Effect of nano-carburization of mild steel on its surface hardness

by

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Submitted in accordance with the requirements
for the degree of

MAGISTER TECHNOLOGIAE
in the subject

CHEMICAL ENGINEERING
at the

UNIVERSITY OF SOUTH AFRICA

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September 2015
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PUBLICATIONS

The following papers have been submitted for review and publication from this study.


DECLARATION

I declare that this report is my own unaided work. It is being submitted for the award of M. Tech at the University of South Africa, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Ajoke Sherifat, **Hassan**

Date
ABSTRACT

There has been progress in the surface modification of low carbon steel in order to enhance its surface hardness. This study contributes to this by investigating the introduction of carbon nanotubes and amorphous carbon in the carburization of mild steel.

In order to achieve the goal, carbon nanotubes were synthesized in a horizontal tubular reactor placed in a furnace also called the chemical vapor deposition process at a temperature of 700°C. Catalyst was produced from Iron nitrate Fe(NO₃)₃.9H₂O and Cobalt nitrate Co(NO₃)₂.6H₂O on CaCO₃ support while acetylene C₂H₂ was used as the carbon source and nitrogen N₂ was used as contaminant remover. The as-synthesized carbon nanotubes were purified using nitric acid HNO₃ and characterized using scanning electron microscopy (SEM), thermo-gravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR). It was found that as-synthesized carbon nanotubes had varying lengths with diameters between 42-52 nm from the SEM and the TGA showed the as-synthesized CNTs with a mass loss of 78% while purified CNTs had 85% with no damage done to the structures after using the one step acid treatment.

The as-synthesized and purified carbon nanotubes were used in carburizing low carbon steel (AISI 1018) at two austenitic temperatures of 750°C and 800°C and varying periods of 10-50 minutes while amorphous carbon obtained by pulverizing coal was also used as comparison. The mild steel samples were carburized with carbon nanotubes and amorphous carbon in a laboratory muffle furnace with a defined number of boost and diffusion steps. The carburizing atmosphere consisted of heating up to the varying temperatures at a speed of 10°C/minute, heating under this condition at varying periods, performing a defined number of boost and diffusion processes at the varying temperatures and cooling to room temperatures under the same condition. The carburized surfaces were observed with the Olympus SC50 optical microscope and the hardness distribution of the carburized layer was inspected with a Vickers FM 700 micro-hardness tester.

The as-synthesized and purified CNT samples showed higher hardness on the surface of the mild steel than the amorphous carbon. In the same vein, the change in the microstructures of
the steel samples indicated that good and improved surface hardness was obtained in this work with the reinforcements but with purified CNT having the highest peak surface hardness value of 191.64 ± 4.16 GPa at 800°C, as-synthesized CNT with 177.88 ± 2.35 GPa and amorphous carbon with 160.702 ± 5.79 GPa which are higher compared to the values obtained at 750°C and that of the original substrate which had a surface hardness of 145.188 ± 2.66 GPa. The percentage hardness obtained for the reinforcement with the amorphous carbon, the CNT and the pCNT showed an increase of 5.47%, 10.04% and 15.77% respectively at 750°C when compared to that of the normal substrate carburized without reinforcements. Furthermore, at 800°C, the reinforcement with the amorphous carbon, the CNT and the pCNT show a percentage hardness increase of 7.04%, 14.68% and 22.05% when compared to that of the normal substrate carburized without reinforcements. Comparing the reinforcement potential of the amorphous carbon, the CNT and the pCNT at 750°C, the percentage hardness reveal that using pCNT displayed an increase of 10.89% over that of amorphous carbon and of 6.37% over that of CNT. In addition, the use of CNT as reinforcement at 750°C displayed a percentage hardness increase of 4.83% over that of the amorphous carbon carburized at the same temperature.

Key terms:
Carbon steel; Surface hardness; Reinforcement; Carbon nanotubes; Amorphous carbon; Carburization; Chemical vapor deposition; Characterization techniques; Microstructures, Microhardness; Austenitic temperature
DEDICATION
This dissertation is dedicated to the loving memory of my late father Alhaji Idris Kolawole Hassan, and to the beautiful people in my life, my mum, siblings and amazing family.
ACKNOWLEDGEMENTS

I am eternally grateful to almighty Allah, the beneficent and the merciful for His grace and abundant mercies and to the memory of my late father, may Allah forgive his shortcomings and grant him eternal rest.

I would like to acknowledge the following people for their valuable contributions which helped in the completion of this project:

• My supervisors, Prof Ayo Afolabi and Dr Michael Daramola for their guidance, encouragement, constructive criticism, suggestion, mentoring and supervision of this work.
• Kwame Ansah, Dr. Kehinde Shobiyi and Dr. Enoch Ogunmuyiwa for their advice, moral and technical support and my dear colleague, Olawumi Sadare for assisting with sample preparations.
• My mum, my jewel of inestimable value, the core of my support system for her unending love, prayers, words of encouragement, advice and sacrifices.
• My siblings and most especially my brother AbdulLateef Hassan, for being there at all time and never tired of my intolerable excesses.
• My dearest uncle, Prof Femi Adeogun for always being there and my ever supportive sister and best friend, Yemisi Messigah for her time and never giving up on me even when I doubt myself.
• Chemical Industries Education and Training Authority (CHIETA) for their financial assistance.
• I also acknowledge my newly found family, the Afolabis’ for their time and love and to everyone who has rendered some sort of assistance. May God bless and always meet you all at your point of needs.

Thank you.
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<tr>
<td>Fe(NO$_3$)$_3$·9H$_2$O</td>
<td>Iron nitrate</td>
</tr>
<tr>
<td>Co(NO$_3$)$_2$·6H$_2$O</td>
<td>Cobalt nitrate</td>
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<tr>
<td>CaCO$_3$</td>
<td>Calcium carbonate</td>
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<tr>
<td>HNO$_3$</td>
<td>Nitric acid</td>
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<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
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<td>H$_2$SO$_4$</td>
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<tr>
<td>SiO$_2$</td>
<td>Silicon dioxide</td>
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<tr>
<td>Al$_2$O$_3$</td>
<td>Aluminium oxide</td>
</tr>
<tr>
<td>CaO</td>
<td>Calcium oxide (lime)</td>
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<td>CAD</td>
<td>Cathodic arc deposition</td>
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<td>CVD</td>
<td>Chemical vapor deposition</td>
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<td>CNT</td>
<td>Carbon nanotubes</td>
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<td>pCNT</td>
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<td>Oxide polishing suspension</td>
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<tr>
<td>Fe</td>
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<td>H$_2$</td>
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$N_2$  Nitrogen
$\text{Mg}$  Magnesium
$\text{H}_2\text{O}$  Water
$\text{Au}$  Gold
$\text{Pd}$  Palladium
$k\text{Pa}$  KiloPascal
$\text{Hv}$  Vickers hardness
$\mu\text{m}$  micron
$\text{nm}$  nanometers
$\text{cm}$  centimeters
$\text{min (s)}$  minute (s)
$\text{ml}$  milliliters
$\text{g}$  gram
$\text{kg}$  kilogram
$\text{wt \%}$  weight percentage
$\%$  percentage
$\text{°C}$  Degree celsius
$\text{FTIR}$  Fourier transform infrared spectroscopy
$\text{SEM}$  Scanning electron microscopy
$\text{TGA}$  Thermogravimetric analysis
$\text{GPa}$  GigaPascal
$\text{SWNTs}$  Single walled carbon nanotubes
$\text{MWNTs}$  Multi-walled carbon nanotubes
CHAPTER ONE

1.0 Introduction

1.1 Background and Motivation

Steel is essentially a metal alloy that is principally composed of carbon and iron and commonly used in construction and other applications (Ashby and David, 1992). It is categorized as carbon steel when no minimum given amount of elements like nickel, cobalt or chromium are added to obtain the expected alloying effect (Gonzalez et al., 1997). Carbon steel, also called plain-carbon steel, is a metal alloy containing two major elements namely iron and carbon with manganese as another alloying element and other residual elements like copper and silicon which quantities are minute to affect the properties (George, 2006). Irrespective of heat treatment processes, high carbon content reduces the weldability and lowers melting point of steels (Smith and Hashemi, 2006). Carbon steels are characterized according to their carbon content and are grouped into the following categories:

- Mild (low carbon) steel: It is the most common and readily available type of steel because of its low price. It contains between 0.01% to 0.25% carbon content which makes it ductile with a relatively low tensile strength but easy to shape and its surface hardness can be increased by carburizing. Its applications include deep drawing parts, chain, pipe, wire, nails and automobile panel bodies (Krauss, 1990; George, 2006).
- Medium carbon steel: This contains about 0.3% to 0.54% carbon content. It has the ability of balancing ductility, strength and has good wear resistance. Its uses include forging, car parts, cylinders, crankshafts, heat treated machine parts and where high mechanical properties are desired (Davis, 1997).
- High carbon steel: This has about 0.55% to 0.95% carbon content and has a high tensile strength, hardness, very good wear resistance and moderate ductility. It is used for high-strength wires, screw drivers, hammers and wrenches (Capudean, 2003).
- Very high carbon steel: This has a composition of 0.96% to 2.1% carbon content which makes it a very strong material. It is usually processed specially to produce specific atomic and molecular microstructures. Its properties include very high strength, ductility, hardness and wear resistance (Ross, 1992).
Steel can be heat treated to allow parts to be constructed in a readily-flexible state depending on the carbon content which enables hardenability so as to increase strength and wear resistance. It involves controlled heating and cooling processes to alter the microstructure, physical and mechanical properties (Grafen and Edenhofer, 1999; George, 2006).

However, mild steel is reported to be unarguably the cheapest and the most commonly used construction material with its usage ranging from tanks, vessels, pipes and others but because of its low strength, structural shortcomings and due to slenderness issues leading to cracks, breaks or buckling when load is applied (Heidarpour et al., 2011; Heidapour et al., 2014) which has become a major of concern and has led to seeking protective measures to enhance its surface hardness (Pierre, 2007; Ali et al., 2013).

