deformation behaviour of material (Haghshenas et al., 2016). It controls ductility properties of metal hence high SRS and work hardening values delay the onset of localized deformation under tensile stress, resulting in improved ductility and help to reduce plastic instability (Cabibbo et al., 2018). The importance of Strain rate sensitivity is during machining as it tells the responds of material during machining (Koch et al., 2014). Two factors that are govern SRS of FCC metals are deformation temperature and grain size reduction (Cabibbo et al., 2018). Strain rate sensitivity of Al-MWCNTs composites at room temperature are shown in figure 4.0.29. Al-1wt. % MWCNTs composite exhibits the highest strain rate sensitivity while pure aluminium composite had the least strain rate sensitivity. High strain rate sensitivity of Al-1wt. % MWCNTs composite is attributed to high ductility while low strain rate sensitivity of Al-0.5 wt. % MWCNTs composite is attributed to low ductility (Koch et al., 2015). Al-1.5 wt. % MWCNTs composite were expected to have higher strain rate sensitivity than all the consolidated Al-MWCNTs composites due to higher MWCNTs content (MWCNTs strengthening effect) but literature had shown that strain rate sensitivity is depend on deformation temperature, grain size reduction, penetration depth, loading strain rate and indentation size (Cabibbo et al., 2018; Koch et al., 2014; Zhao et al., 2018).

