



EFFECTS OF CASSAVA-LEAF-ENHANCED CARBONITRIDING ON CASE-HARDENING OF BARITE MINING TOOLS

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CERTIFICATION

This is to certify that the thesis titled “EFFECTS OF CASSAVA LEAVE CARBONITRIDING ON CASE-HARDENING OF BARITE MINING TOOLS.” submitted to the school of postgraduate studies, African University of Science and Technology (AUST), Abuja, Nigeria for the award of the Master's degree is a record of original research *carried out by Olanrewaju, Yusuf Afolabi in the Department of Materials Science and Engineering.*

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BARITE MINING TOOLS

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ABSTRACT

This study presents the results of an experimental study of the effects of cassava leaves carbonitriding on the microstructure, hardness and abrasive wear behaviour of AISI 1065 and AISI 1070 steels used for barite mining operations. The pack-biocyaniding of the mining tools was achieved using processed cassava leaves powder mixed with BaCl₂ as an energiser in the heat-treatment process. Heat treatment was done at different temperatures of 400°C, 450°C, 500°C and 550°C for 3 hours to allow the diffusion of nitrogen and carbon into the interstitials of the low-alloy steel samples and then cooling in air. The experimental work showed that at carbonitriding temperature of 550°C, maximum hardness was achieved for the steel specimen of AISI 1070 and AISI 1065, from 255HV and 241HV to 327HV and 295HV respectively. A pin-on-disc wear tribometer machine was used to evaluate the wear characteristic of materials. The test results showed that at carbonitrided temperature of 550°C, the harder steel specimens gave the highest wear resistance and also the wear rate was reduced by $2.56 \times 10^{-3} \text{mm}^3/\text{m}$. The implication of these results revealed that the hardening of steels with locally pulverised cassava leaves increased the hardness and wear resistance of the steel specimens as a result of diffusion. Also, the use of waste cassava leaves for improving hardness of steel specimens saves on cost and is environmentally friendly compared to conventional means.

DEDICATION

This work is dedicated to Almighty God for His mercy, guidance and strength, for seeing me through the completion of the thesis work. I also dedicate this work to my loving parents and my beloved brother, Mr. Dauda Olanrewaju.

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CHAPTER ONE INTRODUCTION

1.1 Background

Barite is a non-metallic mineral composed of barium sulphate (BaSO_4) in the proportion of 66% BaO and 34% SO_3 (Grigorova, Dzhamyarov, & Ivan, 2015). Though it is ordinarily a colourless or milky-white substance, it can be found in different colours due to the presence of impurities (strontium and iron oxides), which might be trapped in the crystals during their formation (MacDonald et al., 2011). Barite is chemically inert and insoluble; and has a hardness of 3.0 – 3.5 on Mohs scale, and a specific gravity (SG) of 4.50 (Ariffin, 2004). The high SG of barite makes it suitable for a wide range of industrial, medical and manufacturing uses.

More than 77% of barite worldwide is used as a weighting agent for drilling fluids in oil and gas exploration to suppress high formation pressures and prevent blowouts. The non-magnetic properties of the mineral make it more useful for this purpose as it does not interfere with the magnetic measurements of the borehole during oil exploration process. As a well is drilled, the bit passes through various formations, each with different characteristics. The deeper the hole, the more barite is needed as a percentage of the total mud mix. Barite is also used as a filler in paint and plastics; for sound reduction in engine compartments; as the coating material of automobile finishes (for smoothness and corrosion resistance); as a friction product for automobiles and trucks; as radiation-shielding cement, in glass ceramics and medical applications (Spar, 2017). Barite occurs as a vein filling and as a gangue mineral. It is commonly found in lead-zinc veins in limestones, in hot spring deposits and with hematite ore. It is often associated with one or more of the following minerals: celestine (SrSO_4), galena (PbS), sphalerite (ZnS), pyrite (FeS_2), quartz (SiO_2), calcite (CaCO_3), dolomite ($\text{Ca,Mg}(\text{CO}_3)$), marcasite (FeS_2), chalcopyrite (CuFeS_2), fluorite (CaF_2), siderite (FeCO_3) and witherite (BaCO_3) (Labe, 2015).

Barite as a mineral is found in many regions around the world, including Nigeria. Locations where barite are mined in Nigeria include the Benue State, Nasarawa State, Cross Rivers State, Plateau State, Bauchi State and Taraba State. The deposits in the Nasarawa State and Benue State have been estimated to be 730,000 and 307,657 metric tonnes. Over 7.5 million tonnes of barite have been reportedly identified in Cross River State, Benue State, Taraba State and Bauchi State. The states hosting the most barite mining activity are Nasarawa State, Benue State, Taraba State and Cross River State (O'Driscoll, 2017). However, despite the substantial deposit of barite in Nigeria, the country is not on the list of the world 20th largest producers of barite. Currently, mining of minerals in Nigeria accounts for only 0.3% of its GDP, due to the influence of oil resources. The domestic mining industry is underdeveloped as most of the mining activities are still mainly carried out at the informal sector with over 95% of mining activities being artisanal and small scale, leading Nigeria to importing more barite than can be produced domestically. In order to boost local mining of barite in Nigeria, the Federal Government of Nigeria (in the year

2003) imposed a ban on the importation of barite. Though the ban was aimed at stimulating the development and use of domestic barite resources in Nigeria; the issues in the supply chain were due to the fact that most of the mining and minerals processing operations in Nigeria are carried out by artisanal and small-scale miners. Their mining excavations were merely littoral, and tools are hoes, pick axes, chisels and shovels. They became the reason for most of the oilfield service companies to claim that the local production of barite in Nigeria cannot meet the desired volume and the American Petroleum Institute (API) specifications of the oil industry. As a result, the oil companies applied for the lifting of the ban on barite importation in 2014 (O'Driscoll, 2017). Now, Nigeria's barite sector is hoping to enter a new era of development that will enable it to compete more favourably with the dominant and superior quality barite imports; there is a growing need in ensuring machine efficiency, as losses can dramatically reduce production.

1.2 Problem Statement

The technology of mining and mineral processing faces a challenge with the increasing demand for processed minerals by a growing number of end-users, as a result from an increasingly industrialised economy. The growing rate of the mining industry is assured through the activity of the high-performance machineries. Therefore, low-alloy steels are normally used as materials for mining tools. In most cases, alloy steels do not have enough anti-wear properties. Mostly, abrasive wear produces the premature failure of many components of the extraction machinery in the mining industry. However, the hardness of barite which is about 1.7 – 2.0, together with the impurity minerals present therein causes both significant damage to the mining tools and economic loss to the mining investors. The mining tools are used in tough environments that cause the tools to be exposed to wear and tear. Barite associates with one or more of the following minerals such as quartz and silica, accounting up to 60% of the earth's crust and ranges from 7.5 – 10 of Mohs scale of hardness (Bodin & Mason, 2017). This is in exception of the surface or underground material to be excavated before reaching the vein. With the presence of these hard minerals, mining tools, including hard martensitic steels, with a hardness range of 7 – 8 still wear away over time. The most commonly replaced tools in mineral extraction and processing are the excavating tools, such as the excavator bucket teeth and the pickaxe tools. The wear behaviour of these tools is often assumed to be a function of temperature processing and the structure materials; the properties of the abrasive material; and the nature and severity of the interaction between the metal-to-mineral wear. In the process of digging and loading of barite onto the mining pickaxe and the shovel, there is significant abrasion between the barite impurity and the mining tools.

During mineral and mining processing, relatively large amounts of material are removed causing wear to the excavator bucket teeth; with a resulting decrease in its operating efficiency due to the changes in the dimensions of the wearing surface (Hawk & Wilson, 2001). Failure due to wear reduces the lifespan of the mining tool, and so increases the cost of the mining of barite, in general. Therefore, there is the need to minimise friction and wear in order to extend the lifespan

of these tools. The use of surface coatings opens up the possibility for a material design in which the specific properties are located where they are mostly needed. The substrate material can be designed for strength and toughness while the coating is responsible for the resistance to wear. In order to achieve the above goal, the technology of surface hardening of steels heat treatment is attractive for the industry which is considered for improvement.

1.3 Aim and Objectives

The aim of this work is to investigate the effects of carbonitride on the case hardness and abrasive wear behaviour of barite mining tools. The specific objectives of this work are:

1. To improve the wear resistance of mining tools by increasing the hardness and strength of steels through the diffusion of carbon and nitrogen into interstitial holes in the metal.
 1. To benchmark the mechanical behaviour of the barite mining tools by characterising their microstructure, before and after the carbonitriding process.
 2. To determine the wear and hardness properties of the mining tools after carbonitriding at intermediate temperatures.

1.4 Justification

Several attempts have been made by researchers to improve the case hardness of mining tools. In most cases, conventional heat-treatment processes were carried out using expensive gas chambers or salt baths. In small- and medium-scale enterprises, salt bath treatment has been the most common method probably due to its relatively low cost and reduced treatment time. Unfortunately, a substantial amount of toxic, corrosive and non-environmentally friendly gases is liberated from the fused salt mixture into the atmosphere. The disposal of the spent salt mixture is hazardous to both the flora and fauna of the environment. This work attempts to investigate the use of locally available oven-dried pulverised cassava leaves in improving the case hardness and wear resistance (at intermediate temperatures) of some barite mining tools.

1.5 Scope

The scope of this work is limited to the study of the effects of pack bio-carbonitride on case hardness and abrasive wear behaviour of mining tools, which use locally available pulverised cassava leaves.

CHAPTER TWO LITERATURE REVIEW

2.1 Introduction

Mining industries have been viewed as key drivers of economic growth and the development process (Bradshaw, 2005). In some countries, lead sectors drive economic expansion, which can lead to higher levels of social and economic wellbeing (Bridge, 2008). However, Nigeria has been one of those countries in Africa that has a wide variety of different natural resources. Nigeria's abundant solid minerals constitute some of the largest known deposits in recent years under different categories made up of precious metals, stones and industrial minerals, like coal, tin, gold, marble, limestone, barite and others (Merem et al., 2017).

Mining in Nigeria is over 2,400 years old; initial mining took place in the form of artisanal mining as practised by communities while searching for natural resources within their environment for their social and economic benefits (Greenland, 2011). The history of organised mining in Nigeria began in 1903 when the Mineral Survey of the Northern protectorates was created by the British colonial government. German foreign mining companies such as the amalgamated Tin Mining Company of Nigeria introduced mechanised mining. This led to higher productivity in the mines and consequently land devastation as no law was put in place by the colonial government to guide mineral extraction (Stephen, 2012). In the 1940s, Nigeria was a major producer of tin, columbite and coal. The core of these mineral deposits scattered across the country remains a major attraction for informal and conventional mining activities, even though they are yet to be fully exploited on a large scale. Statistically, the level of exploitation of these minerals is very low in relation to the extent of deposits found in the country. Currently, most of the mining activities are carried out by artisanal and small-scale miners who lack appropriate technology and sufficient funds; and are reluctant to imbibe best practices in their operations. The processes greatly affect Nigeria's mineral development and the environment.

2.2 Barite in Nigeria

Various studies have found that the barite deposits in Nigeria occur in the Benue Trough (Lower, Middle and Upper) (MMSD, 2013). The Benue Trough is believed to have originated as a failed arm of an aulacogen at the time of the opening of the South Atlantic Oceans during the separation of the African plate and the South American plate. The Benue Trough contains as much as 6,000m of cretaceous tertiary sediments, including those predating the middle Santonian, which have been compressionally deformed, faulted and uplifted in several places. Economically, mineable barites mineralisation in Nigeria occurs in the Lower and Middle Benue Trough (MMSD, 2013).

Barite occurs in a large number of depositional environments, and is deposited through a number of processes including biogenic, hydrothermal and evaporation (Hanor, 2000). The occurrence of

barite mineralisation in Nigeria was first reported by the Nigerian Geological Survey Agency, around the Keana, Alosi, Akiri, Wuse, Gbande, Gboko and Shata/Chiata/Ibi areas within the Middle Benue Trough, with tentative reserves of about 40,000 tonnes (Tate, 1959). The mineral occurs in the country as vein infilling materials associated with lead-zinc lodes and veins in the both pre-Cambrian basement and cretaceous sedimentary rocks of the Lower, Middle and Upper Benue valley (MMSD, 2010).

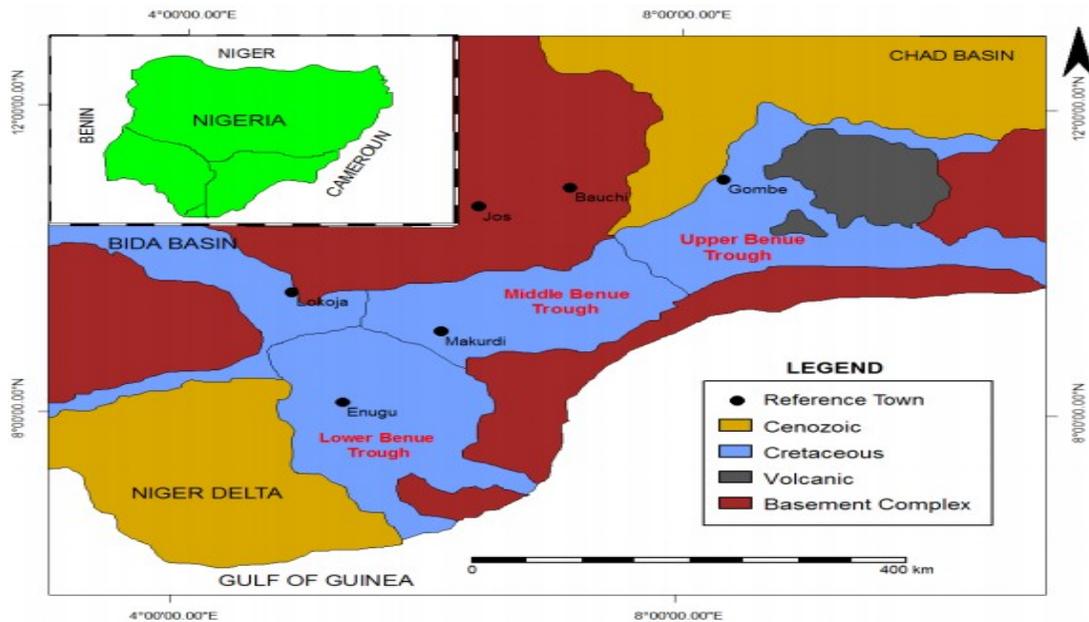


Figure 2.1: Modified map of the Benue Trough of Nigeria (Obaje, Abaa, Najime, & Suh., 1999)

The width of the veins found in some of these locations ranged from a few centimetres to 5.3m and the lengths of the veins also vary from a few to above 4500 m (MMSD, 2010). Only two types of barite occurrences have been seen in the field so far, these are; sediment-hosted, stratiform concordant type or ‘mineral flat’ (Fyfe et al., 1978). This type of occurrence is much less frequent and has only been seen in Alifokpa (Cross River State) and Gidanwaya in Ibi (Taraba State). It is hydrothermal in origin, lensoid in shape and is frequently multi-layered.

In 1975 to 1980, earlier works on the barite mineralisation in Nigeria indicated that the mineral is associated with quartz, galena, sphalerite, iron minerals, copper and fluorite as gangue, see Figure 2.2. Detailed exploration work on barite deposit has been reported in the Azara district part of Nasarawa State in north central Nigeria. About 20 veins have been mapped in Azara, most of them represented by narrow, winding structures. Conservative estimates carried out in three rich veins, out of the 20 occurrences in this locality, indicated a reserve of about 730,000 tonnes of barite; this was established over the area and for only a depth of 10m (Maiha,1996).