Wanga et al., (2003) reported that there have been cases of mild carbon steel failures such as low hardenability and poor wear resistance initiating from the surface and are sensitive to microstructure and properties of the surface. It is therefore understandable to apply surface modification to enhance the properties of a surface layer while the chemical composition remains unchanged relative to the core, hence the need for surface modification with carbon at nanosize which can be referred to as surface nano-carburization which is expected to provide a new approach to deepen the research and widen the application of nanomaterials.

The main purpose of heat treatment of steel is to change its microstructures and improve its mechanical properties such as hardness, and yield strength with slight alteration in the electrical and thermal conductivity while Young’s modulus (elasticity) is unaffected (Robert and Peter, 1996). Heat treatment processes begin with heating the steel to an austenitic phase except spherodizing and process annealing (Dossett and Boyer, 2006). This is followed by quenching at a high temperature leaving cementite to precipitate and remaining pure steel to coagulate. The rate at which the steel is cooled affects the rate at which carbon diffuses out of the austenite and forms cementite. There are various processes of heat treatment but carburizing will be considered in this study and it is essentially done by adding carbon to the mild substrate’s surface at appropriate temperature (Colin et al., 2011). The strength and wear
resistance could be increased by diffusing carbon onto the surface of the steel leaving a significant hardness in the core and it is applied to low carbon steel usually after machining.

Carbon nanotubes (CNTs) are presently receiving significant attention because of their excellent and unique properties which culminate to their wide range of applications. Their synthesis is on the increase so as to meet the technological development, progress and applications from agriculture, medicine, automobiles, power etc. (Heer, 2004; Afolabi et al., 2011). CNTs are allotropes of carbon with a cylindrical nanostructure. They are classified as single-walled nanotubes (SWNTs) with a structure that can be described as wrapping a one-atom thick layer of graphite called graphene and multi-walled nanotubes (MWNTs) consisting of multiple rolled layers of graphene (Salvetat and Angel, 2002). They possess many distinct properties which have enabled them to be useful in many chosen applications and of these are their superior strength, stiffness in tension and its electrical properties which are similar to those of semi-conductors (Berber et al., 2000; Collins et al., 2001). Their exceptional mechanical properties with a well-defined primitive cell, surface, possibility of transport (Dresselhaus et al., 2001) including light mass and ability to improve strength and stiffness (Chen et al., 2002) makes them potential modifying materials for scientific studies as well as wide range of application including high strength composites (Naiqin et al., 2006; Yaser et al., 2011). All of these characteristics make CNTs a good reinforcement in this study as there have been reports of buckling in mild steel due to poor strength retention and possible slenderness hence the need for an innovative way of increasing its surface hardness without sacrificing other properties (Shepherd and Burgess 2011; Heidarpour et al., 2014).

Amorphous carbon is a free, reactive carbon without crystalline structure. It comprises of carbon atoms in a non-crystalline and irregular shape. It is obtained by heating any carbon-rich materials between 650-980°C in a limited supply of air so that complete combustion does not take place. It is present as powder and is the main constituent of charcoal, soot and activated carbon (Falkowski et al., 2000). Natural amorphous carbon can be made and it contains microscopic crystals of other allotropes of carbon like graphite and sometimes diamond. Falkowski et al. (2000) also reported that it possesses no defined shape as it consists of small uneven crystals, but on the nanomicroscopic level, it is made of well-arranged carbon atoms.
Coal and soot are both products of decomposition of a substance by heating which does not give true amorphous carbon under normal conditions (Gorman et al., 2003). Coal is divided into grades depending on the carbon content in the sample compared to the amount of impurities. The highest is anthracite with about 90% carbon and 10% other elements. Bituminous coal has about 75-90% carbon and lignite with 55% carbon (Anderson and Rosenfeld, 1999).

The production of true amorphous carbon materials and films is presently achievable using chemical vapor deposition (CVD) and cathodic arc deposition (CAD). This is due to the evolution of modern thin film deposition and growth techniques in the 20th century. The properties of the carbon produced vary depending on the parameters as well as method used for production. Research is still going on into ways to characterize and increase on the range of properties offered by amorphous carbon materials with interest moving away from silicon to mild steel and other metals which might produce better samples with outstanding properties like strength and high hardness with its biocompatibility opening new fields for applications such as protective coatings for implants, biosensors and other metal substrates (Steffen et al., 2000; Yang et al., 2003; He et al., 2005).

Surface modification as an important objective in this study, has been extensively explored with chemical modification of carbon materials such as graphene though similar to SWNT, but is a single atomic layer of crystalline graphite connected into hexagons and fullerene (Kordatos et al., 2001; Niyogi et al., 2002; Tasis et al., 2006; Richard McCreery, 2008) using processes such as the Prato and photochemical reactions (Lang and Krueger 2011; Liu et al. 2004) but modification with carbon nanotubes remains relatively unexplored (Tagmatarchis and Prato 2005). Other attempts made include some phosphate and chromate base treatment which is been replaced with other alternatives because of negative environmental effects (Hanawa and Ota, 1992; Fedel et al., 2010; Tomachuk et al., 2010) likewise organic coating which is reported as expensive and are only efficient for a limited period (Spinks et al. 2002; Gordon et al., 2009).
Thus, this study sought to systematically investigate the effects of surface treatment of mild steel with carbon nanotubes and amorphous carbon on its surface hardness. It aims at reinforcing the surface of mild steel with carbon nanotubes and amorphous carbon at some selected austenitic temperatures and studies the mechanism of the interactions of these reinforcements on the surface of the mild steel at the temperatures under study.

1.2 Research questions

This investigation provided answers to some pertinent questions emanating from the study. Some of these questions which arose after comprehensive literature review on some keywords as well as analyses of experimental results obtained in the study. Some of these questions are:

• What will be the effect of carbon nanotubes (CNTs) and amorphous carbon on the surface hardness of mild steel?
• What will be the effect of increase in temperature on the surface hardness of the mild steel?
• What will be the mechanisms of both carbon nanotubes and amorphous carbon interactions on the substrate at equal carburization periods and other austenitic temperatures?

1.3 Research aim and objectives

The aim of the study was to investigate the effect of carburizing mild steel with carbon nanotubes (CNTs) and amorphous carbon to enhance its surface hardness. The aim was achieved through the following objectives:

• Preparation of Fe-Co catalyst on CaCO$_3$ for the synthesis of carbon nanotubes.
• Synthesis of CNTs by chemical vapor deposition (CVD) method using acetylene carbon source and nitrogen carrier gas on Fe/Co catalyst prepared on CaCO$_3$ support.
• Purification and characterization of the synthesized CNTs using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA).
• Heat treatment of mild steel sample with carbon nanotubes at various austenitic temperatures of 750°C and 800°C at different periods of time of 10, 20, 30, 40 and 50 minutes.
• Heat treatment of mild steel sample with amorphous carbon at various austenitic temperatures of 750°C and 800°C at different periods of time of 10, 20, 30, 40 and 50 minutes.
• Determination and comparison of the surface hardness of the mild steel samples carburized with both carbon nanotubes and amorphous carbon using a microhardness tester.
• Investigation of the mechanism of surface hardness interaction of the steel with carbon nanotubes and amorphous carbon samples using optical microscopy.

1.4 Scope of study
The study involved the preparation of catalyst using the wet impregnation method on CaCO₃ using Fe(NO₃)₃ and Co(NO₃)₂, synthesis of the carbon nanotubes by chemical vapor deposition method using acetylene as the carbon source, purification of the synthesized CNTs to remove the residual catalyst and other nanoparticles and characterization of the CNTs using SEM, TGA and FTIR. Mild steel sample was carburized with synthesized CNTs and amorphous carbon in a furnace and comparison was drawn from the carburized samples to investigate which reinforcement has stronger effect in the enhancement of the surface hardness of the mild steel samples.

1.5 Expected contributions to knowledge
On completion, this study provided information on:

(i) Nanocarburization of mild steel with carbon nanotubes and amorphous carbon samples at various austenitic temperatures under study.
(ii) Comparison of the surface hardness of mild steel sample treated with carbon nanotubes and amorphous carbon at the various austenitic temperatures.
(iii) The mechanisms of the interface interaction between the carbon nanotubes and the mild steel and that of amorphous carbon and mild steel.
1.6 Structure of dissertation

*Chapter one:* The background and motivation of this project are described in this chapter as well as, the research questions, the aim and the objectives, the scope of the project and the expected contribution to knowledge.

*Chapter two:* This chapter reviews the literatures on the methods used to carburize and enhance mild steel’s surface hardness as well the various processes used in the synthesis of carbon nanotubes especially the chemical deposition method and the purification methods and the use of amorphous carbon and characterization techniques used in the analysis of the samples.

*Chapter three:* This chapter describes the materials and chemicals as well as the methods and experimental procedures used to prepare the catalyst, synthesize and characterize the carbon nanotubes and the steel samples as well as equipment used. The analytical methods as well as the procedures used to determine the steel’s hardness are also described.

*Chapter four:* The results from the experiment which include the analysis of the SEM, TGA and FTIR of the CNTs, analysis of microstructural and microhardness of the steel samples are presented and discussed in this chapter.

*Chapter five:* This chapter contains the conclusions as well as the recommendations of this project.
References


CHAPTER TWO

2.0 Literature review

2.1 Review of surface modification

Surface modification is a generic term that involves a wide variety of techniques used to improve the wear resistance of parts without affecting the softer tough interior of the substrate (Davis, 2002). It involves many applications where low or moderate core properties with a high degree of surface hardness can be obtained using cheap fabricated low carbon steel with minimal problems of distortion and cracking which is associated with thick section parts (Dossett and Totten, 2013).

The major processes that are conventionally used to enhance surface hardness and wear resistance are classified as thermochemical, thermal and coating or plating. The thermochemical process include carburizing, nitriding, and carbonitriding while thermal or applied energy treatments include flame and induction hardening and coating or electroplating include hard chromium plating, electroless nickel plating and various hardfacing methods. The various methods used in modification all have the same objective which is enhanced surface with most already been used in fabricating thin film devices, circuits, plasma, magnetic and electrical field but their application to steel is relatively new (Davis, 2002).