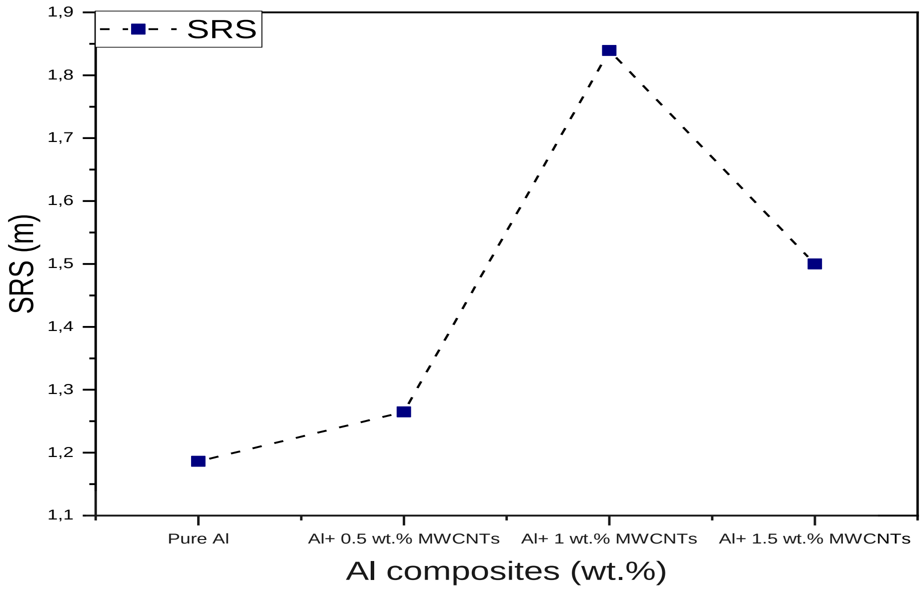

Figure 4.0.30. Strain rate sensitivity of Al-MWCNTs composites

Using ultra Nanoindentation tester, SRS can be obtained by applying time-displacement data through the relationship between creep stress and strain rate i.e. m=$\frac{\partial ln\sigma}{\partial ln\varepsilon}$ (Ma et al., 2017). After comparing the SRS data obtained in this work with research study of Ma et al. (2017) for different aluminium alloys, the current research study showed similar SRS results trend. AA225C0.7 had higher SRS than AA225C15 and A45C0.7 had higher SRS than A45C15 which is seen in the current study between Al-1 wt. % MWCNTs and Al-1.5 wt. % MWCNTs. Strain rate sensitivity results of aluminium alloy obtained using Nanoindenter by Koch et al. (2014) is shown in table 4.0.11 below. At higher temperature the strain rate sensitivity increases. The highest strain rate obtained in the current study is 1.8 on Al -1wt. % MWCNT composite which is the same strain rate sensitivity as aluminium alloy when nanoindentation test is run at 180℃ (Koch et al., 2014). The relationship between strain rate sensitivity (m) and hardness is presented in figure 4.0.31 . The values of m decreased with increasing hardness in all Al-MWCNTs composites. Based on the theory, the value of m is inversely proportional to hardness according to the equation m =$3\sqrt{3}\frac{KT}{H\times V}$. Obtained values of m and hardness of all Al-MWCNTs composites support theory (Zhao et al., 2018).

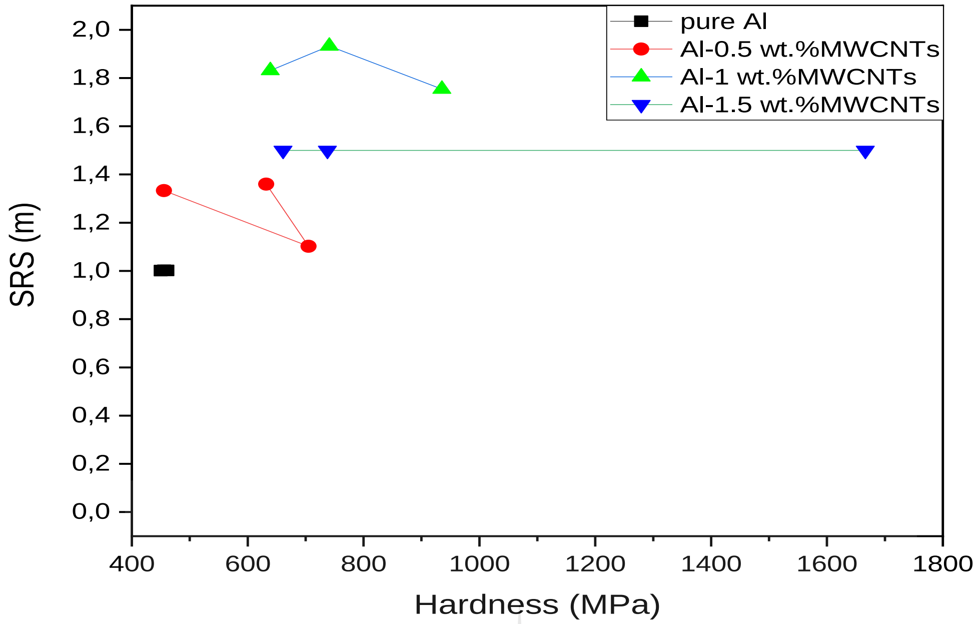

Figure 4.0.32. The relationship between strain rate sensitivity and hardness of Al-MWCNTs composites

Table 4.0.12. Strain rate sensitivity of AA2030 alloy at varied testing temperature

Temperature	**Strain rate sensitivity stage 1**	**Strain rate sensitivity stage 2**
25	0.0227	0.114
180	0.036	0.185
240	0.082	0.170
400	0.159	0.226
480	0.158	0.345

4.2.6 Stiffness of Al-MWCNTs composites

Figure 4.0.33 show stiffness of Al-MWCNTs composites. Al-1.5 wt. % MWCNTs composite exhibits greater stiffness compare to pure Al, Al-0.5 wt. % MWCNTs and 1 wt. % MWCNTs composites. The improvement of stiffness is associated with strengthening effect of MWCNs in Al matrix. During ultra Nanoindentation test, stiffness is deduced from unloading curve and influence by pressed depth (Ma et al., 2017).