Figure 2.2: Vug in barite sample from Bunde with shiny black crystals of galena, greenish-yellow coloured crystals of sphalerite and reddish grains of iron oxide

In quality, the Nigerian barites is moderate to high. The major impurities are quartz, iron oxide (goethite), fluorite and carbonates of iron, calcium and magnesium. These impurities tend to reduce the SG of the unprocessed barites; increase the cost of the processing and wear out the mills rapidly. Some of these impurities can be removed by magnetic and gravity separation. Once it is processed, the quality of the barite increases up to a SG of 4.2, which meets the standard specified value of American Petroleum Institute (API). The importance of barite (BaSO_4) as an economic mineral is seen from its utilisation as a major constituent of drilling mud, in production of industrial wares such as glass, radiation shields and as a source for barium-based chemicals. Currently, occurrences of barite are found in nine states within the Benue Trough. The areas of mineralisation are Cross River State and Ebonyi State in Lower Benue Trough; Benue, Nasarawa, Plateau and Taraba States in Middle Benue Trough; and Gombe, Adamawa and Bauchi States in the Upper Benue Trough. Beyond Benue Trough, investigations by Nigerian Geological Survey Agency has revealed barite mineralisation in Zamfara State (MMSD, 2013). Preliminary survey carried out by the Geological survey of Nigeria in 1959 put the estimated reserve at 41,000 tones for the Benue valley deposits. Also, the Nigerian Mining Corporation estimated the resource of 70,000 tonnes in the Azara deposit in the Nassarawa State. Recently the Nigerian Geological Survey Agency embarked on the evaluation of newly reported deposits in Cross Rivers State, Benue State, Nassarawa State, Plateau State and Taraba State. The inferred resource estimated for four of the states (Benue, Cross River, Nassarawa and Taraba) where mining is considered viable is 21,123,913 metric tonnes (MMSD, 2010).

2.2.1 Barite in Benue State

The barite resource of Benue State is found in the igneous-metamorphic rocks of the pre-Cambrian, as well as in sandstones (cretaceous sediments) and shale of the Benue Trough sedimentary formations (MMSD, 2010). These are known to be the most consistent rock types that host barites in the trough. The mineralisation is vein-type displaying distinct features suggestive of open-space deposition and cavity fillings such as large, interlocked, euhedral

crystal growths, cocks-comb structure, mineral inclusions. The only two vein trends in the trough are; the NW-SE trend, which tends to be orthogonal to the axis of the trough; and the N-S to NNE-SSW trend, which is younger than the former (Oden, 2012). The mineral occurs as white, reddish-brown and clear varieties, as show in Figure 2.2; with SG varying between 3.7 and 4.5. Chemical analysis shows that most samples contain between 76 – 87% BaSO₄, impurities of between 5 and 21% silica and up to 3% iron (iv) oxide (MMSD, 2010).

There are at least ten barite fields in the trough, each containing swarms of veins or concordant stratiform minerals flats of hydrothermal origin. The Guma field in the Benue State is made up of Torkula, Kaseyo, Zanzan, Iye, etc to which the veins in the University of Agriculture campus, at Makurdi can be added.



Figure 2.3: Variety of colours of barite occurrence at Tokula mining site, Benue State.

The highest concentration of barite veins in this field is within and around Torkula and because of its size, this field holds a lot of promise even though its known veins are currently fewer than that in Azara field. Also, Lessel field in Benue State is another large field in terms of number of veins and occurs mainly south of Gboko, while the Yandev deposit north of Gboko, which is also added to this field. Included in this field are Lessel Bunde, Lessel Mbato and Lessel Mbagwa, with over 20 veins currently in production. Other locations of barite in Benue State are Tombu, Korinya, Yandev, Orgba, Ambua, Ihugh and Logo (Oden, 2012). The inferred resource of barites for the state is more than 307,657 metric tonnes based on an average SG of 4.0 and the depth of vein is more than 20m (MMSD, 2010).

2.2.2 Barites in Nasarawa State

Barite in Nasarawa was first detected in Azara in the early 1960s. The resource is hosted by assorted sedimentary rocks, like shale, mudstones siltstones and limestones. The barites occur in the form of veins having a width varying between a few centimetres to 3.5m (MMSD, 2010). Veins persist along strike for distances varying between just under 1,000m to over 4,000m. Laboratory studies conducted on samples from the state show that SG of mine materials varies between 3.9 and 4.4; this is within specification of the API. However, some samples have SG values of less than 3.6. Such samples are silica rich varieties that are not suitable for use unless

beneficiated. The impurities indicated by the analytical data are quartz, celestite (SrSO) and iron oxide (MMSD, 2010). The inferred resource of barites in the state is 3,243,376 metric tonnes calculated using an average SG of 4.0 and a vein depth projected to 20m. The barites filed locations are delineated based on availability of an optimum number of veins for large scale operations. The Azara field in Nasarawa State includes; Azara, Ribí, Wuse and Akiri. This field has a large number of over 20 veins, although quality of material is generally low, except at Ribí. Also, the Keana field in Nasarawa State including; Alosi, Ambua, Chiata, Kuduku (Oden, 2012).



Figure 2.4: Barite mining site in Azara in Nasarawa State, Nigeria (Oden, 2012)

2.2.3 Barite in Cross River State

Barite deposits in the Cross River State is composed of sedimentary rocks, which constitute the Calabar flank and metamorphic and intrusive rocks; they crop out in the Oban massif and Obudu Plateau. In the Calabar flank, which is in the lower Benue Trough, the outcrops are widespread but mineralisation is generally concealed. Barite occurrence has been studied in 22 localities and the host rocks include; sandstones, shales, dolerites, granite and gneiss. Shales and sandstones have the greatest occurrence of barite in the state (Ekwueme & Akpeke, 2012). The mineral occurs as veins trending NE-SW, N-S and NW-SE. Barite occurrences have been reported in many localities and some are already being mined. Some locations where barite are found in Cross River State are; Alifokpa, Gabu, Osina, Alesi, Ekpokpa, Edondon, Iyamitet, Ndam, Okokori, Okumurutet, Okangha, Agoi Ekpo, Agoi Ibami, Akpet, Akpet Central, Okurike, Lefin, Bitol, Ugbem (Oden, 2012). High-grade deposits are found in include Akpet, Ekukunela, Oshina – Gabu, Okumurentes, Iyamitet, Newekwete in Obudu. Currently, this state is the largest producer of barite in Nigeria. The veins width is often between 2.5 and 5.3m; and SG for the samples analysed range from 3.0 – 4.4. Traces of galena and sphalerite are often associated with barite occurrences. Total vein length varied between 1,000 and 6,000m. The inferred resource for the entire state is 8,612,880 metric tonnes and is distributed almost evenly between north and south (MMSD, 2010).

2.2.4 Barite in Taraba State

Barite in the Taraba State is located in five LGAs; Sardauna, Karim Lamido, Yoro, Lau and Ibi. Some of the barite fields include; Mbanga Petel, Juo, Gidan Waya, Kauyen Isa, Bakuyu, Ibia, Kumar, Pupule, Apawa, Didango, Suwa (Oden, 2012). The resources are hosted in porphyritic granites and fine-grained sandstones. Vein lengths are persistent over distances varying from 3,500 to 5,000m and the width from 3.5 to 5m. Impurities consist of quartz and sulphide minerals such as galena. The figure obtained for the inferred resource is 8,960,000 metric tonnes to a depth of 20m. The quality of the resource is good with most SG values close to 4.2 (MMSD, 2010).

2.2.5 Barite in Zamfara State

The Zamfara State is the only state outside the Benue Trough where barite mineralisations is found. The mineral occurs in Dareta near Anka, Rekebu near Chafe, Yarkatsina (GidanSaro) and Tofa Forest Reserve. Barite mineralisation in the Zamfara State is linked to epigenetic hydrothermal fluids, which leached barium from adjacent rocks and precipitated in the vein. The vein deposits show great variations in their properties, especially in their thickness. The veins have variable widths from 0.6m – 2m, and lengths of longer than 100m. The majority of the veins have probably formed from rising hydrothermal solution, which precipitated the barites in the veins. The barites are large to granular with uneven fractures and the colour varies from white to the reddish-brown type (MMSD, 2010).

2.3 Mining Equipment and Operations

A rapid growing rate of the mining industry is assured through the high performance of machineries with complex mechanisms. Earthmoving equipment like excavators, loaders, haulers are commonly used in mining industries. The primary function of this equipment is to excavate below the natural surface of the ground. Commercial barite mining includes open-pit mining and underground mining, with the former being the most popular method. In open-pit mining, barites are usually quarried at residual talus deposits and outcrops and shallow depth ore deposits. In underground mining, barites are usually quarried through the shrinkage method, filling method and stage caving method. Excavators are used in the underground mining operation of barite and its ore. During the operational life of the excavator, several resistive forces act against the bucket teeth; causing failure of the machine parts. Resistive forces include impact, wear, abrasion and chemical action. In the selection of appropriate material for bucket teeth, it is necessary to make an accurate analysis, as the replacement of worn out teeth on a monthly basis causes an increase in cost; which becomes an important economic factor in the mining industry (Fernández, Vijande, Tucho, Rodríguez, & Martín, 2001). Generally, alloy steel is used to make an excavator bucket tooth. In most cases these alloys do not have enough anti-wear properties and coatings are employed as a good alternative, so that its life will improve against abrasive wear (Singla, Shibe, & Grewal, 2011).

2.4 Introduction to Steel and Surface Hardening

Steel is an alloy of iron and carbon combined with any other alloying elements. Carbon steel is by far the most widely used kind of steel. The properties of carbon steel depend primarily on the amount of carbon it contains, and are known as low-carbon steel, medium-carbon steel and high-carbon steel. Generally, with an increase in the carbon content from 0.01% - 1.5% in the alloy, its strength and hardness increase but still such an increase beyond 1.5% causes an appreciable reduction in the ductility and malleability of the steel. In many engineering applications, the surfaces of mining tools, dies and the majority of the machine parts are commonly subjected to higher stresses, abrasive wear and corrosive damages. In such working conditions, surface properties are important for reliable and long economic service life. In order to reduce this loss, therefore, properties of the surfaces should be improved. The diffusion of atoms of different elements into the surface of the materials is a commonly used technique to improve surface properties of tools and mechanical parts.

Case-hardening or surface hardening is the process of hardening the surface of a metal, often low-carbon steel by infusing elements into the metal surface to form a hard, wear resistance skin, while allowing the metal underneath to remain soft and tough, thus forming a thin layer of harder metal (called the "case") at the surface. Most often it is used to improve the wear resistance of parts without affecting the softer, tough base materials necessary to resist impact occurring during operation. Surface hardening includes a wide variety of techniques. For iron or steel with low-carbon content, which has poor to no hardenability of its own, the case-hardening process involves infusing additional carbon into the surface layer (Jayakody, 2010). Mostly, the strength of steel is influenced by its microstructure, the type of crystal patterns, which is controlled by the arrangement of the atoms of the various elements in the steel. Heating and cooling of the steel influences this atomic arrangement (Aweda, Dauda, Dagwa, & Dauda, 2015). However, the heat-treatment process involves a combination of time-controlled heating and cooling operations of metal without changing the product shape that will produce the desired mechanical properties (Fadare, Fadara, & Akanbi, 2011).

The case-hardening is usually done after the part has been formed into its final shape in order to increase the hardening element content of the tools to be used. Both carbon and alloy steels are suitable for case-hardening; typically, mild steels are used, with low-carbon content, usually less than 0.25%. These mild steels are not normally hardenable due to the low quantity of carbon content, so the surface of these types of steel is chemically altered to increase the hardenability (<https://en.wikipedia.org/wiki/Case-hardening>). There are various surface hardening and surface modification techniques that are used in the steel industry. Such case-hardening process may be achieved by diffusing carbon (carburisation), nitrogen (nitriding), and/or boron (boriding) into the outer layer of the steel at an elevated temperature, then the surface layer is heat treated to the desired hardness (Davis, 2002). Other kinds of surface treatment processes include; carbonitriding, nitro-carburising, titanium-carbon flame hardening, induction hardening, laser

hardening, electron beam hardening and ion implantation; which is applied to gears, ball bearings, railway wheels, mining tools, etc.

2.4.1 Carburising

Carburising is the addition of carbon to the surface of low-carbon steels at temperatures within the austenitic region, i.e. below the melting point, of the steel concerned, which is between 850°C – 950° for mild steels. This temperature range has a high solubility for carbon, as it is a stable crystal structure. Carburisation is the most widely used method of surface hardening. It enriches the surface layers of low-carbon or mild steel with up to 0.8% - 1% of carbon. Hardening is accomplished when the subsequent high-carbon surface layer is quenched to form martensite, so that a high-carbon martensitic case with good wear and fatigue resistance is superimposed on a tough of low-carbon steel core (Krauss, 1980). The carburisation process is a diffusion-controlled process, the longer the steel is held in the carbon-rich environment the greater the carbon penetration will be and the higher the carbon content (<https://en.wikipedia.org/wiki/Case-hardening>). The major influencing parameters in carburisation are the holding time, carburising temperature, carbon potential and the quench time (Hochman & Burson, 1966). There are five carburising methods; pack, gas, liquid bath, vacuum and plasma. Both the pack and gas carburising will be discussed further.

2.4.1.1 Pack Carburising

Pack carburising is the process of packing parts in a high-carbon medium such as carbon powder or cast iron and heated at 900 °C in a furnace for 12 – 72 hours. During this process, the sample part, which needed to be carburised, is packed in a steel container and surrounded by granules of charcoal. The charcoal is treated with an activating chemical such as barium carbonate (BaBO_3) that promotes the formation of carbon dioxide (CO_2) (Davis, 2002). At high temperatures, the carbon in the charcoal diffuses into the sample at the surface layer of the steel. This is usually done at the austenising temperature, forming a thin surface layer of high-carbon steel, with the carbon content gradually decreasing deeper from the surface (Abdulraoof, 2016). Once the temperature is brought down, usually through quenching or normalising, the austenite that is formed is converted into martensite or bainite. These are responsible for bringing about the hardness at the surface depth up to which the carbon diffuses into the steel, which is controlled by time and temperature. This method is slow compared to the other methods and has heating inefficiencies due to the difficulty in maintaining an even temperature.

Abdulraoof (2016), studied the pack carburisation of low-carbon steel AISI 1010 rod. This was examined at 850°C, 900°C, and 950°C with the constant time of 2 hours for the carburising process. The result of the experimental work showed that at carburising temperature, the hardness of the steel was increased from the inside to the outside. Also, the low-carbon steel carburised at the temperature of 950°C shows the highest value for hardness as shown in Figure 2.5.

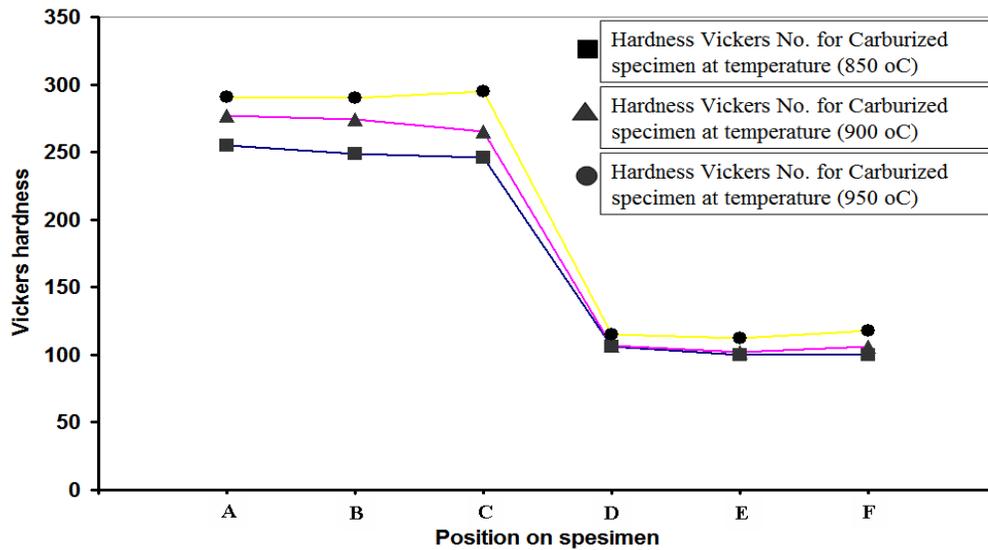


Figure 2.5: Comparison of Hardness Vickers No. for Carburised specimens at 850°C, 900°C and 950°C (Abdulraoof, 2016)

Singh et al. investigated the three heat-treatment processes, where mild steel was heated at 860°C for different soaking times of 2 hours, 2 hours 30 minutes and 3 hours. Then it was tempered at a constant tempering temperature of 200°C with a constant soaking time of 60 minutes. After the heating process, the mild steel was subjected for various tests including an abrasive wear test for the different loads of 75N, 200N and 375N; a hardness test and a tensile test. The results showed that as the wear rate increases, the hardness increases for the different soaking times. Also the tensile strength increases with increasing the soaking time from 2 hours to 3 hours (Singh, Singh, Sachan, & Arya, 2013).