However, there are two distinct approaches to the control of surface modification which are:

(i) Deposition of coatings/layers to modify surface composition relative to substrate or intentional buildup with methods like fusion hardfacing, thermal spray and coatings. These processes become less cost effective as production quantities increases when entire work pieces surfaces has to be hardened and the fatigue performance of coatings and films can also be a limiting factor depending on the strength of bond between substrate and added layer (Schneider et al., 2013).

(ii) Methods that involves surface and subsurface modification without increase in parts dimensions or intentional buildup to modify existing phases or segregate one or more elements from the substrate alloy to the surface diffusion with methods like carburizing, nitriding, carbonitriding, nitrocarburizing. These methods allow effective hardening of
entire surface of a part by modifying the chemical composition of the surface with hardening species like carbon, nitrogen and can be used when a large number of parts are to be surface modified (Brady et al., 2005).

The use of surface modification allows the possibility for material design to meet the demands of specific properties where they are the most needed hence, the need for development of surface modification processes to improve the hardness, resistance, thermal stability and wear resistance of steel and its surface (Jibo et al., 2011). A key advantage to surface modification is that the substrate can be optimized for its wear resistance and hardness properties (Nicholls, 2003).

Various methods of carburization as surface modification treatments to improve hardness and wear resistance are an area of increasing interest in modifying steel surfaces which are borderlines for enhancing hardness in steel as there has been great recent interest due to their combination of properties including their ability to be easily machined (Zhao et al., 2001).

2.1.1 Carburization

Treating steel components to improve the surface properties through carburization is a well-known technology. Carburizing process is used to modify and enhance the surface hardness and wear resistance of metals by diffusing carbon atoms into the metal substrate. It is done at high temperatures generally between 850°C and 980°C in a carbon medium such as solid, liquid or gas (Baek et al., 2000; Sharidah et al., 2012). It involves direct interplay between the substrate’s surface and that of carbon powders.

Chen and Wang, (2000) defined carburization as a method of enhancing surface hardness. It can be further defined as a type of thermochemical treatment in which objects of low-carbon steel surface layer is infused with carbon by diffusion as the steel is heated in an appropriate medium leaving a carbon enriched zone formed in the steel surface layer. It was developed for improvement of the mechanical properties of workpiece over normal methods and specifically for parts that are susceptible to pitting wear with utmost importance given to core
toughness (Nakayama, 1992; Chen and Wang, 2000). Its main purpose is to increase the hardness and wear resistance of the surface of the substrate; and as well to increase the mechanical and chemical properties of steel components in automotive, aerospace and mechanical devices (Grafem and Edenhofer, 1999). It is a diffusion-controlled process so the longer the steel is in carbon-rich atmosphere, the greater the carbon infiltration and the higher the carbon content and the quality of the carburized parts depends on the carbon distribution (Zajusz et al., 2014).

The process is defined by the rapid absorption of carbon atoms by the steel surface layer because of the steel surface’s catalytic effect on the carburizing atmosphere and this leads to carbon atoms being absorbed and diffused in to the steel surface (Kula et al., 2005). The absorption of carbon may result in solid solution strengthening, precipitation hardening, phase transformation or changes in the microstructure of the substrate causing modification of its surface properties and the extent of carbon absorption may differ depending on the carburizing process used (Loganathan et al., 2011). The capability of the carburizing atmosphere to release carbon atoms as a result of disintegration of the components has to be very high as well as the carbon potential and at low pressure carburizing processes (Kula et al., 2005).

The conventional method involves the use of coal as the carburizing compound which generates CO gas by heating up the charcoal. The CO gas reacts with the surface metals thereby carburizing them and though it has the advantage of low cost, it was difficult to control the carburized depth. This was followed by the gas carburizing which was developed by the American Gas Furnace company in 1910. It involves the use of air and butane or propane at high temperatures leaving products like CO, CO₂ and H₂O to react with metal surfaces thereby carburizing them. Much as it has the advantage of easy continuous operation, the quality was marred by the existence of CO₂ and H₂O products which acts as oxides of metals called intergranular oxidation (Yada and Watanabe 2013).

While the basic principle of carburization remained unchanged since its introduction, the methodology has experienced continuous progress as its initial application involved parts
been placed in a container and covered with carbon powder and while this proved effective, the method was exceedingly very slow. As demand in production increased, newly modified forms of carburizing processes were introduced and among these techniques, the gas carburizing process is commonly used as it involves the use of gaseous carbon sources likewise the vacuum process and it is carried out at pressures below atmospheric pressure (Krauss, 1985).

Vacuum carburization is a heat treatment process designed to produce hardened surface/layer with a large amount of carbon atoms/carbides. It is also used in strengthening the surface of low quality metals and in most applications because the absence of oxygen in the furnace atmosphere helps in getting rid of grain-boundary oxidation and allows carburizing temperature to be increased gradually without the risk of surface or grain boundary oxidation (Schneider et al., 2013; Yada and Watanabe, 2013) and provides a friendly environment (Okumura and Iwase, 1998).

It was reported to be firstly used in 1968 by C.I. Hayes Inc. engineers and now being widely utilized as a way to reduce energy cost as well as carburizing time. The high temperature used in the furnace allows larger carbon transfer compared to the conventional carburizing methods giving reduction in carburization time (Pierre, 1989) and it is also free of pollution and intergranular oxidation (Pierre, 1989; Yada and Watanabe, 2013).

A renewed and increase in the process has been currently observed as a result of the progress in the recent and modern furnace designs for thermochemical treatment under low pressure and improved understanding of chemistry of the process (Kula et al., 2005). Vacuum carburizing has gained more attention as an alternative method to other forms of carburization especially atmosphere gas carburizing as it can be carried at temperatures higher than those applied in gas carburizing which reduces processing time and giving its major advantage as ability to prevent oxidation at grain boundaries. It allows processing in a wide temperature range and can also be carried out below 900°C should shallow case depth be required (Zajusz et al., 2014). The process is characterized by the decomposition of carburizing gas, the convection exchange which takes place in the boundary layer between
the steel surface and the atmosphere, and the diffusion of carbon atoms into the steel substrate (Okumura and Iwase, 1998).

Liu and Chen, (2004) investigated and used acetylene in vacuum carburizing steels in a two-chamber vacuum furnace at temperatures ranging from 900°C to 1050°C. They reported that effective case depth and total case depth of a carburized layer is a function of its alloy elements and corresponding concentration especially carbon content of the steel substrate. They further suggested that acetylene which is an unsaturated gas and can be exothermically decomposed be used as carburizing gas as it takes lesser time to decompose and reduces sooting risk unlike propane, a saturated hydrocarbon used in conventional gas carburizing which requires several decomposition steps to reach equilibrium.

They also reported moderate hardenability and improvement in wear resistance of low alloy steel samples which were carburized in a vacuum furnace in a repeated cycle at a temperature of 950°C for 30 minutes with 0.6 kPa acetylene pressure and were allowed to cool between 720-740°C in a cooling chamber at approximately 60 seconds using 1-bar nitrogen pressure with a radiation pyrometer through a glass window to determine the cooling temperatures of the specimen. The SEM results as reported showed that the first and second cycles were used to build up the carbon atoms used as nuclei for the succeeding carburizing cycle which showed large quantity of the carbon precipitated and accumulated and that the carbon content of the carburized specimens increased as a function of the treating cycles. The hardness of the carburized layer was determined using a micro-hardness tester with a load of 0.3 kg (Liu and Chen, 2003).

Kula et al, (2005) however gave a detailed analysis and concluded that for carbon atoms to be deposited on a substrate’s surface, an efficient use and delivery of carbons to substrate’s surface is only feasible if the process is divided into two stages: The boost stage; where a significant amount of the carbon atoms is delivered to the surface from the carburizing atmosphere which is reported to be a result of catalytic reaction of the carburizing atmosphere with the charge surface leading to carbon release in the form of atoms. The absorption of it by the surface and precipitation in the form carbon deposit and the diffusion stage which holds
charge at the same process temperature without further supply of the carbon atoms followed by their transformation into fine crystalline until all atoms are absorbed (Grafen and Edenhofer, 1999; Gorockiewicz, 2011). Such process is said to be beneficial as the carbon atoms solubility in austenite is bounded and a solid carbonaceous layer is created on substrate’s surface in case of excess (Gorockiewicz and Lapinski, 2010).

In carburizing steel, Kula et al, (2005) used samples of mild steel and alloyed steel at 920°C and 950°C in a single-chamber laboratory vacuum furnace with gas quenching which was a part of the equipment at different time intervals using the boost and diffusion stages. They concluded that various surface phenomena which takes place during carburization is of great importance and influence but could be problematic for the process control and suggested that the time interval of the boost stage should be too long so as not to exceed the maximum solubility of the carbon atoms in the austenite as it could lead to them appearing on the surface and this could in turn change the mechanism of the diffusion thereby decreasing the deposit of fresh carbon atoms and difficulty in obtaining the depth of carburization.

Vacuum carburization is considered in order to prevent oxidation, eliminate toxic off-gases with parts left clean and dry with no washers or disposal of liquid waste required. It allows quick cooling of product, no open flames or flame screen is required and most importantly, it has low running cost and can be processed in a wide range of temperature. It also allows carburizing at high temperatures and the mechanism serves as the motivation for introducing carbon atoms which are carbon nanotubes (CNTs) and amorphous carbon to interact with the surface properties of mild steel thereby increasing the surface hardness.

2.2 Mild Steel
Mild Steel is a common type of steel that has become an imperative material for many industries. The low-carbon steel also known as mild steel has a 0.1-0.25 % carbon with ability for increased strength, hardness and reduced formability. Mild steel also called low-carbon steel as important structural materials used in the development of modern industry and as engineering materials are expected to meet increasing and stringent requirements for mechanical and chemical properties hence the need for strengthening and modification (Shin
et al., 2000). They are designated as carburizing or casehardening steels which depends on the nature of the part; the properties required and preferred processing methods (Itami and Kawashima, 1992).