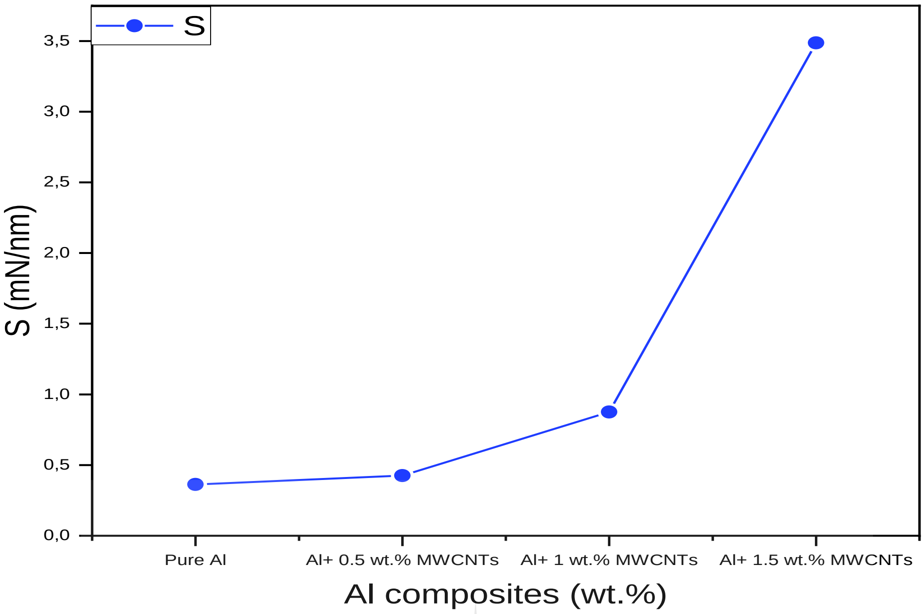

Figure 4.0.34. Stiffness Al-MWCNTs composites

4.3 Fracture analysis of Sintered Al-MWCNTs composites

Fracture surfaces obtained by using SEM are represented in figure 4.0.35 (a-d), which show the fracture surface of Al-MWCNTs composites. The present of many dimples in Al matrix is attributed to strong adhesion between particles. Rough fracture surface with large dimples corresponds to ductile fracture.

Ductile material usually shows micro voids coalescence type of fracture. MWCNT bridges were observed in all MWCNTs composites regardless the amount of MWCNTs addition as shown in figure 23b (Al-0.5 wt. % MWCNTs,), figure 23c (Al-1 wt. % MWCNTs) and figure 23d (Al-0.5 wt. % MWCNTs). MWCNTs bridges play a crucial role in improvement of mechanical properties. No changes of MWCNTs were observed in Al matrix this indicates that MWCNTs didn't include formation of aluminium carbide (Kwon et al., 2016).