2.4.1.2 Gas Carburising

Gas carburising follows the same procedure applied in pack carburising. However, in this process the carbon monoxide (CO) is fed into the furnace to improve diffusion, which is not done in the pack method. The main carburising agent in this process is any carbonaceous gas such as methane, propane or natural gas. The process has safety issues as CO is a poisonous gas, which could be inhaled by persons working inside the plant. The gas method is preferred in carburising large volumes of metal.

Dhankhar and Khokhar (2015) investigated the effect of methane carburisation on mild steel. The heat treatment was done at different temperature ranges of 860°C, 900°C and 940°C, after which it was tempered at 180°C for 1 hour 30 minutes. The results were reviewed after it was subjected to a hardness test, which indicated the process of carburisation greatly improves the hardness at range of 52HRC – 56HRC. This was high for the mild steel carburised at temperature of 940°C, which must be a preferred process for the required applications.

Izciler and Tabur (2006), studied the abrasive wear behaviour of different case depths. In their work, gas carburised AISI 8620 with gear steel for different case depths were examined. It was observed that the gas carburising time affects the case depth, and in turn, the specimen with a higher case depth showed better wear resistance. In addition to this, as the case depth increased, the hardness of the material also increased.

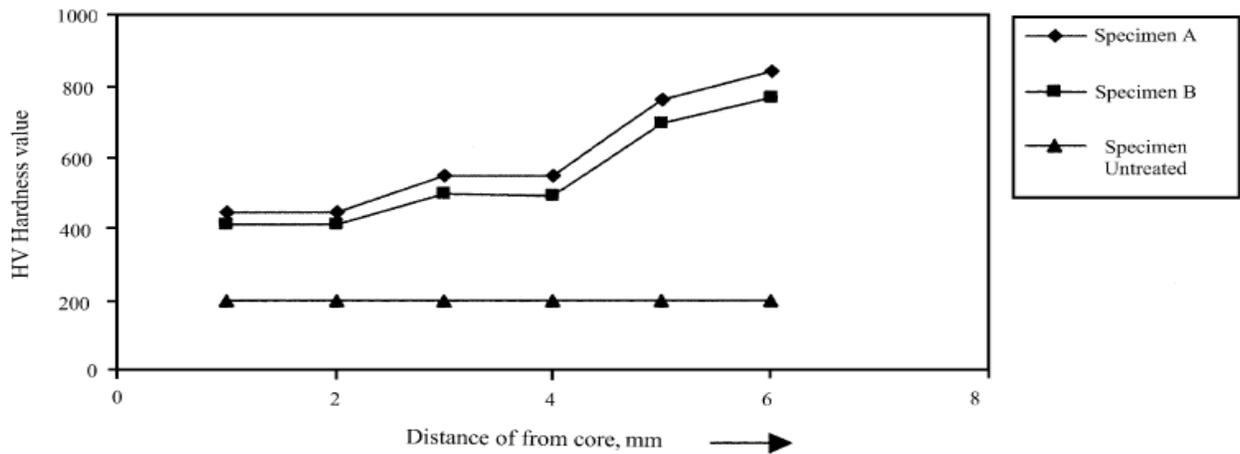


Figure 2.6: Hardness distribution of the specimens (Izciler & Tabur, 2006)

2.4.2 Nitriding

Nitriding is a surface-hardening heat treatment that introduces nitrogen into the surface of steel at a temperature range of 500°C – 600°C, while it is in the ferrite condition. Thus, nitriding is similar to carburising in that the surface composition is altered, but different in that nitrogen is added into ferrite instead of austenite. As nitriding does not involve heating into the austenite phase with quenching to form martensite; nitride components exhibit minimum distortion and excellent dimensional control (Pye, 2003).

After the nitriding process, a compound layer and an underlying diffusion zone, i.e. the case, are formed at the surface of the steel. The compound layer, which is also called the white layer, consists predominantly of ϵ -Fe₂(N,C)_{1-x} and/or γ' -Fe₄N phases, see Figure 2.7 (Du, Somers, & Agren, 2000). In the region beneath the compound layer, called the diffusion zone or case, for pure iron, nitrogen from the outside dissolves interstitially in the ferrite lattice at the nitriding temperature. For the steel containing nitride forming elements, alloy nitride precipitates are also formed in the diffusion zone (Pye, 2003). The compound layer has an improved wear and corrosion resistance.

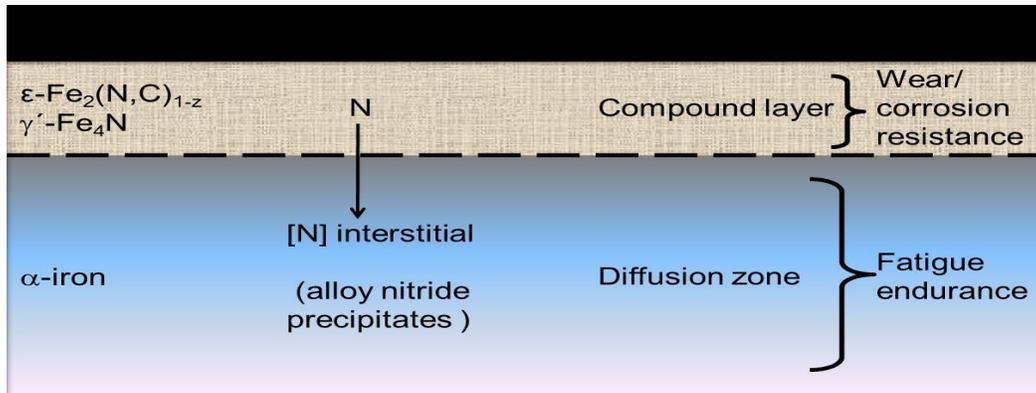


Figure 2.7: Schematic compound layer and diffusion zone structure of nitrided iron/steel

The nitride treatment on steel enhances the surface hardness, thereby increasing the wear and scuffing resistance. Nitriding is used in the case-hardening of the following components such as; gears, cylinder sleeves, camshafts and other engine parts, in order to increase their wear resistance and to operate in high temperatures. The properties produced by nitriding in the area of applications can be summarised as follows (Pye, 2003):

- High wear resistance
- Abrasive wear resistance
- Improved corrosion resistance for non-stainless steels
- High strength
- High torque
- Low fatigue notch sensitivity because of the residual compressive stress
- High surface hardness
- Reduced risk of scuffing and galling

The disadvantage of this surface technique is the long treatment time caused by the slow diffusion process at a low temperature when a deep case depth is required. Conventionally, nitriding can be done according to the medium used to provide the nitrogen, which can be classified as gas nitriding, plasma nitriding, pack nitriding and salt bath nitriding. Each nitriding technique has distinct advantages and disadvantages over each other.

Cesconettoa, Franco Jr and Vieiraa (2015) studied the micro-abrasive wear resistance of an API 5L X-70 micro-alloyed steel using plasma nitride. The heat treatment was done at different temperatures of 410°C, 440°C and 470°C for 1 hour, 3 hours and 5 hours. The results showed that plasma nitriding performed at 440°C for 1 hour led to the formation of a compound layer constituted mainly of ϵ -Fe₂-3N nitride and a diffusion zone with large needle-like nitride, giving the highest wear resistance. Also, the amount of γ' -Fe₄N phase was found to increase with the plasma nitriding time, thereby decreasing the wear resistance of the material.

The effects of nitriding on the mechanical and corrosion properties of SACM 645 steel was studied (Yeh, Chiu, & Chang, 2011). Treatments were carried out in a gas nitriding furnace and the process parameters used in the nitriding of steel was set at 530°C for 12 hours, 24 hours, 48 hours and 96 hours. The result showed that the surface hardness of the nitride specimens reached values of between 1000HV_{0.1}– 1100HV_{0.1} and the wear resistance and corrosion resistance of the nitride specimens was significantly improved by extending the nitriding duration.

2.4.3 Boriding

Boriding is a thermochemical surface treatment that involves diffusion of boron into a substrate at elevated temperatures of between 850°C – 1000°C. The diffusion of boron into the surface of metals and alloys can be done by gaseous, liquid or solid substances to form intermetallic borides (Rodríguez-Castro et al., 2009). The resulting metallic boride provides high-hardness wear resistance, high-temperature resistance and corrosion resistance (Davis, 2002). During boronising, boron atoms diffuse and subsequently absorb into the metallic lattice of the component surface. As a result, an interstitial boron compound is formed with either a single-phase or double-phase layer of boride; depending on the boron potential of the pack, temperature and treatment time. However, the single-phase boride layer consists of Fe₂B composition, while the double-phase layer consists of an outer phase of FeB and an inner phase of Fe₂B. The FeB phase is brittle and forms a surface that is under high tensile stress. The Fe₂B phase is preferred as it is less brittle and forms a surface with a high compressive stress, the preferred stress state for a high-hardness, low-ductility case (Davis, 2002). However, only the pack and paste boronising techniques are able to be processed for many applications while other techniques, such as the liquid and gas boronising techniques, are incapable of application because of toxicity problems. Boronising can complement the technology gap between the conventional heat treatment and the chemical/physical vapour deposition; therefore, it is used to replace many applications in carburising and nitriding (Sinha, 1991).

Calik et al., (2009) studied the hardness and wear behaviour of carburised and boronised AISI 8620 steel. Using the two techniques, steel samples were heated in an electrical resistance furnace for 4 hours at 1210K under the atmospheric pressure. The result showed that boronising treatment increased the hardness of AISI 8620 steel from 395HV_{0.1} to a maximal of 1610HV_{0.1}, compared to the carburised steel, and also improved its wear behaviour. From the obtained results, it can be concluded that boronising is an effective surface-hardening method for improving the wear properties of AISI 8620 steel (Calik et al., 2009).

Ucar et al., (2012) investigated the temperature behaviour of the boride layer of a low-carbon micro-alloyed steel. The study was carried out in a solid medium using the powder-pack boronised method at a temperature range of 973K – 1273K for 4 hours. After boronising, a boride layer and the presence of both FeB and Fe₂B phases were revealed with classic metallographic techniques and x-ray diffraction (XRD) analysis. It was found that the higher

boronising temperatures resulted in an increase in the layer of thickness, from 7 μ m to 105 μ m. In addition, the boride layer had a hardness of over 910HV_{0.1} and 1320HV_{0.1} for 973K and 1273K, respectively, while the substrate's hardness was approximately 145HV_{0.1}.

2.5 Carbonitriding

Carbonitriding is the modification technique of surface hardening heat-treatment process of materials where carbon and nitrogen diffuse into the austenite of steel at temperature ranges between 750°C and 950°C (Michael, Timken, & Madhu, 2013). The modification consists of introducing a large amount of ammonia into the gas carburising atmosphere in order to add nitrogen to the carburised case as it is being produced. The carbonitriding of steel is often used to promote the surface hardening of engineering components via the dissolution of carbon (C) and nitrogen (N) in austenite and ferrite (Davis, 2002). The presence of nitrogen increases hardness, reduces distortion and retains or stabilises the austenite phase, especially in alloy steels. Case structures achieved from these diffusion processes are suitable in applications where wear resistance is paramount. Various methods are used to produce the C and N for thermochemical treatment processes; these include pack-based methods and the in situ processing of C and N.

The convectional process of carbonitriding is done in such a way that the carbon is provided by introducing methane, and nitrogen is provided by introducing ammonia to the furnace under the controlled carrier gas (Herring, 2002). A thin skin of carbon and nitrogen rich steel, see Figure 2.8, is obtained when proper ratios of the working gases are maintained. The carbonitrided case depth is usually between 0.075mm and 0.75mm deep and generally has a higher hardness than a carburised case. Carbonitriding treatment is similar to carburising in that the austenite composition is changed and high surface hardness is produced by quenching to form martensite. Therefore, the presence of nitrogen in the austenite accounts for the major differences between carbonitriding and carburising, which makes it possible to form martensite in plain carbon and low-alloy steels that initially have low hardenability (Davis, 2002).

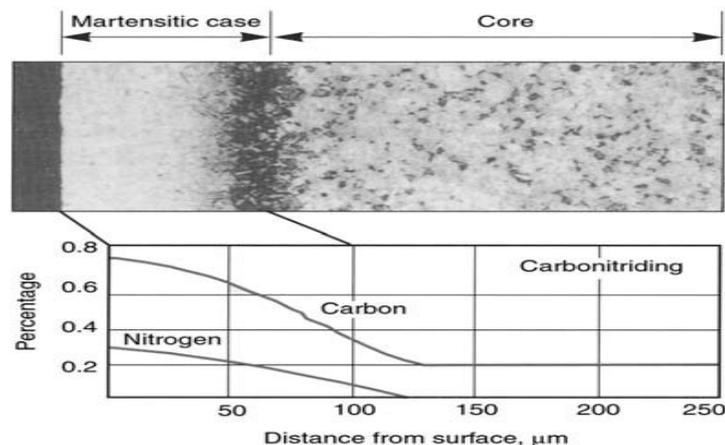


Figure 2.8: Surface layers produced by carbonitriding of steel at 850°C, where carbon predominates in the formation of a martensitic layer (Herring, 2002)

A study was conducted on low-carbon steel using pack carbonitriding method (Puspitasari et al., 2016). The specimen placed inside the carbonitriding media consists of 50% charcoal and 50% urea in a pack stainless steel box. The temperatures for pack carbonitriding was at 700°C, 750°C and 800°C with a soaking time variation of 1 hour and 2 hours, respectively. The results showed that at 700°C and 750°C with an hour variation, the steel hardness increased from 85.7HRB to 95.7HRB, and at 800°C the hardness decreased to 93.1HRB.

Taweejun and Kanchanomai (2015) investigated the effects of carbon and nitrogen on the microstructure and mechanical properties of carbonitrided low-carbon steel. The carbonitriding was performed at 870°C for 2 hours, with a high flow rate of ammonia. The results indicated that an increase in nitrogen content resulted in a high amount of retained austenite in the case of carbonitrided low-carbon steel, caused a reduction to hardness, case depth and strength. However, the elongation was improved, and the distortion was reduced.

2.6 Cyaniding

Cyaniding, or salt bath carbonitriding, is a type of case-hardening process that produces a file-hard, wear-resistant surface on ferrous parts. The process is fast and efficient, when preheated steel is dipped into a heated alkali cyanide bath and allowed to soak. The surface of the steel absorbs both carbon and nitrogen from the molten bath. Upon removal, it is quenched in mineral oil, paraffin-base oil, water or brine and then rinsed to remove any residual cyanide. Bath operating temperatures for cyanide hardening vary between 760°C and 870°C. The process makes the steel develop a hard surface layer, or case, that contains less carbon and more nitrogen than the case developed in activated liquid carburising baths (Davis, 2002). The major drawback is that cyanide salts are poisonous when exposed to the environment.

2.7 Pack-Cyaniding

Various surface modifications and coating techniques have been employed by technologists to enhance the life of production parts and tools. Among the techniques, carbonitriding of pack cyanide (CN) seems to be cost effective. Pack-cyaniding at high and intermediate temperatures, which is different from the conventional treatment of liquid cyaniding, provides a hard surface layer for low-carbon steels and ductile irons (Arthur, et al., 2015 and Adetunji et al., 2008). The process makes use of dried cassava leaves that have been pulverised to various particle sizes.