Its low carbon content and mechanical properties have made it relevant for many applications and its properties are determined by its composition (Higgins, 1993). Its ductility and good weldability makes it a widely used structural material but with a poor wear resistance (Lampman et al., 1990; Jyotsna, 2008). There have been reports of wear and fatigue at surface level creating defects which have led to premature failing of engineering materials (Rao et al., 2012; Grandra et al., 2014).

Due to this advantage, there have been several modification processes to improve and increase its strength and surface such as hot rolling and quenching (Nasipov et al, 1987; Pedroza et al., 2012). Considering the potential material applications like machine parts, constructional steel and because of its ability to be easily shaped, become harder and stronger through heat treating, mild steel can be considered as a potential candidate to effect the superior tensile strength and stiffness of CNTs as reinforcement because of its low carbon content and low tensile strength.

There have been significant research efforts in treating and enhancing steel hardness as they are important structural and engineering materials. The unique characteristic of mild steel’s relatively low tensile strength with its ability to be easily shaped and of its surface hardness to be increased has made it duly considered in this research and in order to optimize, increase its part design and extend its life time, modification processes are required to achieve more suitable surface properties (Pereiraa et al., 2014).

The mechanical properties of steel are controlled by controlling its microstructure and the nature of the phases within the microstructure. This is achieved by choosing appropriate chemical compositions and heat treatments that eventually results to treated steel with modified microstructure. However, the extent of the modification depends on the
composition of the steel and the method of treatments (thermal or mechanical), resulting in the phase transformations of the substrate (Wagner and Heijneman, 2008; Vander Voort and Lucas, 2009).

The phase transformation stages starts from:

**Austenitization**: This is the first step in heat treatment which converts the steel into the FCC solid solution called austenite when the steel is heated into the austenitic phase and held long enough. It is an important phase because it has a direct effect upon the microstructures produced during treatments in where the austenite is transformed into other phases and the steel is finally returned to ambient temperature. The Fe-C phase diagram helps in analysing and selection of suitable temperature in austenitization process which is also important in time selection as the most favourable combination of temperature and time depends on the objectives of the total heat treatment process and upon the microstructure of the steel before austenitization (Cheng et al., 2010). The steel substrate is usually at ambient temperature and has a microstructure comprising a mixture of cementite and ferrite which could also have free ferrite grains, discrete particles of the carbide embedded in ferrite grains and regions of pearlite in which the two phases exist as a lamellar mixture. It is however important to know that cementite and ferrite are phases while pearlite is a microstructure (Heidarpour et al., 2013).

The heating rate is also an important part of the process as the important transformation occurs during austenitization and does so above the austenitic temperature line in the austenite phase. When the carburizing temperature exceeds the eutectoid isotherm, the carbon atoms dissolve but the ferrite cannot accept the carbon atoms without the formation of some austenite which occurs by a nucleation and growth process which occurs on ferrite grain boundaries and on ferrite/cementite interfaces (Heidarpour et al., 2013). The austenite provides a medium for the carbon in the adjacent carbides and the simultaneous growth of austenite and dissolution of carbides to occur and when the temperature is exceeded, the austenite dissolves any remaining ferrite. The rate controlling parameters are the nucleation kinetics and the rates of diffusion of solutes in austenite until the completion of transformation. If the nucleation process is heterogeneous, fine grained ferrite and finely spaced lamellae in pearlite cause the transformation to occur more rapidly than it would in a coarse microstructure and the finer the initial microstructure, then the finer the austenitic
grain size will be when the carbon atoms have all dissolved. The grain size depends on the nucleation rate which as well depends on nucleation sites and the temperature at which the nuclei forms. When austenitization is complete, grain growth takes place at rates higher than its temperature and the completion an austenitization process does not usually correspond to the time taken for the carbides/carbon atoms to dissolve because, while the steel is austenite, its composition is inhomogeneous because the carbon concentration at and near the positions originally occupied by the carbides exceeds the concentration elsewhere hence additional time is required for the austenite to homogenize (Zhu et al., 2013).

The kinetics of producing homogeneous austenite is strongly considered in steels that contain alloy carbides (e.g. molybdenum carbides) because substitutional diffusion is slower than interstitial diffusion hence, the microstructural change to be considered during austenitization is grain growth. Some austenite grains continue to grow and, necessarily, others constrict and disappear causing a decrease in the number of grains per unit volume. The average grain size increases with temperature at a rate that is proportional to the square root which is a function of time and temperature (Hamad et al., 2014). Parts of the sample transform at different times and temperatures during the cooling process and when cooling rates are slow enough to allow diffusion to occur readily, the transformation is completed at high temperatures which occur over a small range of temperature. “Furnace cooling” and “slow cooling” refers to the steel being close to its equilibrium state as its temperature drops. The transformation to ferrite and cementite begins and ends at lower temperatures where the steel is no longer close to equilibrium as it cools. The phase diagram provides reasonable estimates of the volume fractions of various phases to be expected in the final microstructures.
2.3 Carbon nanotubes

Carbon nanotubes (CNTs) were first reported by Iijima (1991) via arc discharge evaporation method (Yaser et al., 2011) and they have received a great deal of attention in many research fields because of their unique properties such as surface property, high tenacity, high electron conductivity which have enabled them to be useful in selected applications till date (Collins and Avouris, 2000).

They are been well studied because of their distinctive mechanical, chemical and optical properties (Hall et al. 2007; Peng et al. 2007) with focus on their synthesis, purification and modification (Huang and Rodrigue, 2013). According to (Roman and Somenath, 2006), they are said to have high capability which can alter and improve metals even with addition at very small fractions and specifically, their superior strength, unusually high thermal conductivity, stiffness in tension, ability to bend reversibly and high surface area to volume
ratio have made them useful systems for fundamental scientific studies as well as for a wideange of applications and technological advancement such as power, medicine, chemical
ensors, composite materials, electronic devices and support in catalysis (Baughman et al.,
002; Thostenson et al., 2003) and have led to its combination with other materials to create
and obtain useful results (Chen et al., 2000; Lordi and Yao, 2000).

2.3.1 Synthesis of carbon nanotubes
In the synthesis of carbon nanotubes, catalysts are reported to play an important role as their
growth can be controlled through the manipulation of nanoparticles size used as catalysts.
Several supports and combinations of transition metals, carbon sources have been
vestigated for their activity in the synthesis of CNTs (Nagaraju et al., 2002; Kathyayini et
al., 2004) in order to improve the yield and quality of CNT production. The most widely used
metals are Fe, Co and Ni as well as their alloys which are supported on materials such as
SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and zeolite that are stable at high temperature which have proven to be
successful in the synthesis of CNTs but has shown difficulty in purification of the product
(Dupuis, 2005) which require processes that may damage the CNT structures and the solvents
used in its purification have to be disposed to minimize environmental issues (Hernadi et al.,
2002). Silica gel or zeolites were used and observed to be good support for catalyst in CNT
synthesis but zeolites as porous supports were reported to be responsible for large build-up of
amorphous carbon during CNT synthesis which requires a multi-step purification process
which can cause structural damage and as well introduce other types of impurities to the
CNTs (Mhlanga et al., 2009). The synthesis of CNTs of metals supported on silica and
alumina with the factors affecting their catalytic process and structures of produced CNTs
have been duly studied while that on CaCO\textsubscript{3} remains relatively unexplored (Dupuis, 2005;
Dervishi et al., 2007).

Magrez et al., (2005) reported that CaCO\textsubscript{3} which is a non-porous, cheap, low surface area and
readily available material has proven to be an excellent support and a good match between
the carbonate decomposition temperature and the CNT growth. It is said to decompose to
CaO (lime) and CO\textsubscript{2} at high temperature and the residual CaO can be removed using only one
step acid treatment of HNO\textsubscript{3} while drying will remove the amorphous carbon (Schmitt et al.,
2006). It is also environmental friendly material and can be easily dissolved in diluted nitric
(HNO₃) or hydrochloric (HCl) acid which enables support to be removed leaving pure materials devoid of impurities and contaminants (Kathyayini et al., 2004; Mhlanga et al., 2009).

As proposed by Magrez et al., (2007) and also reported by Afolabi et al., (2011), the atom efficiency of the reaction at a high temperature using CaCO₃ support to yield CaO and CO₂ is given as equation (i):

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2
\]  

(i)

C(resource)          C(product)  CO disproportionate water-gas shift

The process is followed by the reaction of acetylene C₂H₂ and CO₂ which gives CNTs together with CO and H₂ (ii) and (iii). The processes are said to occur around the support interface so as augment the acetylene conversion to CNTS during the reaction time and temperature used.

\[
\text{C}_2\text{H}_2 + \text{CO}_2 \rightarrow 2\text{C} + \text{H}_2\text{O} + \text{CO}
\]  

(ii)

\[
\text{C}_2\text{H}_2 + \text{CO}_2 \rightarrow \text{C} + 2\text{CO} + \text{H}_2
\]  

(iii)

The temperature used which is usually 700°C aids the CNT growth by the interface (Fe-Co/CaCO₃/C₂H₂) while the water gas shift reaction (iv) or CO disproportionation (v) facilitates the CO₂ regeneration.

\[
\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2
\]  

(iv)

\[
2\text{CO} \rightarrow \text{C} + \text{CO}_2
\]  

(v)

The CO₂ acts an etching gas which prevents catalyst poisoning.

Metals like Fe, Co and Fe-Co on Ca, Mg oxides, carbonates and hydroxides supports prepared using the wet impregnation method have been studied and results showed that the Fe-Co supported catalysts gave the best metal-support interplay which in turn has a major influence on the CNTs and CaCO₃ nanocrystals used as catalyst prepared via wet impregnation method for CVD synthesis of CNTs was also reported to yield high quantities
of CNTs (Kathyayini et al., 2004; Cheng et al., 2005) and reported studies showed that most catalyst-support mixtures were prepared by wet impregnation method using different carbon sources like acetylene-ethylene and carrier gases like argon-nitrogen with similar CNT products obtained but varied diameter distribution (Schmitt et al., 2006; Mhlanga et al., 2009).