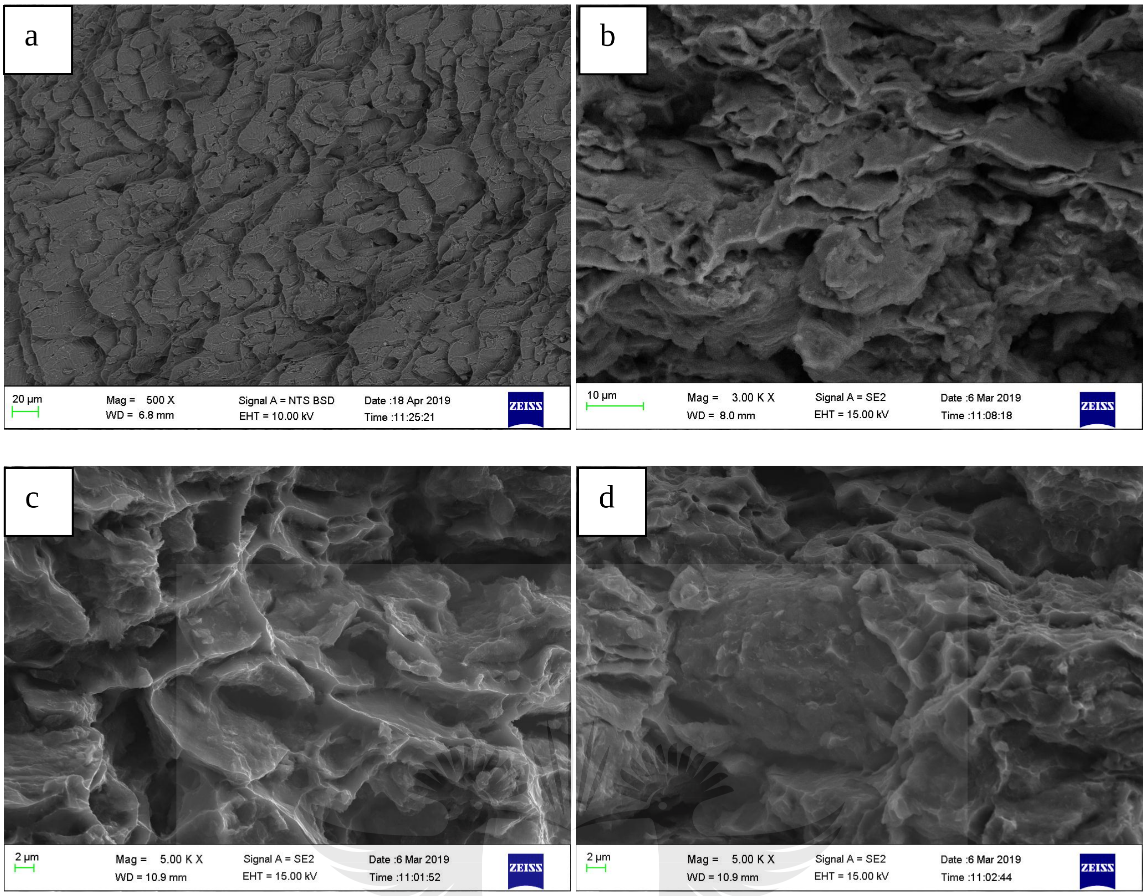

Figure 4.0.36. Fracture analysis of (a) Pure Al, (b) Al-0.5wt. % MWCNTs, (c) Al-1wt. % MWCNTs and (d) Al-1.5wt.% MWCNTs composites

Chapter 5

5. Conclusion and Recommendation

This chapter presents conclusions and recommendations drawn from the study.

5.1 Conclusions

In this research work, efforts have been made to develop and study mechanical properties of Al-MWCNTs composites, which were fabricated using ball milling and spark plasma sintering respectively. Mechanical properties of Al-MWCNTs composites were evaluated using ultra nanoindentation tester. The effect of MWCNTs as reinforcement of Al matrix has been identified and discussed. The following are the conclusions:

1. Pure Al-MWCNTs in weight percentages of 0, 0.5, 1 and 1.5 wt. % were successfully fabricated using ball milling and Spark Plasma Sintering respectively.
2. SEM has shown that the improved mechanical properties are as results of homogeneous dispersion of MWCNTs and good interfacial bonding.
3. TEM confirmed good structural integrity of multi walled carbon nanotubes reinforced within Al matrix.
4. Raman spectroscopy indicated that aluminium carbide formed only after sintering but it was not severe to reduced mechanical properties of aluminium composites.
5. XRD revealed that there are no phases formed during production of the Al-MWCNTs composites.
6. Mechanical properties such as Plasticity, Elasticity, Hardness, Yield strength, Modulus of elasticity, Stiffness and Strain rate sensitivity were improved significantly with the increase in MWCNTs content.
7. Creep behaviour of Al-MWCNTs composites in room temperature was successfully studied, strengthening effect of MWCNTs was observed.

5.2 Recommendation

1. Exploring aluminium application further to take advantage of the improved mechanical properties.
2. Combining the use of tensile and ultra nanoindentation test to study mechanical properties materials is recommended since it will broaden the knowledge of the material's properties.

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