Cassava is a local material that contains some amount of cyanide, which is often removed as waste during processing. It has been reported that the crops contain cyanogenic glycosides linamarin and lotaustralin in a ratio of 97:7 in all its tissues, except for the seeds (Teles, 1995). According to Adewusi et al. (1999) and Azucena-Topor et al. (2008), they showed that the cyanide concentration of the cassava are higher in the leaves than the roots or the tubers. Therefore, in the present work, processed cassava leaves, which are rich in hydrogen cyanide

(HCN), were used in the carbonitriding process to achieve the surface hardening on low-carbon steel. The researcher made an effort in converting the cyanide waste to engineering value, making it of benefit to human use, thereby promoting the nation's health and economy.

In the case-hardening process of cassava leaves, the parts containing cyanide is packed in a steel container (cyaniding boat) and surrounded by powders of the processed cassava leaves, see Figure 2.9, with the addition of energisers (BaCO₃). The energiser is added to increase the diffusion rate and case depth. This approach has both economic and ecological benefits, in that it is potentially an inexpensive and environmentally friendly source of carbonitriding.

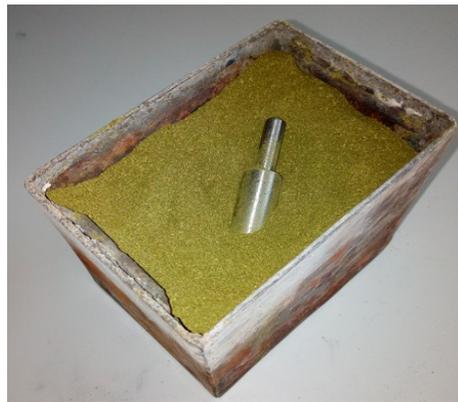
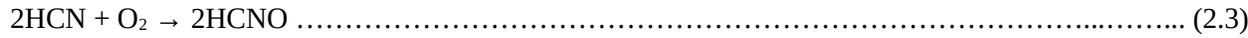


Figure 2.9: Pulverised cyanide packing of low-carbon steel using steel container (cyaniding boat)

2.7.1 High Temperature Pack-Cyaniding

This is usually done at temperatures ranging from 700°C – 950°C and treated together with an activating chemical, such as barium carbonate (BaCO₃), that promotes the formation of carbon dioxide (CO₂). The BaCO₃ serves as an energiser to facilitate the decomposition of CN present in the processed cassava leaves to liberate both nitrogen and carbon. The mechanism of reaction depends on the presence of CO to carry C to the steel surface. Carbon monoxide takes atomic carbon to the surface of the steel for diffusion.

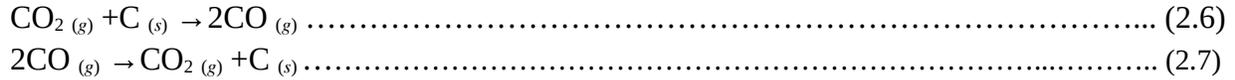
The reactions involve the following:



2.7.1.1 Energiser Reactions

Barium carbonate (BaCO₃) was added as an energiser to accelerate the formation of carbon monoxide. The BaCO₃ energiser, which decomposes during the heating up period, according to the following reactions (Jiménez, Staia, & Puchi, 1999):



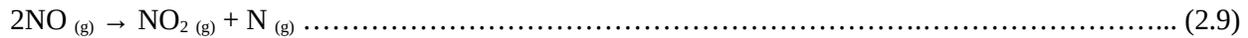


The oxygen of the entrapped air in the cyaniding boat, initially reacts with the carbon of the pack-cyaniding medium as shown in reaction (2.1). As the temperature increases, the CO becomes more in excess where by it decomposes. The decomposition of CO gas occurs at the steel surface and released CO₂ (g) and C (g) as shown in reaction (2.2). The released carbon (C) diffused into the surface of the steel at austenite while the CO₂ formed reacted with the carbon (C) of the cyaniding medium as shown in reaction (2.6) to produce CO, while the cycle of the reaction continues again.

2.7.2 Intermediate Temperature Pack-Cyaniding

The process is carried out at a temperature range of 400°C – 550°C together with BaCl₂ as an energiser. The nitrogen is released when the packed steel is heated at temperatures where the impregnated nitrogen-containing compound, such as HCN, decomposes. Previous work revealed that there is a diffusion of N at low temperatures (Arthur, et al., 2015 and Adetunji et al., 2008). At 550°C the potential of nitrogen is high while that of carbon is low, so only the nitrogen diffuses appreciably into the steel, resulting in nitriding. During nitriding, a white layer of Fe₄N (γ' nitride) and Fe₂N (ε nitride) forms near the outer layer of the surface caused by a high nitrogen potential.

The following mechanism of reaction occurs during the process:



Also, the hydrogen cyanide (HCN) reacted with oxygen gas as follows:



The hydrogen cyanate (HCNO) formed decomposes at the surface of the steel, according to the following reaction:



2.7.2.1 Energiser Reactions

The hydrogen cyanide reacted with the barium ions of the activator substance contained as barium chloride and barium cyanide Ba(CN)₂ which transforms to barium cyanamide BaNCN (Flandro, 2011). In the process, carbon is released, which can diffuse into the components, according to reactions (2.12 and 2.13):



The barium cyanamide reacted further with the atmospheric oxygen to form barium carbonate and nitrogen. The nitrogen then diffuses interstitially into the surface of the steel, according to reactions (2.11 and 2.14).

In addition, researchers have used carbon and nitrogen from cyanide-containing cassava leaves to improve the properties of steels. The pioneering work on the carbonitriding of mild steels with cassava leaves was done by Ibrionke et al. (2004). Their work on the pack-cyaniding of mild steel included case-depth measurement and mathematical modelling. The case depth was studied as a function of time at a temperature of 860°C in pack-cyaniding medium, after which the result reviews the following hardness value of 483.3HV, 519.1HV and 540.02HV for the diffusion times of 2 hours, 3 hours and 4 hours, respectively. Also, the highest case depths of 0.65mm, 1.05mm and 1.65mm were obtained for the three different diffusion times mentioned. After modelling for 5 hours and 6 hours, the resultant case depths increased to 1.68mm and 1.90mm, respectively.

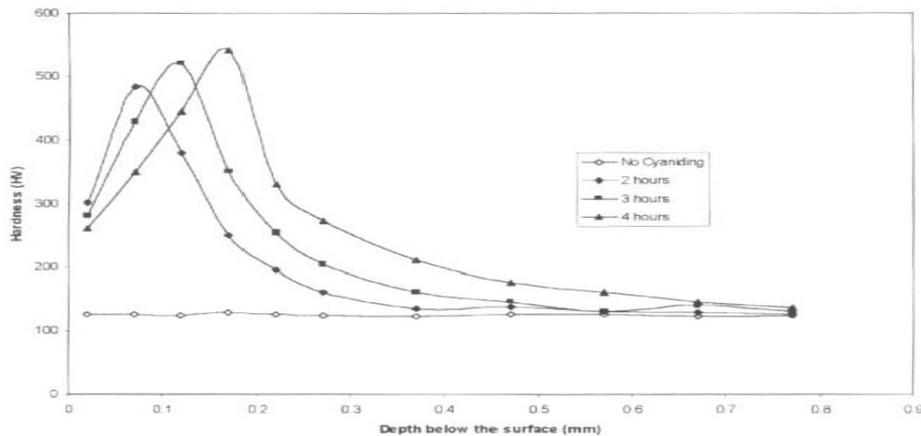


Figure 2.10: Plot of hardness against depth below (Ibrionke et al., 2004)

Adetunji, et al. (2008) studied the metallographic of pack cyanide mild steel using cassava leaves. The process was done in a heat-treatment furnace, varying the temperature from 700°C to 950°C in steps of 50°C. Also, the heat-treatment time varied from 1 hour to 5 hours in steps of an hour. After case-hardening, the result revealed that at a high temperature there is carbon diffusion into the case of mild steel from cassava leaf powder. Similarly, it was found that at low temperatures, there is a diffusion of nitrogen, while the diffusion proceeds from the case into the core of the material with increasing the treatment temperature and increasing the treatment time. Also, from their work, it was found that at high temperatures, the optimum hardness was achieved at 900°C.

Arthur (2011) investigated the wear properties of the pack cyanide mild steel, using processed cassava leaves powder with BaCO₃ as an energiser in the heat-treatment process. In the studies,

four different powder particle sizes of 212 μm , 300 μm , 600 μm and 850 μm were utilised at four different temperatures of 750 $^{\circ}\text{C}$, 800 $^{\circ}\text{C}$, 850 $^{\circ}\text{C}$ and 900 $^{\circ}\text{C}$ and soaked for 3 hours. After the heat-treatment process, the case hardness was observed to decrease with a decrease in particle size and decreasing pack-cyaniding temperature (PCT). Results also revealed that the wear rate of treated mild steel increased with the particle size of the processed cassava leaf powder. This also indicated that the cassava leaf of particle size 850 μm produced the hardest case and highest wear resistance.

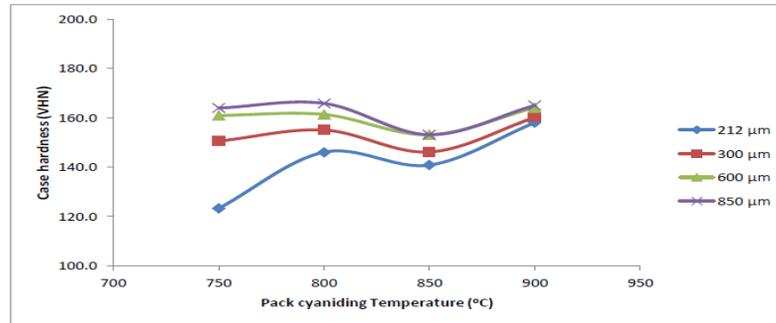


Figure 2.11: Case hardness as a function of cyaniding temperature and particle size

Akinluwade et al. (2012) studied the visible diffusion zone of pack cyanide mild steel in processed cassava leaves using light and electron microscopes. In the process of the study, it was found that the visible diffusion zone is a region of high-carbon concentration owing to the diffusion of carbon from the processed cassava leaf powder. Also, the result revealed that the microstructure of the cases consists of a predominant pearlite phase, see Figure 2.12, with the particle size at a constant soaking temperature.

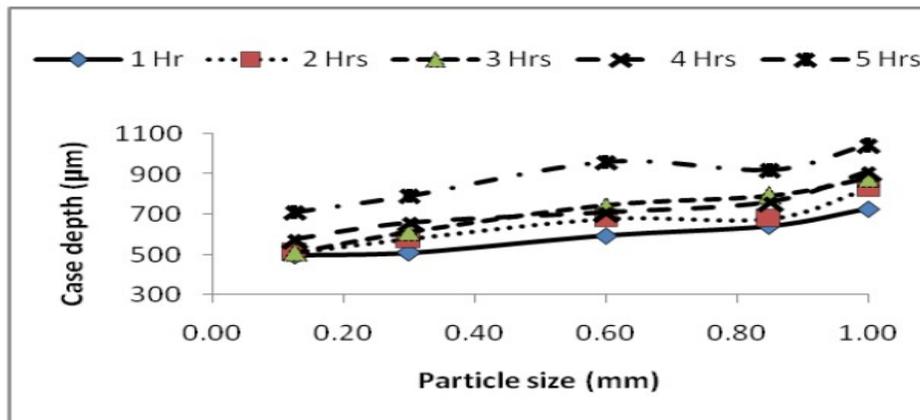


Figure 2.12: Case depth as a function of particle size for high temperature of 950 $^{\circ}\text{C}$ pack-cyaniding method

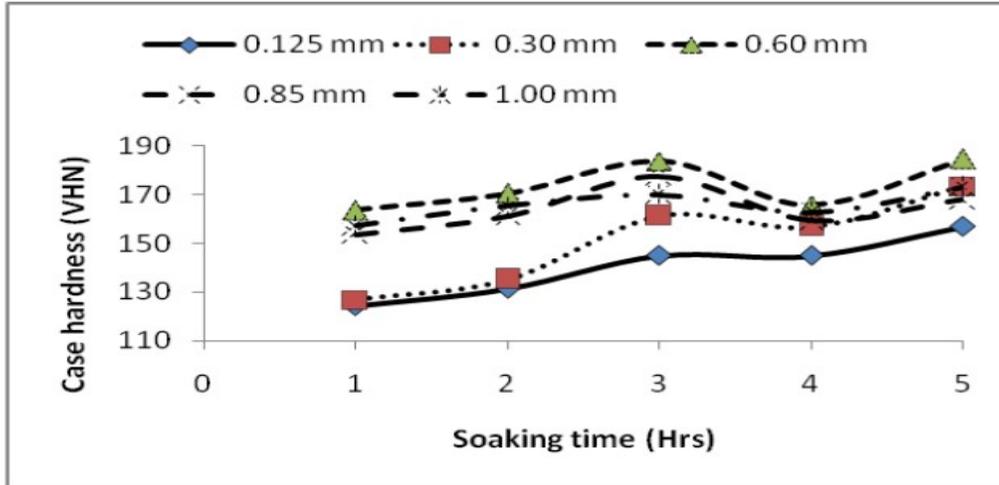


Figure 2.13: Case hardness with respect to soaking time for low temperature of 550°C pack-cyaniding method

In addition to the study of the pack-cyaniding method, Ebechidi (2014), investigated the wear resistance of AISI 1065 and 1070 proeutectoid steels using the pack-cyaniding method. The heat treatment was done at a temperature range of 700°C, 800°C, 850°C and 900°C for 5 hours. After the carbonitriding process, the AISI 1065 steel was quenched and tempered at 300°C for 3 hours, and the AISI 1070 steel was air cooled. The result revealed that the tempered martensitic AISI 1065 steel formed, showed an increase in hardness of 706HV, see Figure 2.14; over that of 540HV obtained in previous studies with the same method. Also, at 900°C, the lowest wear rate, lowest coefficient of friction, see Figure 2.16, highest hardness from 281HV to 706HV, and highest strength from 948MPa to 978MPa were observed for the AISI 1065 carbonitrided steel.

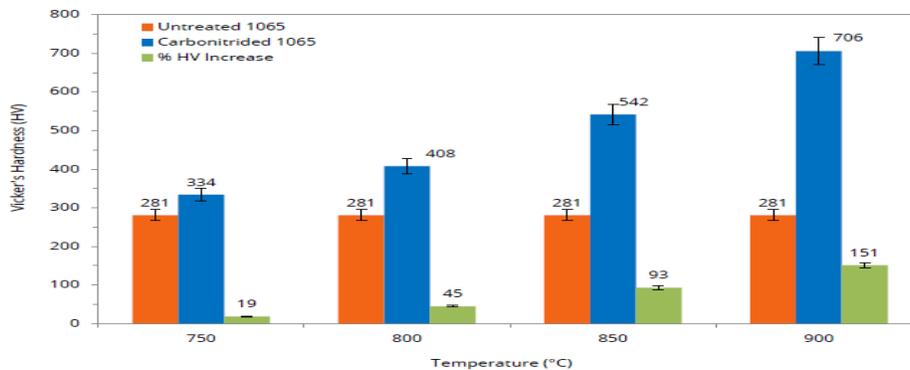


Figure 2.14: Hardness versus temperature for AISI 1065 steel, water quenched and tempered at 300°C

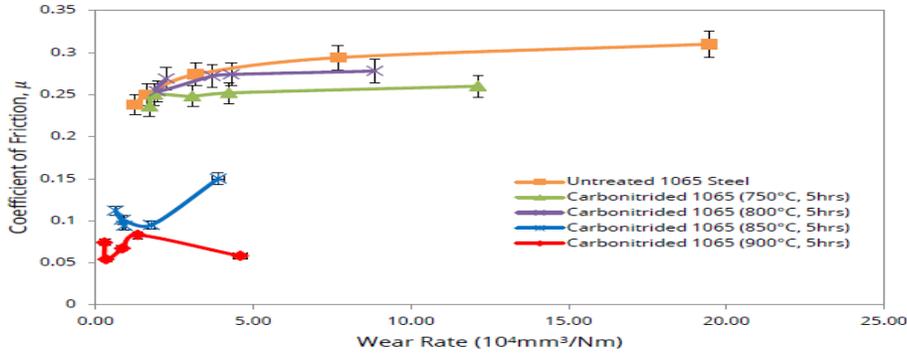


Figure 2.15: Variation of wear rate with weight loss of AISI 1065 steel: carbonitrided temperatures of 750°C, 800°C, 850°C, 900°C at 5 hours versus water quenched and tempered temperature of 300°C at 3 hours

Arthur, et al. (2015) carried out the analytical modelling of carbon and nitrogen concentration profiles of cassava-leaf-enhanced carbonitrided steel. The work was modelled using two analytical models that are based on Fick's second law of diffusion. After the process, the model predictions were compared with the experimental data. Results showed that the trends in the predicted data are consistent with the experimental results. The results also suggest that the simple idealisations of nitrogen and carbon diffusion at intermediate and high temperatures provide reasonable estimates of the case depths from the predictions of carbon and nitrogen diffusion. These estimates can be adopted to guide the surface engineering of improved hardness and wear of cassava-carbonitrided steel surfaces.