Kathyayini et al., (2004) in their study revealed that the order of catalyst activity in the CVD synthesis was Fe-Co/CaCO₃ >> Co/CaCO₃ > Fe/CaCO₃ hence the Fe-Co bimetallic system supported on CaCO₃ will be used in this present study.

There have been various methods devised to synthesize carbon nanotubes (CNTs) but they involve complex processes and attempts have also been made to grow CNTs on uncommon substrates like noble metals, ceramics and semiconducting metals like cobalt and nickel usually as catalysts (Yin et al., 2008; Mazdak et al., 2013; Luca et al., 2011). Vander Waal and Hall (2003) attempted to grow CNTs directly on 304 stainless steel meshes with different surface pre-treatments like oxidation, oxidation–reduction and as well investigated the effects and flow rates of precursor gases like acetylene (C₂H₂)/benzene mixture and CO/benzene mixture on CNTs production and showed that CO has less effect than others.

Other techniques used in CNTs synthesis include arc discharge, laser ablation, plasma which are reported to produce high quality but low yield of carbon nanotubes (Lai et al., 2001; Nozaki et al., 2011) and chemical vapor deposition (CVD) but of all these, chemical vapor deposition is reported to be largely used because of its capability to produce compacted and even deposits, good adhesion, surface morphology of products obtained and wide range in choice of chemical precursors (Choy, 2003; Luca et al. 2011). It has also been reported as the most favorable way of producing CNTs with excellent qualities at a comparatively affordable cost (Guo et al., 2006) and compared to electric arc-discharge and laser-ablation methods, CVD technique is adjudged to be a promising method to synthesize CNTs because of its low cost, high purity, simple configuration and high flexibility in adjustable parameters for controlling the CNTs structures (Harris, 1999; Hou et al., 2002). The structure of carbon nanotubes (CNTs) obtained from the process is dependent on size, alignment and catalyst
composition used so catalyst can be said to play a major role in the production of CNTs (Afolabi et al., 2007; Porro et al., 2007). The quality and quantity of CNTs depends on many parameters such as growth duration, feed gas composition, type of catalyst, nature of support, carbon/catalyst precursor composition, temperature, feed gas flow rate, and carrier gas (Chen et al., 2006; Kunadian et al., 2009).

2.3.2 Purification of carbon nanotubes
All the synthesized CNTs via CVD method contain impurities of amorphous carbon, graphite, nanoparticles and residual metal catalyst regardless of the method used and the presence of these impurities may affect the characteristics of the CNTs (Vairavapandian et al., 2008; Kumar and Ando, 2010). Hence, purification of the CNTs is very important for applications that exploit their intrinsic properties (Zhao et al., 2006).

Purification processes are very vital and usually employed in CNTs because of impurities that are mostly associated with the products either as catalyst used or other parameters like temperature used in the decomposition process. Purification do not only removes impurities but also introduces oxygenated surface groups onto the CNTs whose presence alters the surface chemistry of CNTs (Motchelaho et al., 2011). Porro et al., (2007) reported the effect of purification treatment on structural properties of CNTs which resulted in more available surface area and less concentration of residual catalyst inside the grown materials.

Purification processes such as carbon dioxide oxidation, air oxidation, permanganate oxidation were proposed but they were reported uncontrollable and unscalable (Shi et al., 1999). Chen et al., (2002) reported that when the air oxidation method was used to calcine carbon nanotubes, different temperatures were reported indifferent group and this will result in insufficient purification or damage of the CNTs.

Various methods which have been used and reported are classified into physical and chemical purification of CNTs. The physical process of purifying CNTs such as centrifugation, filtration, size exclusion chromatography uses a different oxidation temperature of
carbonaceous particles from that of CNTs and the persistent problem associated with the method is that materials like transition metallic catalyst particles remain trapped in wall structure and can affect the CNTs performance in many practical applications and are complex (Ebbesen et al., 1994). The chemical purification method include electrochemical treatment, gas treatment and liquid phase treatment (acid treatment and refluxing) which are more efficient and based on the selective oxidation of carbonaceous impurities which can remove the metal catalyst particles remained in the as-grown CNTs as metal catalysts can be dissolved in purification solutions such as acids (Park et al., 2001).

The electrochemical treatment is adequate for purification of vertically aligned carbon nanotubes arrays and can only remove impurities to some extent while the gas phase treatment can be used to remove amorphous carbon and other carbonaceous impurities under air or oxygen condition but the metal catalysts cannot be removed (Hou et al., 2008; Dementev et al., 2009) while the liquid phase removes metal catalysts and carbonaceous impurities by using H$_2$SO$_4$/KMnO$_4$, HNO$_3$, H$_2$SO$_4$/HNO$_3$ (Wepasnik et al., 2011) but the structure of the CNTs can be damaged especially while using concentrated oxidizing agent and strong oxidants hence non-oxidative acid such as hydrochloric (HCl) can be applied but Edwards et al. (2011) reported that iron particles were only oxidized after CNTs were purified with concentrated HNO$_3$ and H$_2$SO$_4$/HNO$_3$ as they were not removed using 5mol/L HCl solution.

Rosca et al., (2005) and Su et al., (2008) investigated the effects of acid treatment on structural properties of CNTs using concentrated nitric acid (HNO$_3$) or nitric/sulphuric (HNO$_3$-H$_2$SO$_4$) acid solutions of various concentrations for various purification times and reported that the sulphuric/nitric acid solution in a ratio of 1:3 for 24h yielded highly pure CNTs and is widely used though there are various suggested methods (Toebes et al., 2004). The methods used depend on the level of material impurities but these steps could sometimes affect the structure of the CNTs so efforts are made to minimize or totally remove impurity content during synthesis as preparation and purification processes involved are quite complicated and not too economical (Afolabi et al., 2007; Jun Huang and Rodrigue 2013). It is therefore important to understand and identify the significant synthesis parameters of the methods to be used and how the parameters to be used interact with each other and enhance
the synthesis of the catalysts for the production of CNTs. The effect of the method used on
the purity and structural changes between the original “as-prepared” carbon nanotubes and
the oxidized CNTs can be determined using the transmission electron microscopy (TEM),
energy dispersive spectroscopy (EDX), thermogravimetric analysis (TGA), Raman
spectroscopy (RS), and the Fourier transform infra-red spectroscopy (FT-IR) (Boehm, 2002).

In order to overcome limitations in its production, chemical vapor deposition (CVD) will be
used in the preparation of carbon nanotubes from catalysts because of its short time cost,
simplicity of the method and suitability for high quality materials.

2.4 Amorphous carbon
Carbon materials have attracted much attention in a vast range of applications such as
protective coatings, energy storage and medical applications. Carbon exists in a variety of
stable forms such as graphite, diamond, nanotubes, fullerenes and amorphous carbon whose
physical properties varies widely with the allotropic form (Robertson, 2002). Amorphous
carbon on its own has attracted enormous interest in recent years because of the emergence of
nanotechnology. It has been extensively used in the last decades for several applications such
as field emission display, surface modification and other areas (Paik, 2001) due to its unique
properties such as high hardness, low friction coefficient, and chemical inertness (Khan and
Silva 2005). It can be easily deposited at ambient temperature which implies that it could be
conveniently deposited on compliant substrates and can be easily combined with other
materials. Its compatibility and surface properties makes amorphous carbon a good choice of
reinforcement and modification (Jelinek et al., 2010; Aoi and Tada, 2013) and its chemical
inertness also makes it suitable for most surface modification (Yang et al., 2003; Bharathy et
al., 2010).

Activated carbon black is often confused with activated carbon which is a common
amorphous carbon characterized by high pore volume (2.25 cm$^3$ g$^{-1}$) and surface area of
4100 m$^2$ g$^{-1}$ (Jaramillo et al., 2010). Its chemical characteristics (acidic/basic) is said to be
dependent on the chemical heterogeneity of the surface i.e. the amount of non-carbon
heteroatoms present in carbon structure (Trogadas et al. 2014). The physical properties,
chemical nature of surface functional groups and the chemical nature of the adsorbate must be known in understanding adsorption mechanism of organic/inorganic species with amorphous carbon as most data derived from literature is difficult to understand because the carbon materials reported are derived from a wide variety of precursors and the adsorbents as well vary considerably in their physical and chemical properties (Chigombe et al., 2005)

In this study, the catalyst was prepared using Fe-Co/CaCO₃ via wet impregnation method with CaCO₃ used as support because of its ability to reduce formation of amorphous carbon and carbonaceous materials on the growth of CNTs. The carbon nanotubes were synthesized from the decomposition of acetylene using Fe-Co/CaCO₃ catalyst via chemical vapor deposition. The CNTs were characterized using the scanning electron microscopy, thermo gravimetric analysis and fourier transform infra-red spectroscopy to evaluate the quality of the carbon nanotubes before and after purification procedures while amorphous carbon was used as purchased and both materials were deposited on mild steel samples as reinforcement for carburization to enhance its surface hardness. The study entailed comparison of hardness between the reinforcements used with mild steel samples and gave discussions on the interplay and comparison between samples hardness.
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CHAPTER THREE

3.0 Materials and Experimental Methods

This chapter describes in detail the materials, experimental methods and equipment used in this study.

3.1 Materials and Chemicals

Carbon nanotubes were produced in the laboratory using the chemical vapor deposition method and the amorphous carbon was obtained by pulverizing charcoal. These two materials were used as the major reinforcements in the carburization of mild steel as described in this project. Iron nitrate Fe(NO$_3$)$_3$ and Cobalt nitrate Co(NO$_3$)$_2$ were the metal used in the catalyst synthesis while acetylene gas was used as the carbon source and nitrogen gas as the carrier gas and as well as purging gas in the CVD. A detailed summary of all materials and chemicals are shown in Table 3.1.