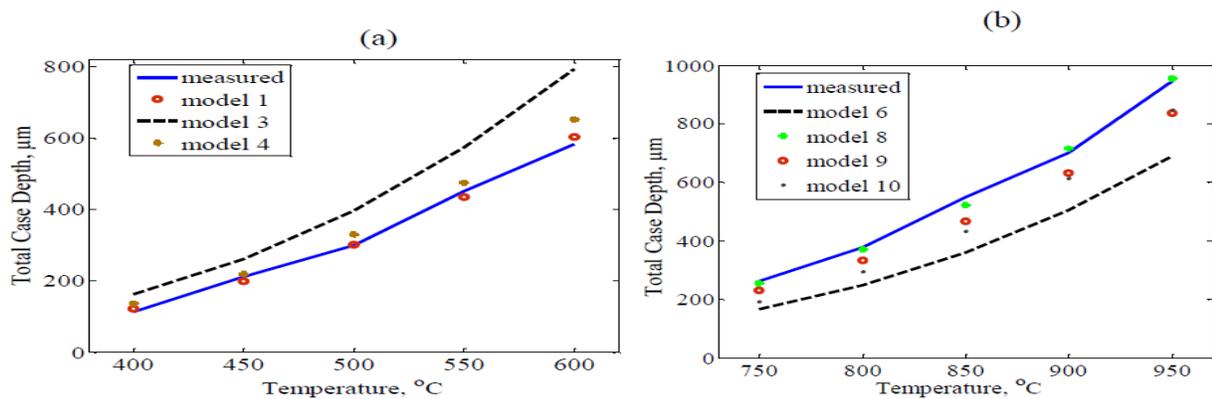


Figure 2.16: Comparison of calculated total case depths for (a) some selected nitrogen in ferrite diffusion coefficient models with measured total case depths and (b) some selected carbon in austenite diffusion coefficient models with measured total case depths

Arthur, et al. (2015) carried out a study on the nano- and macro-wear of bio-carbonitrided AISI 8620 steel surfaces. The carbonitriding method used was a cyaniding process, and the heat treatment was done at temperatures of 400°C, 450°C, 500°C and 550°C for 3 hours. The result obtained revealed that the measured wear volumes at both nano- and macro-length scales increases with decrease PCT. The nano- and macro-wear resistances are also shown to be

enhanced by the in situ diffusion of carbon and nitrogen from cyanide-containing bio-processed waste.

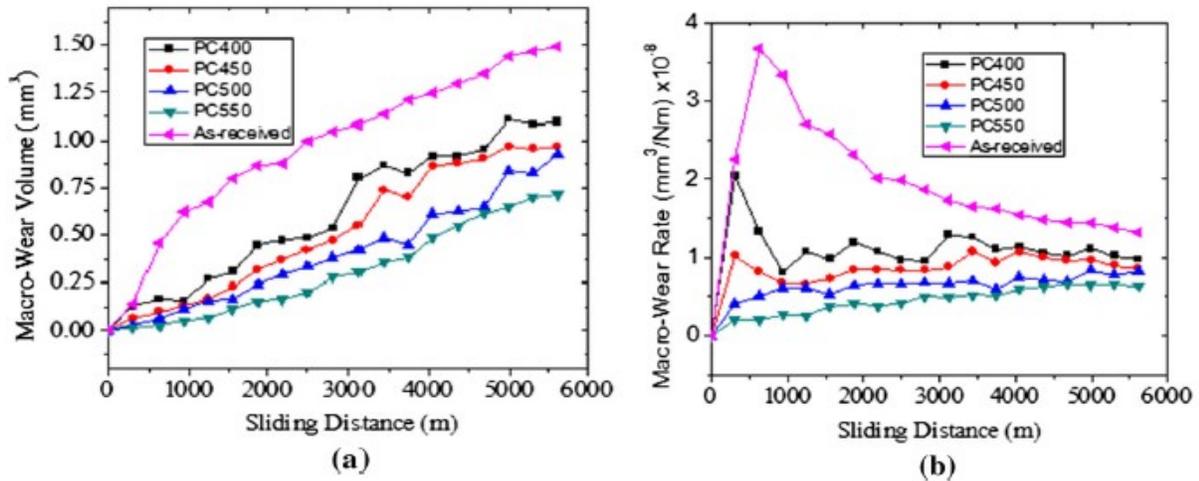


Figure 2.17: (a) Macro-wear volume versus sliding distance for all tested samples, and (b) Macro-wear rate versus sliding distance for all tested samples

2.8 Mechanism and Kinetics of Diffusion

Diffusion is the spontaneous movement of atoms to new sites within the metallic crystal structure (Bradshaw, 2005). The surface modification processes rely on diffusion of new atoms in the work piece to alter the mechanical properties of the surface region. Many reactions and processes that are important in the treatment of materials rely on the transfer of mass either within a specific solid (ordinarily on a microscopic level) or from a liquid and a gas. Hutchings (1992), identified two thermochemical classes of solid state processes where atoms transported by thermally-enhanced diffusion leads to surface modification. In most metal alloys, interstitial diffusion occurs much more rapidly than diffusion by the vacancy mode. It involves atoms that migrate from an interstitial position to a neighbouring one that is empty. This mechanism is found for inter-diffusion of impurities such as hydrogen, carbon, nitrogen and oxygen, which have atoms that are small enough to fit into the interstitial positions (Callister & Rethwisch, 2004).

As the rate of diffusion depends on the concentration gradient and diffusion coefficient, according to the steady-state diffusion expression:

$$J = -D \frac{dC}{dx} \dots\dots\dots (2.15)$$

Where J is diffusion flux, measured in kg/m².s or atoms/m².s, which represents the quantity of the diffusing substance through a unit area perpendicular to the steel surface. The constant of

proportionality D is called the diffusion coefficient, which is expressed in m^2/s , and dC/dx is the concentration gradient measured in kg/m^3 or g/cm^3 .

The temperature has an influence on the diffusivity and diffusion rates. There is a barrier to diffusion created by neighbouring atoms who need to move to let the diffusing atoms pass; thus, atomic vibrations created by temperature assist diffusion. Empirical analysis of the system resulted in an Arrhenius type of relationship between diffusivity and temperature (Callister & Rethwisch, 2004).

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \dots\dots\dots (2.16)$$

Where D_0 is a pre-exponential constant (m^2/s), Q is the activation energy for diffusion (J/mol or $eV/atom$), R is gas constant (Boltzmann's constant), $8.31 J/mol-K$ or $8.62 \times 10^{-5} eV/atom-K$ and T is absolute temperature (K). From the above equation it can be inferred that large activation energy means relatively small diffusion coefficient (Callister & Rethwisch, 2004).

2.9 Wear Theory and Mechanisms

Wear can be defined as the progressive loss or gradual removal of material from a surface due to the relative motion of two surfaces over each other (Williams, 2005). It is often measured as volume or mass loss of material and can be identified through microscopic studies of the surface. The term 'wear' is a commonly occurring degradation mechanism for materials and components in the mining industry, which has been considered to be the main failure form of machine parts. It is known to lower the operational efficiency of machinery and its components, leading to a major source of costs in a number of industries (Tylczak, Hawk, & Wilson, 1999). In mining, and minerals processing, there are frequent mechanical interactions between metals, and between metals and abrasive non-metallic and metallic materials, i.e. mineral bearing ores. The abrasive nature of ores causes significant wear to extracting, handling and processing equipment. Consequently, wear in mining, and minerals processing operations results in the removal of large amounts of material from the wear surfaces of scraping, digging, and ore processing equipment (Hawk & Wilson, 2001). The economic consequence of wear is widespread and pervasive. As the mining industry tends toward the use of large equipment with greater production capacity, the wear of materials results in the need to replace and maintain worn components and surfaces.

Generally, a material's susceptibility to wear depends on its physical and mechanical properties, as well as on environmental factors, i.e. the conditions to which the material is exposed. These include the abrasive properties, the stress conditions on the worn surface, temperature processing, the structure of the material used and the structure and properties of the material(s) in between the two sliding surfaces (Spero, Hargreaves, Kirkcaldie, & Flitt, 1991). Wear is caused by a number of mechanisms, the following four being especially important in the wear process;

abrasion, adhesion, surface fatigue and tribochemical reaction. During the mining and mineral processing of an ore, two of those mechanisms; abrasion and tribochemical reaction, are supposed to have a distinguished action over the others. Abrasion is the most common wear mechanism verified in industry, being accounted for more than half of the wear events in several industrial segments. Concerning the mineral industry, abrasion is the major wear mechanism in mining, as well as in mineral processing operations (Rendón & Olsson, 2009).

2.9.1 Standard Test Method for Wear Test

Tribological systems are used to determine the various parameters of wear. The pin-on-disc, see Figure 2.18, has been described in the ASTM standard, G99, “Standard Test Method for Wear Testing” (Raymond, 2004). The ASTM standard for the test specifies the use of a rounded pin but does not specify any specific values for the parameters; it allows those to be selected by the user to provide simulation of an application. The parameters that can vary include size and shape of the pin, load, speed and material pairs. Generally, it is used as a comparative test in which controlled wear is performed on the samples to study. It has been used extensively to study wear and to rank the various materials (Raymond, 2004). In the test procedure, two specimens are required; one is a pin with a hemispherical tip which is perpendicular to and slides over the other, usually a flat rotating circular disc. The test machine causes either the disc specimen or the pin specimen to revolve about the disc centre. In either case, the sliding path is a circle on the disc surface. The plane of the disc may be oriented either horizontally or vertically. The pin specimen is pressed against the disc at a specified load usually by means of an arm or lever and attached weights. Other loading methods have been used, such as, hydraulic or pneumatic. The amount of wear is determined by measuring appropriate linear dimensions of both specimens before and after the test, or by weighing both specimens before and after the test. The volume loss is calculated by the wear rate of the material. Also, the coefficient of friction is usually measured as a means of understanding some mechanism of wear. As the action performed on all the samples is said to be identical, the wear rate can be used as a quantitative comparative value for wear resistance.

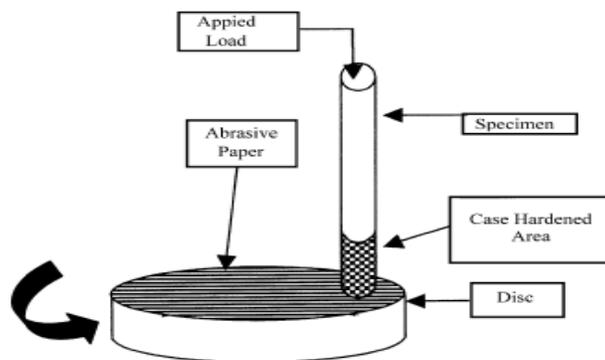


Figure 2.18: Pin-on disc abrasive test apparatus (Izciler & Tabur, 2006)

For the analysis of the abrasive testing procedure, the amount of wear in any system would depend on a number of factors. These factors include applied load, machine characteristics, sliding speed and distance, environmental conditions and the material properties. In this case, the wear rates may be calculated from weight loss measurements by using the following formula:

$$W = \frac{\Delta G}{d \times M \times S} \text{ mm}^3/\text{Nm} \dots\dots\dots (2.17)$$

Where W is the abrasion rate, G the mass loss, M the applied load (force \times length), d the density of the steel and S is the sliding distance (Izciler & Tabur, 2006). With the aid of using these formulae, the weight loss and wear rate can be plotted against sliding distances as well as load.

CHAPTER THREE METHODOLOGY

3.1 Materials and Sample Preparation

One of the mining equipment, such as pickaxes, was being source from Polyguard Investment mining company. The materials tested and were made up of AISI 1070 and 1065 low-alloy steels with a chemical composition illustrated in Tables 4.1 and 4.2. The average chemical composition of the steel was examined using optical emission spectroscopy (OES) (Solaris CCD Plus). The sample preparation was design based on the choice of wear test (pin-on-disc) experiment that will be performed.



Figure 3.1: (a) and (b) indicate the old and new pickaxe

3.1.1 Pin Preparation

With the aid of a milling and lathe machine, ten cylindrical pins were fabricated; five from the new pickaxe and another five from the old pickaxe, which is assumed to be the AISI 1070 and 1065 steels, respectively for the pickaxes. The pins heights are 50mm while the diameters of the pins were varied in steps along with the height. At the bottom, the diameter is 12.5mm covering a height of 28mm, while at the top, the diameter is 6.5mm with a height of 19.5mm, see Figure 3.2a. Also, the hemispherical shape with a radius of 2.5mm was considered for the tips of the pins. This process was achieved with the turning and facing operations from the lathe machine, after which the ten pins, of the above dimensions, were utilised in both the carbonitriding heat treatment and the wear experiment.

3.1.2 Disc Preparation

Eight samples were prepared for the disc with diameter of 44mm and thickness of 6mm. This was machined from both the AISI 1065 and AISI 1070 steels. The samples were made to serve as a base upon which SiC papers with 120 grit size were placed on it in order to serve as the abrasive material with a higher hardness so as to wear off the surfaces of the pins as they slide over them during the wear testing analysis, see Figure 3.2 b. This shape was considered due to the type of wear analysis that will be performed on the tools.

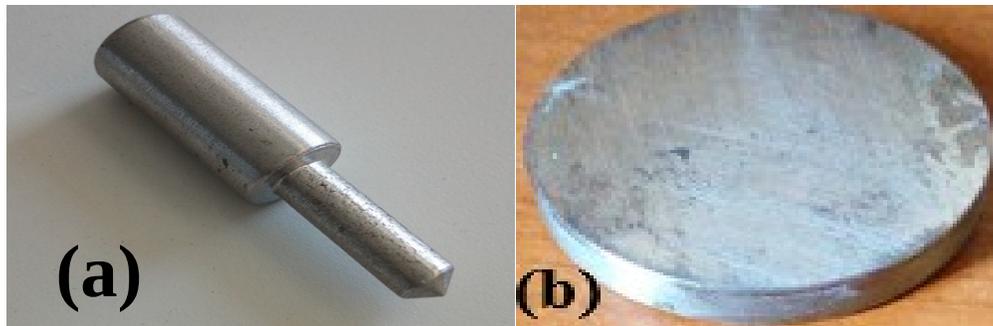


Figure 3.2: (a) and (b) show the prepared pins and discs of the pickaxe tool



Figure 3.3: Grinding, facing and turning operations of the prepared samples

3.1.3 Cyaniding Boat

Five heat-treatment boxes, cyaniding boats, of 70mm × 100mm × 80mm were constructed using mild steel plates of 3mm thickness. The boats were large enough to contain the heat-treatment powder mixture, standard mild steel pin specimen and also the rectangular test specimen.

3.2 Cassava Leaves Powder Preparation

Eight-month-old fresh cassava leaves specie of *Manihot esculenta* (bitter local variety), see Figure 3.4a, were sourced from a farm located at the back of AUST. The bitter local variety for cassava was considered due to its high cyanide content compared to the sweet variety. Random sampling methods were used in harvesting the leaf from the cassava field, after which it was then oven-dried at 75°C for 8 hours, see Figure3.4a. This drying process was carried out in order to reduce the rate of liberation of HCN, which is the component of cassava used in the carbonitriding heat treatment. Afterwards, the dried parts of cassava leaves were pulverised into powder using a grinding machine and sieved to 425µm particle sizes, see Figure3.5a, with an octagon sieve shaker machine. The cyanide content and the functional group of the pulverised leaves were determined using the ninhydrin-based spectrometer of trace method and FTIR spectroscopy, respectively, see Figure 4.1.



Figure 3.4: Varieties of cassava plant: (a) the bitter variety with yellowish leaf stalk (b) the sweet variety with reddish leaf stalk

3.3 Intermediate Temperature for Carbonitriding Treatment Procedure

Eight samples, four each from AISI 1070 and AISI 1065 steels were utilised for the pack-cyaniding process with the pulverised cassava leaves. The pulverised powder was mixed in a proportion of 80% cassava powder to 20% by weight of BaCl_2 and were loaded into the mild steel boats and closed tightly.

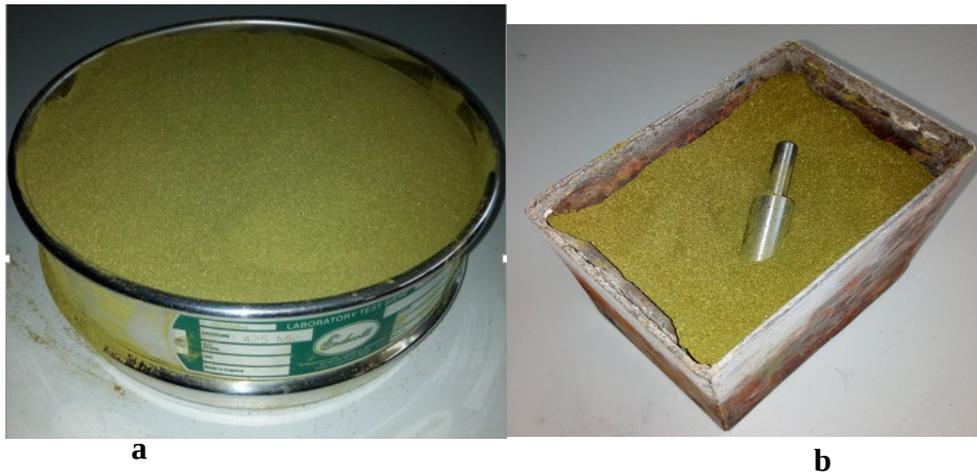


Figure 3.5: (a) Cassava leaf sieved to 425µm particle sizes using octagon sieve shaker machine (b) steel pins in the pulverised cyanide pack

Each of the boats were covered with a mild steel lid and sealed with fire clay to entrap the gases generated and to also provide a reducing atmosphere in the boat. The BaCl_2 was added as an energiser to increase the diffusion rate and case depth. The boats were then heated in the heat-treatment furnaces of 1200°C capacity in a fume cupboard, varying the temperatures from 400°C to 550°C in steps of 50°C for 3 hours at the AUST Lab, Abuja – Nigeria, see Figure 3.6a. Then the specimens were air cooled to room temperature. These procedures were repeated for the four

pin samples of AISI 1065 and AISI 1070 steels. After being carbonitrided, the samples were subject to comparison tests such as wear and hardness.



Figure 3.6: (a) furnace for heat treatment of steel samples (b) a cyaniding boat removed from the furnace for air cooling

3.4 Wear Test Experiment

Two distinctly different approaches were used to measure the wear of the samples. The first method was the pin-on-disc wear test experiment; this was done for only the pin and disc samples (treated and untreated) for the AISI 1070 and AISI 1065 steels. The ISC-200 Tribometer system, see Figure 3.7, was used to perform the wear test experiment and this was done in a room fully exposed to ambient environmental conditions of 25°C. Deadweight of 20N was applied vertically on the arm to press the pin against the counter face of the rotating disc with a wear track radius of 13mm, corresponding to the normal load required for the test. During the test, the pin was kept stationary in such that one of the faces (tip) is forced to press against the abrasive that is fixed on the revolving disc. Hence it was the abrasive paper that tends to wear the surface of the samples. When the disc rotates for a particular period of time, the sample was loaded at the top to press against the disc with the help of a lever mechanism. The abrasive track radius and the revolutions counter were set to the operation conditions using the radius knob and RMP knob. After each wear test, the weights of the pins were determined to measure the weight loss. The depth of the wear track was determined after the wear test, using sliding velocity of 0.25m/s and total sliding distance of 225m; the wear volume and wear resistances of the tested samples were evaluated. In the experiment, the test was conducted with the following parameters.

Table 3.1: Pin-on-disc wear experiment parameters

Wear Parameters	Test	
Applied load		20N
Speed of rotation		185rpm
Radius of wear track		13mm
Duration of each test		15

	minutes
Sliding velocity	0.25m/s
Total sliding distance	225m

The wear rate of each sample was calculated from the weight loss; the amount of wear was determined by weighing the specimen before and after the test using precision electronic weighing machine. As the weight loss is measured, it is then converted to volume loss using the density of the steel sample. Hence wear volume, wear rate and wear resistance can be calculated as follows (Hutchings, 1992):

$$\text{Wear Volume (mm}^3\text{)} = \frac{\text{weight loss}}{\text{density}} \text{ (Eqn 3.1)}$$

Density of the steel sample $\approx 7.86\text{g/cm}^3$

$$\text{Wear Rate} \left(\frac{\text{mm}^3}{\text{m}} \right) = \frac{\text{Wear Volume}}{\text{Sliding distance}} \text{ (Eqn 3.2)}$$

$$\text{Sliding distance (m)} = V \times \text{time} = \frac{2\pi RN}{60} \times t \text{ (Eqn 3.3)}$$

Where R is the wear track radius of the disc at 13mm

$N = \text{Speed of rotation (185 rpm)}$, $\pi = 3.142$ (constant), $\text{Time} = 15 \text{ mins}$

$$\text{Wear Resistance} \left(\frac{\text{m}}{\text{mm}^3} \right) = \frac{1}{\text{Wear Rate}} \text{ (Eqn 3.4)}$$

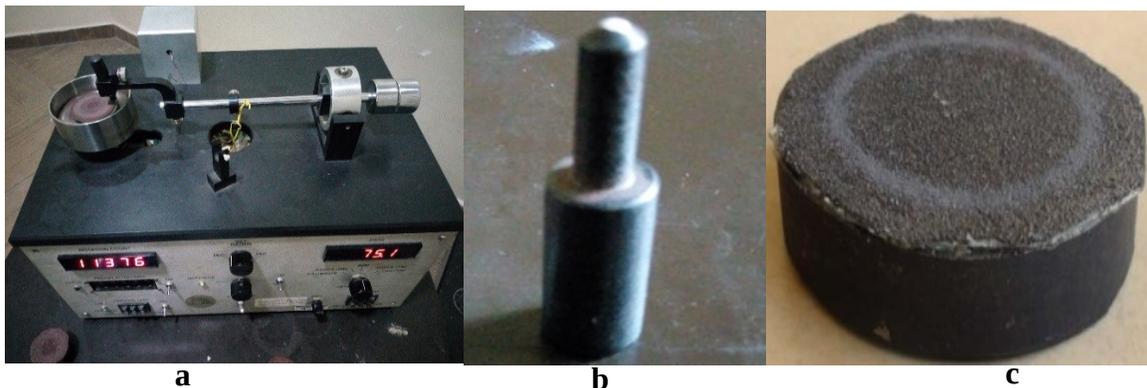


Figure 3.7: (a) ISC-200 type pin-on-disc tribometer. (b and c) the experimental process of wearing of pin-on SiC grit paper

3.5 Metallography Preparation

The microstructural studies of low-alloy steel start with the sample preparation. Each of the pack cyanide pins specimen was cross-sectioned for about 18mm from the bottom in a direction perpendicular to the flat surface. After that, the cross-section was rough ground and polished by using 60 μm , 120 μm , 240 μm , 400 μm , 600 μm , 1000 μm and 1200 μm of SiC grit size on the Buehler grinding machine to remove the scales or scratches in the surface, the specimen was kept cool by being frequently dropped in water during the grinding operation. After that, it was polished with 0.1 μm diamond suspension paste to obtain a mirror finish, and subsequently etched by 2% nital solution (2% concentrated nitric acid and 98% ethanol) for a few seconds, washed under a running tap of water and then dried using a hand blower. Thereafter, observed with an optical microscope.

3.6 Hardness Measurement

The hardness of the steel samples was measured with the use of a micro-hardness testing machine on the sectioned pins, for both the treated and untreated AISI 1070 and AISI 1065 steels. The hardness was taken on a three-spot measurement, varying it from the core to the edge, using a load of 10kg (98N), with load time of 10s through a diamond pyramid indenter at the polished surface of each sample. The average hardness of the received samples for AISI 1070 and AISI 1065 steels were 255VH and 241VH, respectively. The hardness of the treated samples was measured and recorded, see Table 4.7a and b.



Figure 3.8: Micro-hardness test measurement

CHAPTER FOUR RESULTS AND DISCUSSION

4.1 Composition Analysis of Samples

The chemical composition, as received, the excavator bucket teeth and the pickaxe samples are shown in Tables 4.1 and 4.2, respectively. This was characterised at SCC Pipe Yard – Lab Section, Bwari – Abuja, Nigeria. These results are summarised for the excavator bucket teeth as well as both the new and the used pickaxe.

Table 4.1: Chemical composition of as received AISI 1070 steel for the new pickaxe

Element	C	Si	Mn	P	S	Cr	Al	Cu	Co	Ti	Fe
Wt. %	0.72	0.17	0.97	0.02	0.01	0.00	0.00	0.00	0.00	0.01	98.02
	3	2	8	2	9	8	5	4	3	0	7

Table 4.2: Chemical composition of as received AISI 1065 steel for the old pickaxe

Element	C	Si	Mn	P	S	Cr	Al	Cu	Co	Ti	Fe
Wt. %	0.67	0.32	0.75	0.02	0.02	0.02	0.03	0.06	0.00	0.01	97.98
	0	0	4	0	6	8	1	5	6	0	6

From the summary Tables 4.1 and 4.2, the steels used contained carbon and manganese as the major alloying elements and the weight of carbon present is about 0.6% – 0.73%, which makes them high-carbon steel. Both steels' compositions are reasonably close to the nominal composition of AISI 1070 and AISI 1065 carbon steels as their carbon and manganese content falls within that classification of the AISI (Timken Steel, 2016). Their hardness and strength are expected from the high-carbon manganese, while other residual elements such as copper, titanium, aluminium, chromium and phosphorus are also present to add additional strength; which is very low in this case. Some of the element contents like molybdenum, nitrogen, nickel present in the result are too low (<0.002); for this reason, they were excluded from Tables 4.1 and 4.2 (Steel Dynamics, 2010).

The quality of the hardness and strength of these steels were improved with the carbonitriding method of case-hardening, which is discussed in the next section.

4.2 Functional Group Analysis of Cassava Leaves

The Fourier Transform Infrared (FTIR) Spectroscopy presents the FTIR spectra obtained for the pulverised cassava leaves.

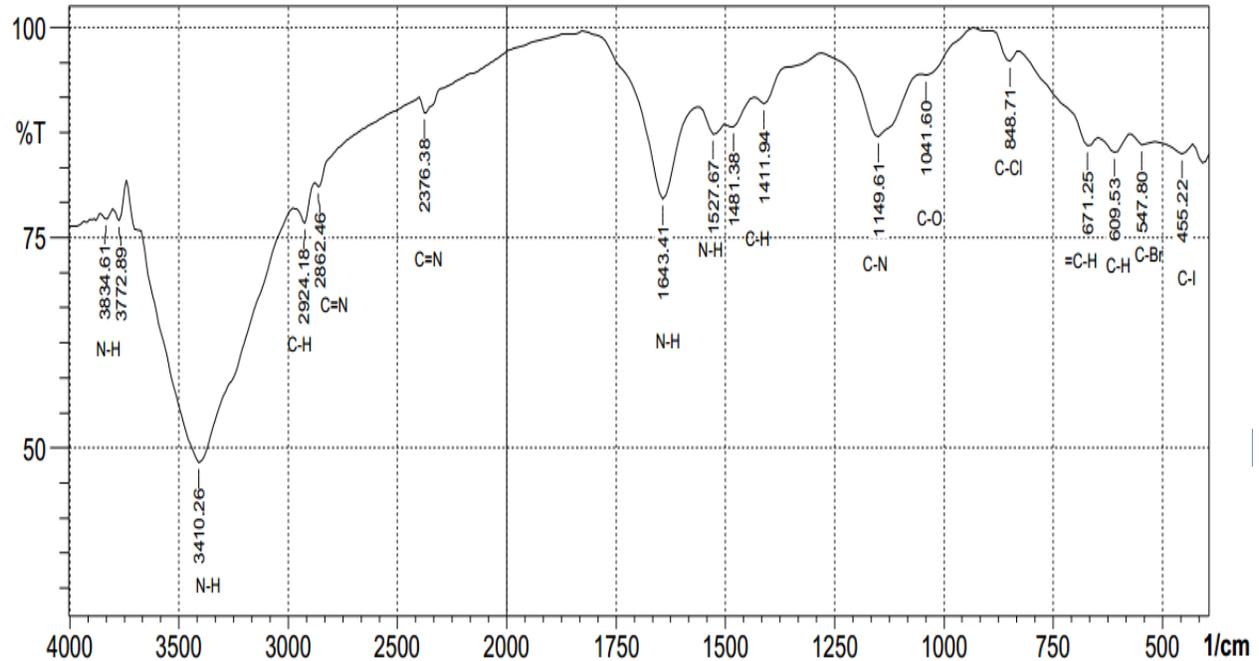


Figure 4.1: FTIR spectra for the pulverised cassava leaves

The spectra revealed a number of peaks, indicating the complex nature of the examined pulverised cassava leaves. The peaks observed at 455cm^{-1} , 547cm^{-1} and 848cm^{-1} can be attributed to C-I, C-Br and C-Cl stretch of the alkyl halides group. The functional groups assigned to the 609cm^{-1} , 671cm^{-1} and 1041cm^{-1} are C-H and C-O stretch of aromatic respectively. The spectra observed from 2376cm^{-1} and 2862cm^{-1} are indicated as -C-N and -C=N stretch (amine and nitriles) group, respectively. Also, the band observed from 1149cm^{-1} may be attributed to C-N stretch from amine molecules that are present in the *Manihot utilissima*, *M. esculenta* plant. Inspection of the spectra corresponding to the presence of the most significant bands at 1411cm^{-1} and 2924cm^{-1} , representing C-H aromatic groups. Furthermore, the bands at 1527cm^{-1} , 1643cm^{-1} , 3410cm^{-1} , 3773cm^{-1} , and 3834cm^{-1} may be assigned to nitrogen-containing groups (amine) where N-H at 3410cm^{-1} shows a strong, stretching band. Hence, the functional groups determined from the FTIR spectrum confirmed the existence of C-O, amine (N-H, C-N), nitriles (C=N), and carboxylic groups.

4.3 Microstructural Analysis

The different processing stages have a strong dependence on the microstructure development, which has a direct relationship to the final mechanical properties. After the heat-treatment process at various temperatures for the alloy steels, the microstructure was revealed using the metallurgical microscope. Each paired micrograph shows microstructures of the specimen's cross-section that proves case formation.