<table>
<thead>
<tr>
<th>Materials/chemicals</th>
<th>Form</th>
<th>Colour</th>
<th>Purity (%)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron nitrate (Fe(NO$_3$)$_3$)</td>
<td>Metal salt</td>
<td>Silver</td>
<td>98</td>
<td>Sigma-Aldrich (Pty) SA</td>
</tr>
<tr>
<td>Cobalt nitrate (Co(NO$_3$)$_2$)</td>
<td>Metal salt</td>
<td>Reddish brown</td>
<td>98</td>
<td>Sigma-Aldrich (Pty) SA</td>
</tr>
<tr>
<td>Calcium carbonate (CaCO$_3$)</td>
<td>Powder</td>
<td>White</td>
<td>-</td>
<td>Rochelle Chemicals (SA)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Gas</td>
<td>Colourless</td>
<td>99</td>
<td>Afrox Pty (SA)</td>
</tr>
<tr>
<td>Acetylene</td>
<td>Gas</td>
<td>Colourless</td>
<td>99</td>
<td>Afrox Pty (SA)</td>
</tr>
<tr>
<td>Nitric acid (HNO$_3$)</td>
<td>Liquid</td>
<td>Colourless</td>
<td>55</td>
<td>Merck Chemicals (SA)</td>
</tr>
<tr>
<td>Amorphous carbon</td>
<td>Powder</td>
<td>Black</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mild steel</td>
<td>Rectangular Bar</td>
<td></td>
<td></td>
<td>Stewarts &amp; Lloyds (SA)</td>
</tr>
</tbody>
</table>
3.2 Experimental methods

3.2.1 Preparation of catalyst

Iron nitrate Fe(NO$_3$)$_3$.9H$_2$O and Cobalt nitrate Co(NO$_3$)$_2$.6H$_2$O (Sigma-Aldrich) were used to prepare the catalyst using the wet impregnation method so as to make a 10wt% metal-loaded catalyst comprising 5wt% each of both iron and cobalt. Calculated amount of 3.62 g of Fe and 2.47 g of Co nitrates were measured using an electronic measuring balance (AND EK-610i, max 600 g d=0.01, JAPAN) into a beaker and dissolved in 30 ml of distilled water to make a precursor solution. This 30 ml solution was filled into a burette and let in dropwise into the measured 10 g of CaCO$_3$ (Rochelle Chemicals) support in a beaker while stirring using a magnetic bar and electronic stirrer (FMH instrument STR-MO) for 30 minutes. The metal-support slurry was left to stir for another 30 minutes so as to obtain a homogenous mixture and was dried in an oven at 120°C for 12 hours. After allowing the catalyst to cool to room temperature, it was ground to fine powder. (Kathyayini et al., 2004; Mhlanga et al., 2009). The schematic in Figure 3.1 shows the preparation of the catalyst used in the synthesis of the carbon nanotubes.

![Figure 3.1: Schematic for the preparation of Fe-Co nanoparticles using wet impregnation.](image-url)
3.2.2 Synthesis of carbon nanotubes

Carbon nanotubes were synthesized by the decomposition of acetylene C$_2$H$_2$ (Afrox, 99% purity) in a horizontal tubular reactor placed in a furnace also called the chemical vapor deposition process. Nitrogen N$_2$ (Afrox, 99.99%) was used as the carrier gas and the furnace was electronically operated to ensure that the reaction temperature, heating and gas flow rates are duly monitored and maintained. The setup is similar to that used by Fan et al. (2006) and Afolabi et al. (2011). This is generally referred to as the “CVD". The operation of the equipment is simple and effective as it is electrically controlled so as to regulate the heating rate, reaction time and flow rate of gases used in the decomposition of acetylene over the catalyst in order to produce carbon nanotubes. This was used and operated by using Nitrogen gas N$_2$ as an inert gas which is also called the carrier gas as a means to purge and as well rid the furnace of air and other impurities. The N$_2$ gas was passed over the catalyst which was placed in a quartz boat in a quartz tube and centered in the furnace but prior to this, the temperature, reaction time and flow rate was set as preferred before the introduction of the carrier gas and carbon source acetylene C$_2$H$_2$ which signaled the commencement of the reaction and turned off after a preset reaction time of 60 mins leaving the N$_2$ gas flowing over the sample till it cooled to room temperature. The result of this was a black powder which was ground into fine powder and measured. Figure 3.2 shows a schematic of the horizontal CVD reactor furnace.

In synthesizing carbon nanotubes, 1 g of the 10 wt% Fe-Co/CaCO$_3$ catalyst was measured and spread to form a thin layer in the quartz boat which was placed in the centre of the quartz tube and inserted into the reactor. The furnace was heated from room temperature to 700°C at 10°C/ min under the flow of N$_2$ at 180 ml/min so as to purge and heat up the reactor and on attaining the temperature of 700°C, acetylene (C$_2$H$_2$) was introduced at a constant flow rate of 90 ml/min which signals the commencement of the reaction and N$_2$ at 180 ml/min at a pressure of 200kPa. After a reaction time of 60 minutes, the flow of C$_2$H$_2$ was stopped and the furnace was left to cool to room temperature under the continuous flow of N$_2$ (180 ml/min). The boat was then removed from the reactor and the carbon deposit produced was collected, weighed and recorded.
3.2.3 Purification of carbon nanotubes

In the purification of the produced CNTs, a single step acid treatment (Toebes et al., 2004; Su et al., 2008) was employed where a measured amount of 0.5 g of the produced CNTs was measured and soaked in 100 ml of 55% HNO₃. The CNTs and acid mixture was stirred vigorously stirring using a magnetic bar and electronic stirrer (FMH instrument STR-MO) for 4 hours at room temperature so as to remove amorphous carbon, traces of catalysts and their supports completely then transferred and soaked in 200 ml of water for 12 hours. The resulting mixture was thoroughly washed and filtered using the N022AN.18 electric pump with distilled water and pH paper as indicator until a pH of 7 was attained indicating its neutrality. The filtered sample was dried in an air oven at a temperature of 110°C overnight and the purified CNTs were allowed to cool and measured with a noticeable mass loss of 0.12g. The treated CNT samples were characterised using the SEM, TGA and FTIR. The electronic stirrer (FMH instrument STR-MO) was also used in stirring the metal-support while preparing the catalyst which was carried out at 500 revolutions at 30 minutes and 4 hours respectively for the metal-support slurry and CNTs-HNO₃ mixture with a magnetic bar stirrer in them. Figure 3.3 shows the electronic stirrer while stirring the sample mixture and Figure 3.4 shows the schematics of the electric pump which is fixed to a conical flask with a tube where the water used in washing the sample is filtered into.
3.2.4 Mild steel sample preparation

Mild carbon steel samples (AISI 1018) were cut into smaller sizes of 10mm×10mm×6mm and polished with a surface grinder to obtain even and uniform surfaces. Cross-sections of as received and carburized mild steel were carefully polished after hot mounting in struers polyfast resins while grinding was carried out to achieve a flat surface and to remove scratches using struers 320, 600 and 1200 grit, silicon carbide paper. The samples were then polished for 10 minutes using struers MD Largo with 9 and 6 µm and MD Dac with 3µm diamond paste and 1µm with OPS (oxide polishing suspension) then rinsed in ethanol and dried. The surface hardness and composition of the mild steel sample was determined before
carburizing with CNTs and amorphous carbon using Vickers FM 700 microhardness tester. The chemical composition of mild steel is presented in Table 3.2 (Munroe, 2009).

Table 3.2: Chemical composition of mild steel

<table>
<thead>
<tr>
<th>Mild steel</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.14-0.2</td>
<td>0.6-0.9</td>
<td>&lt; 0.04</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

3.2.5 Carburization of mild steel samples

The mild steel samples of rectangular shape were carburized at the temperatures 750°C and 800°C and at periods of 10, 20, 30, 40, and 50 minutes with carbon nanotubes and amorphous carbon in a laboratory muffle furnace at the Richard Ward chemical and metallurgical department of the University of Witwatersrand. The process employed is similar to that used by (Kula et al., 2005; Gorockiewicz, 2011). A defined number of boost and diffusion steps were carried out at varying temperatures of 750°C and 800°C while the charge consisted of the mild steel with a defined polished flat surface. The carburizing atmosphere consisted of heating up to the varying temperatures at a speed of 10°C/minute, heating under this condition at varying periods, performing a defined number of boost and diffusion processes at the varying temperatures and cooling to room temperatures under the same condition. The carburized surfaces were observed with the Olympus SC50 optical microscope and the hardness distribution of the carburized layer was inspected with a Vickers FM 700 micro-hardness tester.
Figure 3.5: Schematic of the carburization furnace

3.3 Equipment used
The following pieces of equipment were used in the investigation of this research.

3.3.1 The surface grinder
The HMI surface grinder was used to produce smooth and polished surface on the mild steel samples. Its operation comprises a rotating abrasive wheel, a chuck which holds the workpiece in place while it is worked on and a rotating table.
3.3.2 The muffle furnace

The EI60S/GI/J4 muffle furnace with a Toho P4 programmable temperature controller was used in the heating up and carburizing the steel samples with the reinforcement (carbon nanotubes and amorphous carbon. It is operated electronically so the temperature, heating and gas flow rates are well monitored and it also has metal plates which holds the steel samples in place and centralized as well as a long fork which is used to place and remove the plates from the furnace. The temperature controller was used to preset the temperature and time at which the carburization processes were carried out.
3.3.3 The cut-out machine

The Brilliant Euchner 200 stm1N-2223024 cut out machine was used in cutting the samples into smaller cross sectional sizes for the hot mounting, grinding and polishing process.
3.3.4 The hot mounting machine

This Opal 410 hot mounting machine was used to mount the mild steel sample using polyfast resin before polishing for the microhardness hardness test and Olympus SC50 optical microscope analysis. The steel sample was placed on a balance which slides into the mounting zone then a sufficient amount of the polyfast resin was measured and poured in before closing the machine which is programmed to heat to 200°C and cool in 6 minutes.