Table 4.3: Optical micrograph of as received AISI 1070 steel

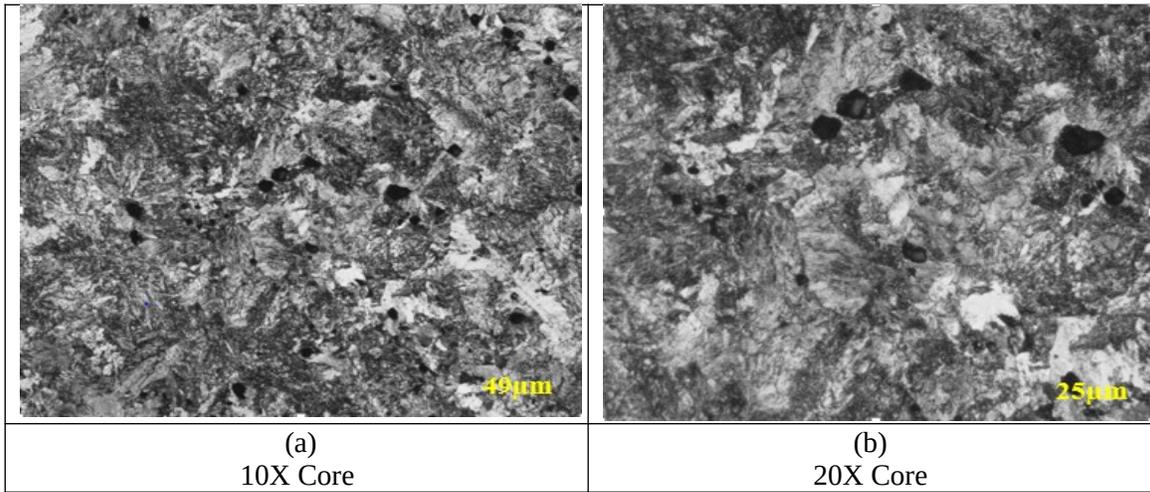
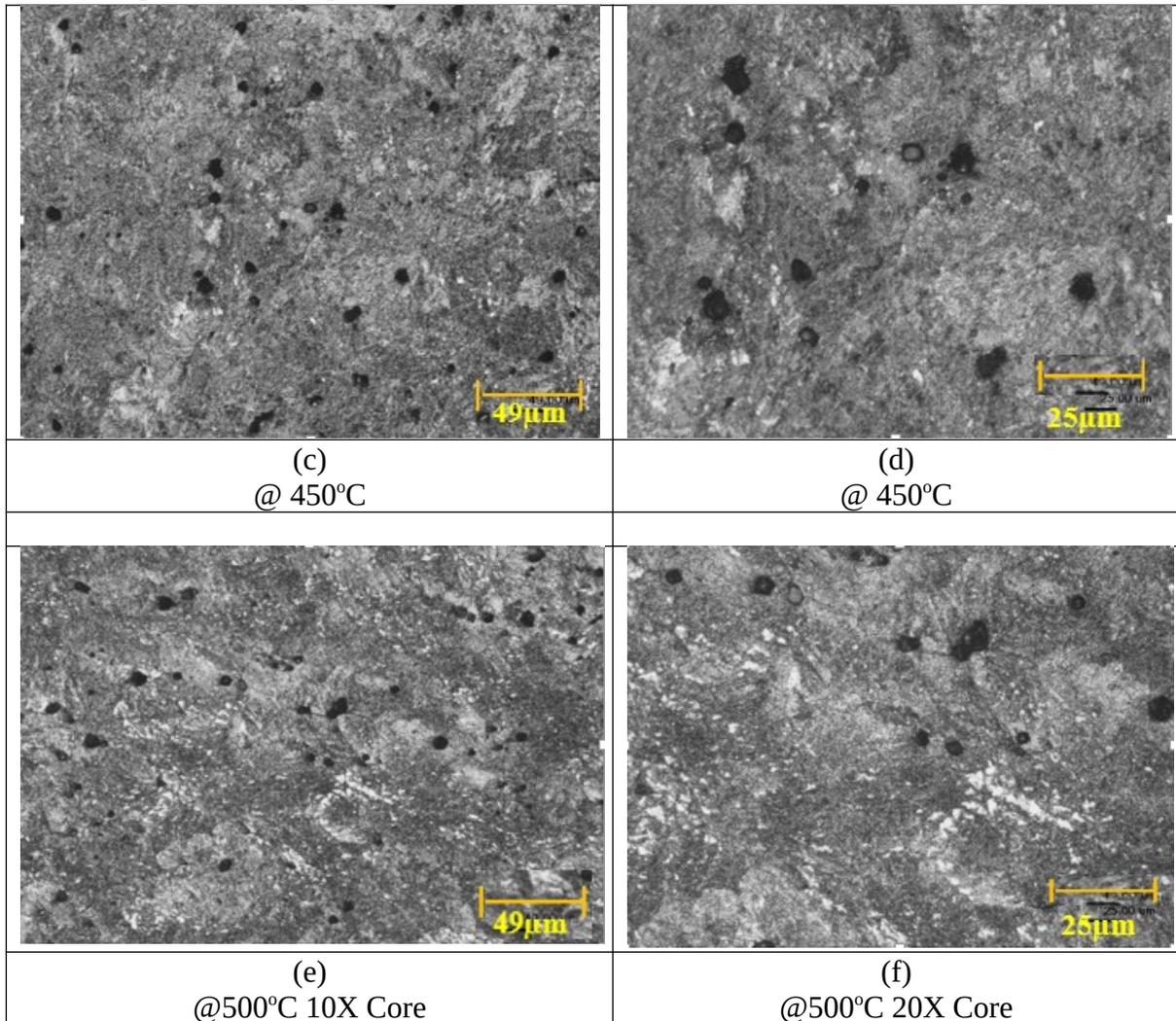
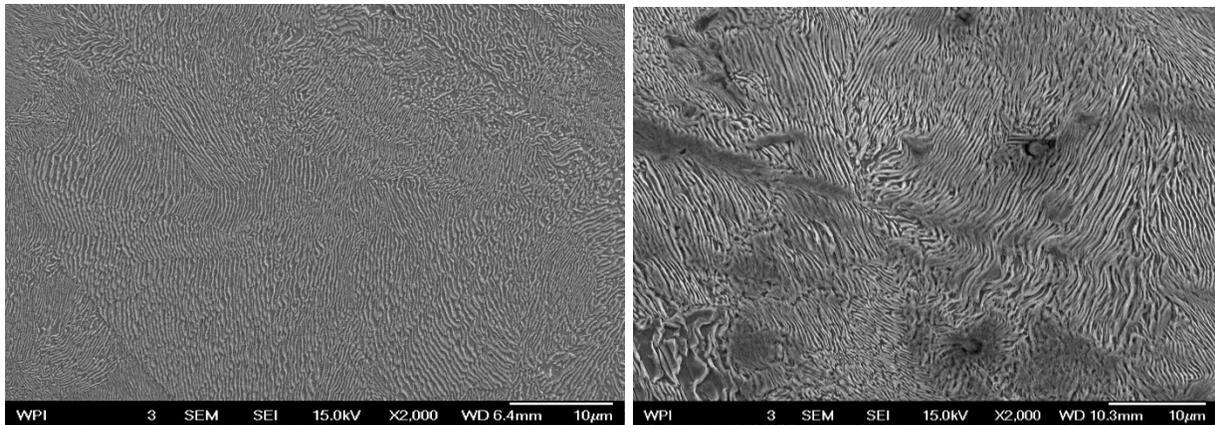


Table 4.4: Optical micrograph of AISI 1070 steel after carbonitrided at 3 hours





(g)

Figure 4.2: SEM image of AISI 1070 steel (g) as received sample, (hour) treated at 500°C for 3 hours

Table 4.5: Micrograph of as received AISI 1065 steel

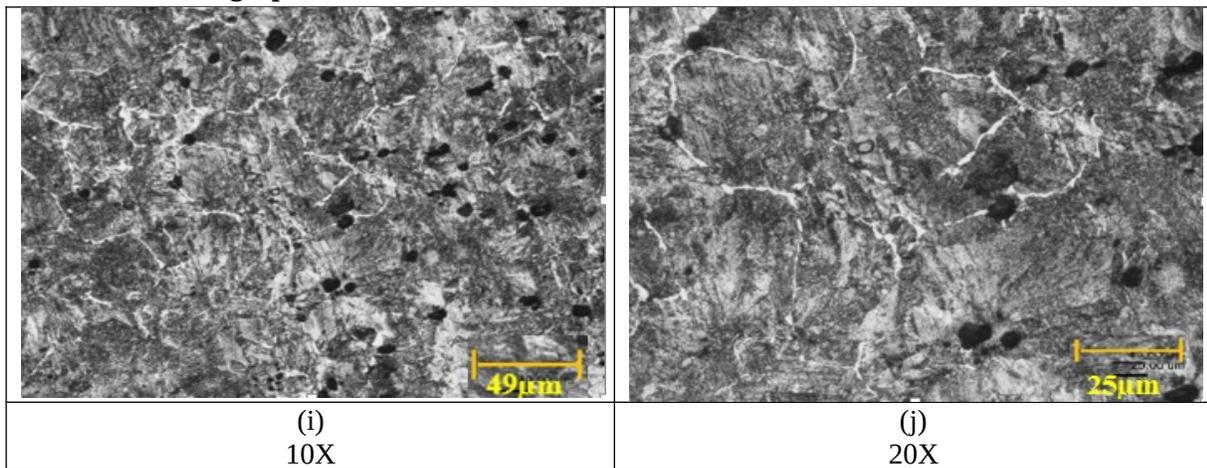
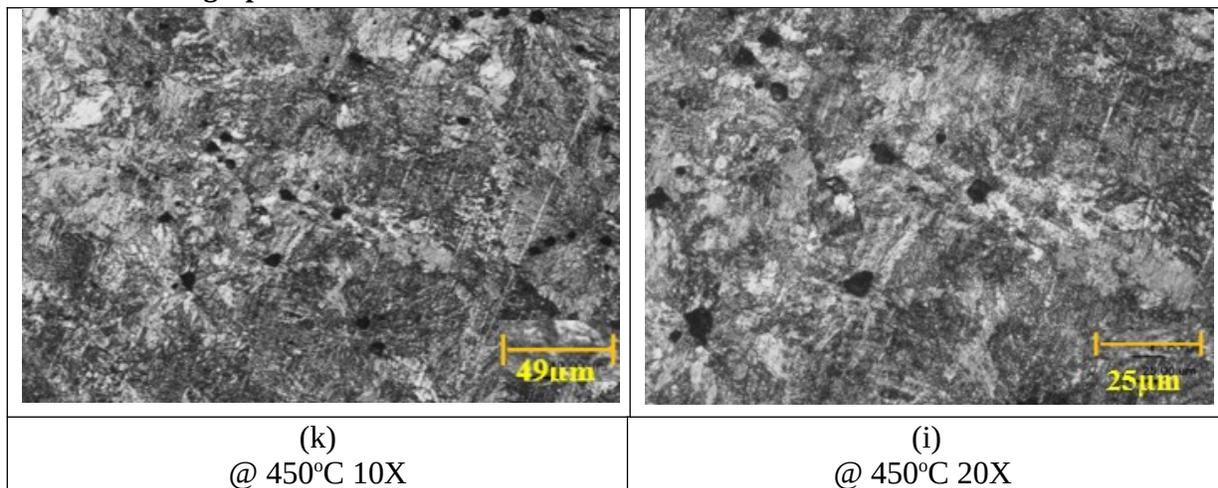


Table 4.6: Micrograph of AISI 1065 steel after carbonitrided at 3 hours



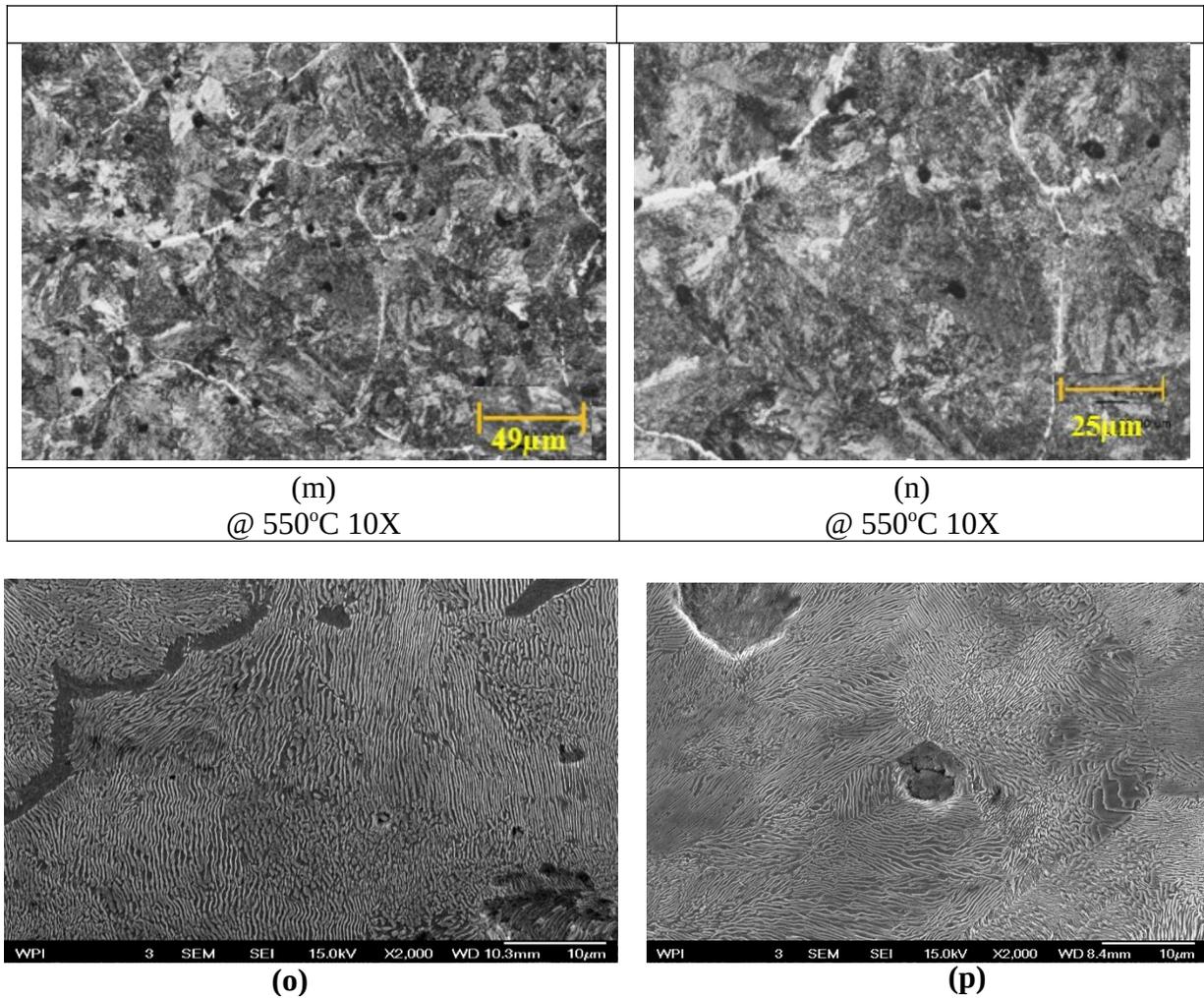


Figure 4.3: SEM image of AISI 1065 steel (o) as received sample, (p) treated at 550°C for 3 hours

Tables 4.3 a and b and 4.5 i and j, presents the ferrite (α -Fe) and pearlite (mixture of α -Fe and Fe³C) structures that were observed in the hypo-eutectoid microstructure of as received AISI 1070 and AISI 1065 steels. Tables 4.4 and 4.6 illustrate the optical microstructure of AISI 1070 and AISI 1065 steel samples processed with four pack-carbonitrided temperature at a constant time of 3 hours. As expected, microstructures were observed after the carbonitride process of the samples. Since the diffusion of atoms into the steel depends on the initial microstructure of the steel, it was observed at the core that the variation is little between different carbonitrided, see Tables 4.4 c – f and 4.6 k – n, and as received samples shown in Tables 4.3 a and b and 4.5 c and d; probably due to the same microstructures that appear as the original, pearlite and ferrite. Also, it has been observed that samples with different heat-treated temperatures showed differences in the grain size of diffusion of carbon-nitrogen, where it is bigger at 450°C and smaller at 550°C. At intermediate temperatures, after carbonitriding, interstitial diffusion takes place for nitrogen and carbon atoms and diffusing into steel. The SEM image showed in Figures 4.2 and 4.3 reviewed some concentration diffusion of nitrogen and carbon contents from the biocyanide

particles on the surface of the low-alloy steel during heat treatment as compared to the as received, see Figures 4.2 g and o. This showed that the diffusion process depends on temperature.