![The Opal 410 hot mounting machine](image)

Figure 3.9: The Opal 410 hot mounting machine

3.3.5 The polishing machine

The steel samples were ground and polished on the Leco Spectrum system 2000 using pan clothes of 9, 6 and 3µm respectively with diamond paste.
3.4 Characterization techniques

3.4.1 Scanning electron microscopy

The surface morphology, microstructure, length and diameter of the CNTs samples were analyzed using the scanning electron microscopy (SEM). A Zeiss electron microscope equipped with a microscope fitted to a computer which uses the Axiovision 3.1 software for image analyses operating at 10 KV was used for the analysis of the samples. This required that the samples should be coated before they could be characterized so the carbon nanotubes were coated using 60% gold (Au) and 40% palladium (pd).
3.4.2 Thermogravimetric analysis

The residual mass percent and oxidation temperature of the CNTs were investigated by thermogravimetric analysis (TGA). The analyses were performed on TG SDT Q600 thermogravimetric analyzer. The mass of sample placed in the specimen holder also called the crucible which is made of aluminum was about 6mg and heated in order to eliminate water absorbed by sample. The initial weight reading was set to 100% and the heating initiated at a temperature range from 30°C to 800°C with a heating rate of 10°C/min under a nitrogen flow of 10 ml/min. The TGA curves were determined by the TA universal analysis software package which controls the instrument.
3.4.3 The Vickers microhardness tester

The Vickers hardness tester FM 700 was used to measure the microstructure and hardness of the as received mild steel and carburized samples using the indentation technique with a load of 0.5 kg. It was electronically controlled so as to monitor the dwell time, load on the substrates, the indentations taken at different points on the samples and the distances between the indentations.
3.4.4 The Olympus SC50 optical microscope

The Olympus BX41M optical microscope equipped with SC50 camera was used to observe the obtained structures after carburization and to evaluate the change in the microstructures of the mild steel samples.
References


CHAPTER FOUR

4.0 Results and Discussion

This chapter presents the results obtained from the synthesis and characterization of carbon nanotubes as well as that of the carburized mild steel samples and the hardness profile of the steel samples.

4.1 Characterization of carbon nanotubes

4.1.1 Scanning electron microscopy (SEM)

The comparison of morphology of the as-synthesized CNTs and purified CNTs by SEM is given in Figure 4.1 (see Appendix B1 for images). The images show the CNTs with a spaghetti-like orientation with several millimeters long and the diameters of the CNTs are distributed in the range of 42-52 nm (Wang et al., 2013).

![Figure 4.1: SEM images (a) as-synthesized CNT (b) purified CNT]

Figure 4.1a shows a dense network of the material which shows a vast amount of CNTs which are tightly bonded entangling each other and are quite free of amorphous carbon with a diameter of 52.99 nm. Figure 4.1b reveals the spaghetti strand-like structure with a node-like close end while the other end is capped with the catalysts which have varying lengths with a
spongy appearance. In the purified CNT, it can be observed that there is a lower degree of entanglement as compared with Figure 4.1a and this could be attributed to the functional group introduced during purification (Zhao et al., 2013). However, some catalyst are still at the tips and some twisted areas of the CNT which can be attributed to complex tubes which the acid used could not infiltrate and the ends are not entirely opened as well (Motchelaho et al., 2011; Ling et al., 2013).

4.1.2 Thermogravimetric analysis (TGA)

Figure 4.2 depicts the results obtained from TGA for the as-synthesized CNT and the purified CNT. The TGA was conducted under inert environment using nitrogen gas.

![Figure 4.2: TGA curve of as-synthesized and purified CNT samples](image)

From Figure 4.2, it can be observed that the as-synthesized CNT characterized with a round legend shows a slow weight loss from 27-503°C which was about 0.3%. At temperature greater than 503°C, a sharp reduction was noted which could be attributed to decomposition of water and amorphous carbon leaving 22% of Fe-Co catalyst residue at 594°C which was maintained till the end of the analysis where the percent of the residue remained unchanged.
The as-synthesized CNT sample shows that the sample was thermally stable to 503°C where decomposition starts to take place with a mass loss of 78%. This can be attributed to the presence of impurities possibly from the support used in the sample (Ebbesen et al., 1994). The purified sample shows a significant mass loss of 85% at a thermally stable temperature of 550°C before decomposition commenced at temperatures higher and this was maintained till 600°C. The percentage of residue left shows that CNTs are relatively pure after the acid treatment which reduced the remaining residue to about 15% and that washing in CNT in acid for four hours in enough to remove most catalyst-support residues and impurities. The initiation and decomposition temperatures of the purified CNTs are higher than those of the as-synthesized CNTs and this is ascribed to the reduction of catalyst particles and amorphous carbon (Edwards et al., 2011).

The rate at which the sample decomposed increased from the temperature of 593°C of the as-produced CNTs to 598°C in the purified CNTs shows that the structure of carbon was not damaged by the acids used which in turn improved the thermal stability of the carbon nanotubes (Motchelaho et al., 2011).

### 4.1.3 Fourier transform infrared spectroscopy (FTIR)

The FTIR was performed on all synthesized nanotubes using the Bruker TENSOR 27 FTIR spectrometer. This analytical technique which is non-destructive helps to identify the functional groups in the nanotubes walls. When CNTs were introduced to infrared radiation, a difference in charge due to the stretching and bending of carbon atoms is observed and this induces an electric dipole which is read as signals on the FTIR spectra. The extent of this induced dipole determines the presence of functional groups (Osorio et al., 2008). As-produced CNTs are to be symmetrical and thus generate weak signals which are disrupted by functionalization and in turn increase the charge difference.

Figure 4.3 shows the infrared (IR) spectra for the CNTs and the pCNTs in the same plane. There are three peaks indicated on the plot that substantiates the proper synthesis and purification of CNTs: the C-O peak at 3355 cm⁻¹, C-H at 2950 cm⁻¹ and C=O at 1236 cm⁻¹ which shows the presence of carboxylic groups from acid treatments (Vatanpour et al., 2011). There is a slight peak at the wavenumber of ~997 cm⁻¹ which corresponds to the presence of C-H bond but it is not too defined hence it’s not conclusive enough to prove the presence of
the bond. The individual spectrum for the as-synthesized CNT and purified CNT are presented in Appendix B2.

Figure 4.3: FTIR spectra of as-synthesized and purified CNT samples

4.2 Microstructure and hardness of the mild steel sample

4.2.1 Analysis of microstructures

The samples were etched with natal 2% solution of ethanol and nitric acid solution to reveal the microstructure and analyzed using the Olympus optical microscopy.

Figure 4.4a-c shows the starting microstructures of the low carbon steel which consists of coarse-grained ferrite-pearlite microstructure with the light colored region representing the ferrite while the dark region represents the pearlite which is a mixture of ferrite and iron carbide. There are no significant changes in the samples in Figure 4.4 as there was no introduction of carbon atoms into the substrate hence the microstructures remains slightly the same.
Figures 4.5-4.9 presents and compares the microstructures obtained at varying periods of the carburizing temperature of 750°C. From the micrographs, it can be observed that microhardness varies significantly after carburizing at different periods with the same temperature using the same routine. The surface structures at various saturation times show the presence of carbon deposits. Figure 4.5 shows the beginning of the dissolution of the pearlite into the austenite phase which forms at the pearlite boundary. The layer closest to the carburized surface shows a nucleation of the pearlite transforming into austenite (see Figure 4.6) with varying grain sizes which are slightly bigger in the micrographs with amorphous. This can be attributed to the size of the carbon powders used as amorphous carbon is in µm (Appendix B3) while the CNT is in nm as seen in the SEM and differences can be seen in prior austenite sizes and retained austenite. The grain boundaries as can be seen in Figures 4.7 and 4.8 are more visible and this can be attributed to the slow furnace cooling from the austenitic temperature of 750°C to room temperature. The formation of the austenite from the dissolution of the pearlite at the surface is controlled by the diffusion rate of the carbon atoms showing some pearlitic regions which are not totally dissolved. Hence, leading to formation of high ferrite hardness as the carbon atoms move from areas of dissolving pearlite to regions around the ferrite grains with some inclusions and decrease in pearlite. The heat treated samples have a ferritic matrix with an irregular grain size which could be due to the
distribution of the austenite from a carbon enriched zone of the ferrite from the dissolution of the pearlite grains (Figures 4.7-4.9). However, it can be observed that a more defined austenite grain structure is obtained in Figures 4.7-4.9 especially in those of the CNT and pCNT. This might be due to the increased number of sites which are suitable for the nucleation of ferrite and also the recrystallization of carbon with the initial austenite structure and also present in the grains formed are inclusions which might be as a result of the precipitating carbon atoms as seen in Figure 4.9.

Figure 4.5: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 750°C for 10 mins
Figure 4.6: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 750°C for 20 mins

Figure 4.7: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 750°C for 30 mins
Figure 4.8: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 750°C for 40 mins

Figure 4.9: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 750°C for 50 mins
A similar trend as observed in the 750°C is seen in the micrographs of the microstructures at 800°C (see Figures 4.10-4.14). However, the dissolution of the pearlite into partial austenite can be easily seen in Figure 4.10 leaving a soft core. The layer closest to the surface has austenite leading to ferrite with varying change in grain size in which is as well attributed to the size of the carbon powders. Ultrafine ferritic microstructure with little carbide and defined grain boundaries were obtained with certain inclusions and all composed of ferrite and retained austenite. However, there are bigger grain sizes in the amorphous carbon microstructures and as carbon deposit occurs on the surface of the samples when the carburizing atoms touches the surface of the steel sample, increase in the carburizing temperature leads to carbide precipitation on the surface on some of the samples leading to austenite grains with a thin coat of the carbon deposit on the samples (Figures 4.11-4.13).

Figures 4.11-4.14 shows that the pearlitic microstructures as seen in the starting microstructure did not totally dissolve into austenite even at the high temperature and hold time indicating they were localized as ferrite. This observation strengthens the fact that the structure aids in the decomposition of austenite on slow cooling after the carburization process. The growth process of austenite at 800°C is similar to that of 750°C with variations in the microstructure indicating rapid growth of austenite as a result of the rapid diffusion of carbon at higher temperature (Woo and Chong, 1985).

Figure 4.10: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 800°C for 10 mins
Figure 4.11: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 800°C for 20 mins

Figure 4.12: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 800°C for 30 mins
Figure 4.13: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 800°C for 40 mins

Figure 4.14: Optical micrographs of microstructures carburized with (a) amorphous carbon (b) CNT and (c) pCNT at 800°C for 50 mins
4.2.2 Analysis of microhardness

The microhardness shows the value for each reinforcement used from the surface of the mild steel sample and how it varies with time and temperature. The detailed hardness distribution in the carburization layer as a function of time and temperature is illustrated in Figures 4.15 and 4.16. Each hardness value represents a mean of five indentations and the average hardness was calculated (Appendix C).

![Figure 4.15: Comparison between the Vickers microhardness obtained for amorphous carbon, CNT and pCNT at 750°C](image)

Figure 4.15 illustrates the Vickers Hardness HV of the mild steel samples with the various reinforcements used in carburizing at a constant temperature of 750°C as a function of time. A Vickers microhardness of $159.316 \pm 1.56$ GPa with a load of 0.5 kg (500g) was obtained with CNT signified with the black bar at the period of 10 mins with no noticeable increase in the microhardness at varying periods till 50 mins with a microhardness of $165.98 \pm 4.98$ GPa. The pCNT indicated with a slant lined bar showed a steady increase in its microhardness with increase in time with an initial microhardness of $163.56 \pm 2.89$ GPa till a final microhardness value of $176.408 \pm 3.59$ GPa. The amorphous carbon signified with the cross lined bar at the
period of 10 mins showed an initial value of 152.64 ± 5.89 GPa with slight increase as time progressed to 40 mins where a microhardness of 155.74 ± 4.28 GPa and a significant increase at 50 mins where a microhardness of 157.2 ± 2.27 GPa was obtained.

The microhardness values as compared amongst the reinforcements showed that of the pCNT with the highest value from the initial period (10 mins) till the final (50 mins) with steady increase and that of the amorphous has the least values as there were little increase with time.

The hardness values (see Appendix C) of the reinforcements as compared with the normal substrate and those heated without any reinforcement showed an improved surface hardness was obtained.

Figure 4.16: Comparison between the Vickers microhardness obtained for amorphous carbon, CNT and pCNT at 800°C

Figure 4.16 shows a similar trend as observed in Figure 4.15. The CNT has an increased initial hardness value of 164.32 ± 2.97 GPa as compared to that obtained at 10 mins in 750°C.
with noticeable increase with time. However, the CNT at 20 mins shows no much increase until the 30 mins with a value of 168.3 ± 3.70 GPa and continued till the 50 mins period where a value of 177.88 ± 2.35 GPa indicating a general increase in the carburized sample compared to those obtained at 750°C. The pCNT shows a value of 179.16 ± 4.17 GPa which is higher than that gotten in the 750°C series and this continued progressively till 50 mins where a value of 191.64 ± 4.16 GPa was obtained. In the case of the amorphous carbon, the 10 and 20 mins bar appear equal but however have different values of 156.5 ± 2.77 GPa and 157.48 ± 5.30 GPa with a little increase as at 30 mins with a value of 158.62 ± 4.41 GPa and 159.46 ± 2.99 GPa at 40 mins respectively. The 50 mins showed a noticeable increase with a value of 160.702 ± 5.79 GPa with no clear difference in the heights of the bars as illustrated.

In terms of effect of the reinforcements on the substrates, the pCNT shows a higher hardness compared to the CNT and amorphous carbon. A good and improved surface hardness was obtained in this work with the reinforcements but with pCNT having the highest value compared to the normal substrate which had just a surface hardness of 145.188 ± 2.66 GPa and by comparing Figures 4.15 and 4.16, it can be observed that while microhardness increased with time in Figure 4.15, the values increased in Figure 4.16 which showed increase with time and temperature indicating that samples carburized at 800°C has higher hardness values than those at 750°C which is attributed to higher carbon diffusion in the austenite.
References


CHAPTER FIVE

5.0 Conclusions and Recommendations

This section of the dissertation gives the summary of the major findings or deductions obtained from the discussion of results in chapter four, while recommendations are made for further studies that are not covered during the investigation of this study.

5.1 Conclusions

The aim of this study was to investigate the effect of carburizing mild steel with carbon nanotubes (CNTs) and amorphous carbon as reinforcement on its surface hardness with the synthesis of carbon nanotubes from Fe/Co catalyst prepared on CaCO₃ support via the CVD and was used in carburizing low carbon steel samples with amorphous carbon as well. Thus from the synthesis of carbon nanotubes and carburization of low carbon steel samples with CNTs and amorphous carbon, it can be concluded that:

- The as-synthesized CNT sample showed purity percentage 78% while that of the purified sample showed 85% with no damage to the CNTs with diameter ranging from 42-52 nm.
- The growth process of austenite at 800°C though similar to that of 750°C has variations in the microstructure indicating rapid growth of austenite is a result of the rapid diffusion of carbon at higher temperature.
- The microhardness values obtained from the reinforcements used showed increase in hardness value from the initial value of 145.188 ± 2.66 GPa to a peak value of 157.2 ± 2.27 GPa with amorphous carbon, 165.18 ± 2.05 GPa with CNT and 176.408 ± 3.59 GPa with pCNT at 750°C while those obtained at 800°C showed higher values of microhardness of 160.702 ± 5.79 GPa with amorphous carbon, 175.08 ± 2.39 GPa with CNT and 191.64 ± 4.16 GPa with pCNT.
- The percentage hardness obtained for the reinforcements showed the amorphous carbon with improved percentage hardness value of 5.47%, the CNT with 10.04% and the pCNT with 15.77% at a temperature of 750°C and at 800°C, the reinforcements showed 7.04% with amorphous carbon, 14.68% with CNT and 22.05% with the pCNT over the normal substrate carburized at these temperatures.
- The percentage hardness as compared among the reinforcements showed the pCNT with 10.89% and 6.37% % over amorphous carbon and CNT at 750°C respectively and the CNT has 4.83% over amorphous carbon. The values obtained at 800°C showed higher
percentage hardness with pCNT at 16.14% and 8.64% over amorphous carbon and CNT while CNT has 8.21% over amorphous carbon.

- The microhardness and percentage values obtained showed that pCNT as a stronger reinforcement than amorphous carbon and CNT as pCNT showed significantly more stability and hardness and that higher temperatures and time increased the surface hardness.
- The reinforcements used in this work are promising enough in increasing low carbon steel’s surface hardness as a little amount has resulted in improved surface hardness with pCNT as the best overall reinforcement in this study as it has the highest surface microhardness.
- Increase in temperature showed a slight increase in the surface hardness obtained as compared between values gotten at 750°C and 800°C.
- The CNTs has a more rapid diffusion rate compared to the amorphous carbon which can be attributed to its size and its high capability to alter and improve metals even with addition at very small fractions and specifically, their superior strength, and high surface area to volume ratio which can also be seen in the grain sizes.

5.2 Recommendations

The following suggestions are thereby recommended:

- Further optimization of the content, composition and mechanical properties are needed to help in understanding the microstructural formation of the sample.
- A better technique in introducing the carbon powders to the substrate surface will aid uniform spread and diffusion.
- Lastly, increase in mass of the carbon powders and the carburizing time will also aid in further study.
APPENDICES

This section contains data and images not included in chapter four but which are relevant to the study and that have to deal with the carbon nanotubes and mild steel samples. Detailed discussions on these data and images are already presented in chapter four.

Appendix A: General data

Appendix A1: Calculations of the mass of metal salts used in the catalyst synthesis

10% Fe/Co on CaCO₃ was used as the basis. Hence,

5% Fe × 10 g = 0.5 g
5% Co × 10 g = 0.5 g

Iron nitrate Fe(NO₃)₃.9H₂O
Atomic mass = 55.845 g/mol
Molecular mass of Fe(NO₃)₃.9H₂O
55.845 [14+3(16)] (3) + 9[(2) + 16] = 403.85 g/mol
Molecular mass of Fe(NO₃)₃.9H₂O = 403.85 g/mol
55.845 g = 403.85 g/mol
0.5 g = x
x = 403.85 g/mol × 0.5 g /55.845 g/mol
x = 3.62 g of Fe

Cobalt nitrate Co(NO₃)₂.6H₂O
Atomic mass = 58.93 g/mol
Molecular mass of cobalt nitrate Co(NO₃)₂.6H₂O
58.93 [14+3(16)] (2) + 6[(2) + 16] = 290.93 g/mol
Molecular mass of Co(NO₃)₂.6H₂O = 290.93 g/mol
58.93 g = 290.93g/mol
0.5 g = x
x = 290.93 g/mol × 0.5 g /58.93 g/mol
x = 2.47 g of Co
Appendix B: Characterization techniques

Appendix B1: SEM images of the CNT

Figure B1: High magnification SEM images of (a) as-synthesized CNT (b) purified CNT

Appendix B2: FTIR spectra of as-synthesized and purified CNT

Figure B2: FTIR spectrum of as-synthesized CNT
Appendix B3: Particle size analysis of amorphous carbon

Figure B3: FTIR spectrum of purified CNT

Figure B4: The particle distribution of amorphous carbon
Appendix C: Microhardness values

Table C1: Average microhardness of substrate

<table>
<thead>
<tr>
<th>No of Ident.</th>
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<th>800°C</th>
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Table C2: Average microhardness of amorphous carbon at 750°

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Table C3: Average microhardness of CNT at 750°C

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Table C4: Average microhardness of pCNT at 750°C

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Table C3: Average microhardness of amorphous carbon at 800°C

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Table C4: Average microhardness of CNT at 800°C

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Table C5: Average microhardness of pCNT at 800°C

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