4.4 Micro-hardness Result

Vickers micro-hardness testing machine was used to find the hardness of the different surfaces for the AISI 1070 and AISI 1065 steel samples. Hardness measurements of the specimens were done before and after the heat treatment on a straight line from core to the case by intervals of 1mm under the load of 10kg. The Tables 4.7a and b below present the Vickers hardness result for the three steel samples.

Table 4.7a: Hardness values for as received and carbonitrided AISI 1070 steel

AISI 1070 Steel		Vickers Hardness, HV			
		Point 1	Point 2	Point 3	Average
As received		252	255	259	255 ± 3
Carbonitrided Temperature (°C)	400	263	271	288	274 ± 3
	450	299	303	303	289 ± 2
	500	308	310	318	312 ± 2
	550	326	327	329	327 ± 2

Table 4.7b: Hardness values for as received and carbonitrided AISI 1065 steel

AISI 1065 Steel		Vickers Hardness, HV			
		Point 1	Point 2	Point 3	Average
As received		241	243	240	241 ± 2
Carbonitrided Temperature (°C)	400	258	260	264	261 ± 3
	450	279	273	286	279 ± 5
	500	280	287	318	295 ± 5
	550	299	303	320	307 ± 5

During carbonitriding, both carbon and nitrogen atoms diffuse inward into the AISI 1065 and AISI 1070 steels; this results in the formation of a hardened zone resulting in changes in the mechanical properties such hardness and strength. As it can be seen from the above Table 4.7, hardness of the specimen's changes according to the heat treatment they have been subjected to. The hardness value of the as received samples for AISI 1070 and AISI 1065 from the surface to the core are 255HV and 241HV, respectively, as an average value. All the treated samples showed an increase in case hardness values as compared to as received steel value. For the treated sample for AISI 1070 and AISI 1065 steels, at 550°C carbonitriding temperature, the maximum hardness value achieved are 327HV and 295HV, respectively, which is observed as an average for both the surface and core. Thus, carbonitriding time and temperature play a critical role in the determination of case depth and hardness. At 550°C, the potential of nitrogen is high, while that of carbon is low so only nitrogen diffuses appreciably into the steel resulting in nitriding. The variation in hardness, with respect to cyaniding temperature, is graphically shown

in Figures 4.2 and 4.3. This shows an increase trend in hardness with increase in heat-treatment temperature.

4.5 Pin-on-Disc Wear Results

The results of the pin-on-disc abrasive wear test of carbonitrided steels at different temperatures of 400°C, 450°C, 500°C and 550°C for 3 hours is shown in Tables 4.8 and 4.9.

Table 4.8: Summary of pins-wear parameters for AISI 1070 steel samples

		Weight Loss (g)	Wear Volume (mm ³)	Wear Rate (mm ³ /m)	Wear Resistance(m/mm ³)
Untreated sample		6.5E-03	0.8333	3.70E-03	270.0
Carbonitrid Temperature (°C)	400	4.1E-03	0.5256	2.34E-03	428.0
	450	3.2E-03	0.4103	1.82E-03	548.4
	500	2.8E-03	0.3589	1.60E-03	626.8
	550	2E-03	0.2564	1.14E-03	877.5

Table 4.9: Summary of pins-wear parameters of AISI 1065 steel samples

		Weight Loss (g)	Wear Volume (mm ³)	Wear Rate (mm ³ /m)	Wear Resistance(m/mm ³)
Untreated sample		7.3E-03	0.9359	4.16E-03	240.4
Carbonitrid Temperature (°C)	400	5E-03	0.6410	2.85E-03	351
	450	4.3E-03	0.5513	2.45E-03	408.1
	500	3.5E-03	0.4487	1.99E-03	501.4
	550	3E-03	0.3846	1.71E-03	585.0

4.6 Effect of Carbonitriding Temperature on the Hardness and Wear Resistance of Heat Treated AISI 1070 and AISI 1065 Steels

The effect of carbonitriding temperature on the hardness and wear resistance of carbonitrided steels for the four different temperatures of 400°C, 450°C, 500°C and 550°C is shown in Tables 4.7a and b and Tables 4.8 and 4.9. This was also plotted graphically in Figures 4.2 and 4.3, where it was shown that wear resistance varies directly with the heat-treatment temperature. An increase in temperature increased the nitrogen diffusion, thereby strengthening the steel as a result of hardness. However, this also contributes to the wear resistance as shown in Figure 4.2. This showed the variation at different temperatures for the diffusion of carbonitride, causing an effect to the hardening and wear resistance for the AISI 1070 and AISI 1065 steels.

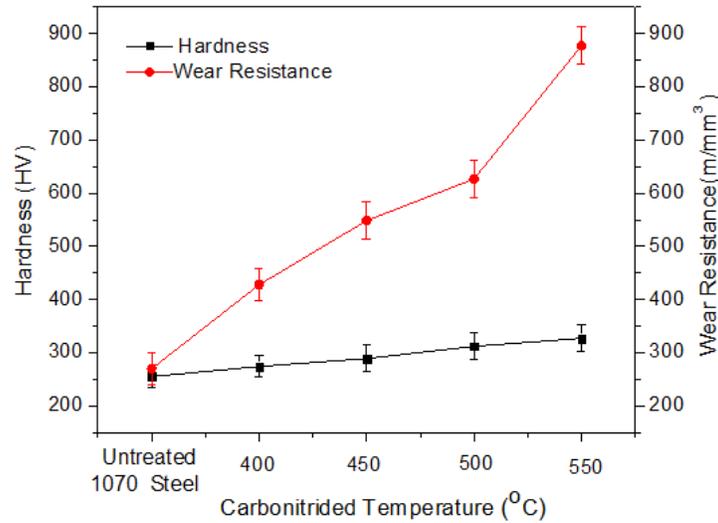


Figure 4.4: Relationship between pack-cyaniding temperature, hardness and wear resistance for AISI 1070 steel

From the graph, it was shown that carbon-nitride for both AISI 1070 and AISI 1065 steel samples at temperature of 550°C gives the maximum hardness and wear resistance and the minimum hardness for the same steels heat treated at a temperature of 400°C. Hence, the steels heat treated at temperatures of 550°C give the best results and is preferred. It is found from the graph that the wear resistance curve, due to abrasion, is highly influenced by the hardness and it varies directly with the hardness, this means that with an increase in the hardness values of carbonitrided AISI 1070 and AISI 1065 steels, the wear resistance, due to abrasion, increases. It is as a result of the increased nitrogen and carbon diffusion on the steel which contributes to the hardness having the greater abrasive wear resistance.

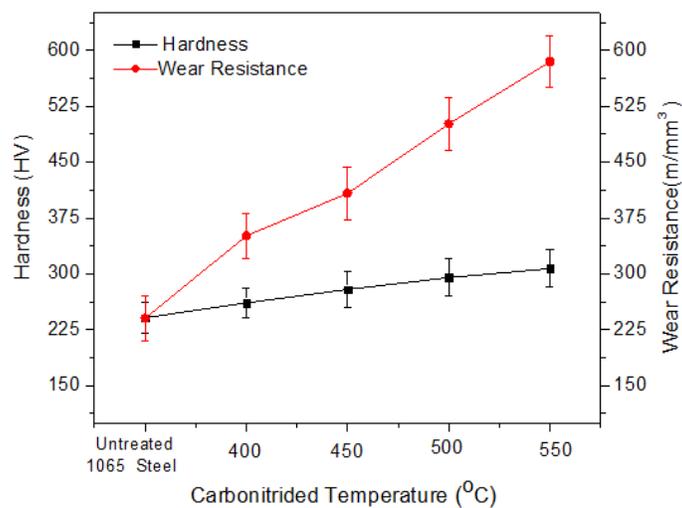


Figure 4.5: Relationship between pack-cyaniding temperature, hardness and wear resistance for AISI 1065 steel

4.7 Effect of Carbonitriding Temperature on Wear Rate of Heat Treated AISI 1070 and AISI 1065 Steels

The variation of carbonitriding temperature with the wear rate, due to abrasion, is shown in Tables 4.9 and 4.10, it was also graphically represented in Figures 4.5 and 4.6. From these results, there is a great reduction in wear rate for the treated steel samples compared to the untreated samples that show the highest wear rate. This also showed that the trends in the wear rate was consistent with the trends in hardness as the nitrogen and carbon diffused to the steel. Hence, the heat treated AISI 1070 and AISI 1065 steels had better wear resistance and greater hardness than the as received materials. The hardness and wear resistance increased with the increasing carbonitriding temperatures of up to 550°C. At 400°C to 550°C, nitrogen diffuses better and increases the hardness in such a way that offers a reduction in wear rate.

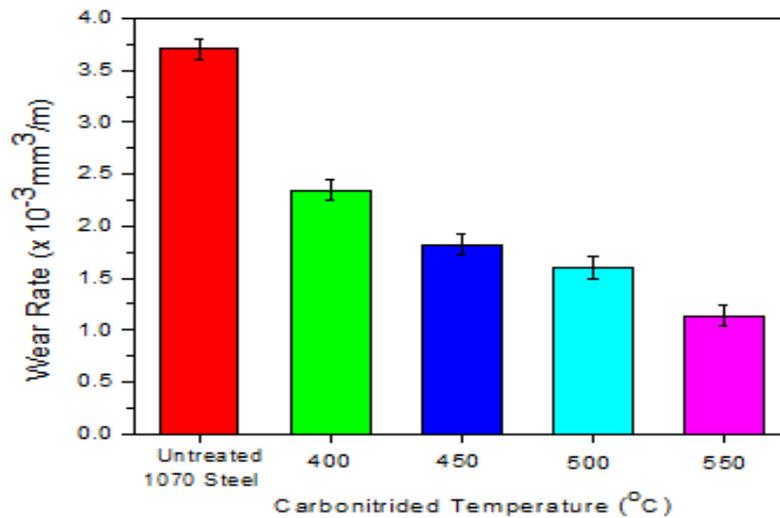


Figure 4.6: Wear rate against carbonitriding temperature for AISI 1070 steel

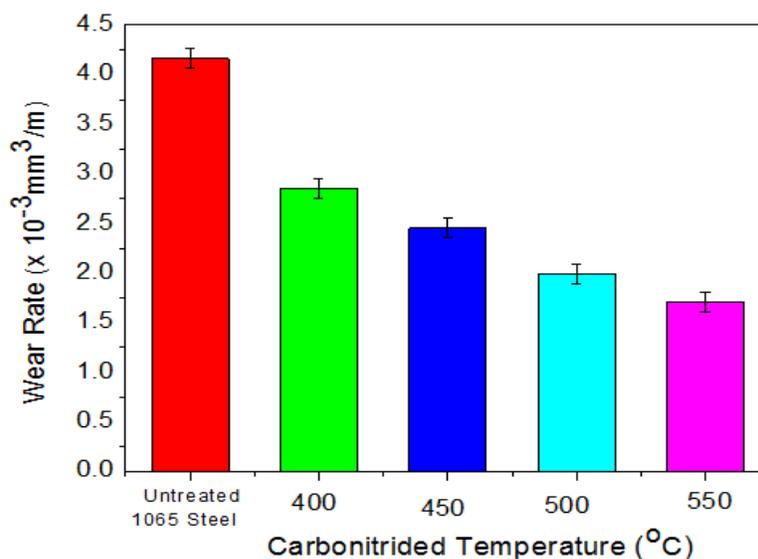
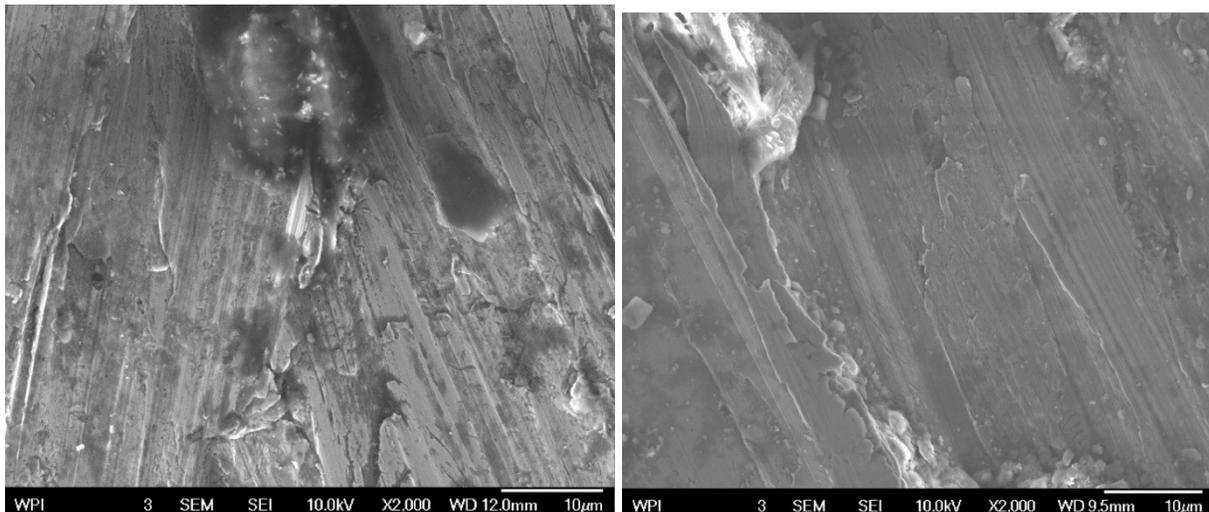


Figure 4.7: Wear rate against carbonitriding temperature for AISI 1065 steel

This is due to the increase in the strengthening rate of diffusion of nascent and atomic nitrogen into the steel as the temperature is increased. From the graph it is shown that the wear rate decreases gradually with an increase in the carbonitrided temperature. This result is expected because as the carbonitriding temperature increases, the hardness of carbonitrided AISI 1070 and AISI 1065 steel increases and due to the increase in the hardness, the wear rate due to abrasion decreases.

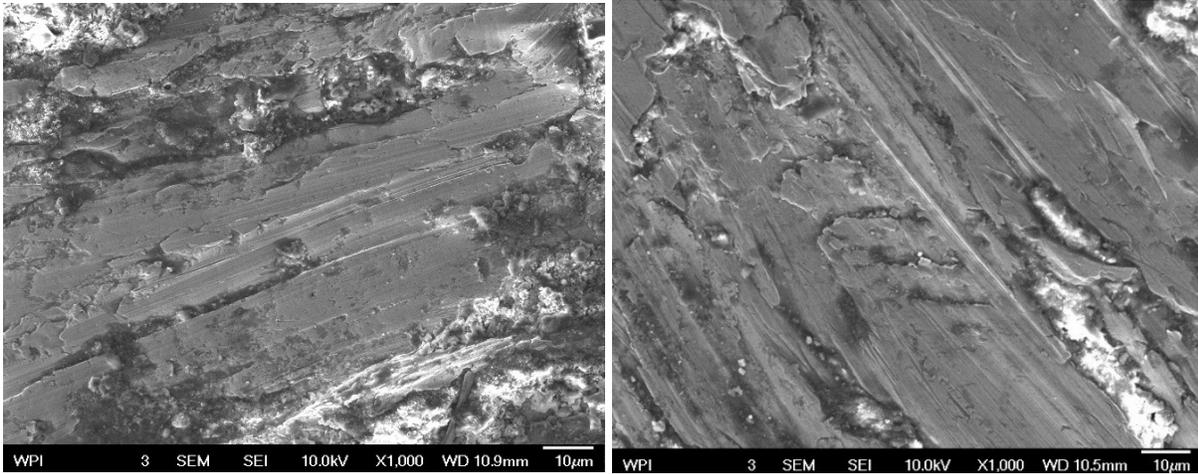
4.8 SEM of Worn Surface

Scanning electron micrographs of the worn surfaces of pins for AISI 1065 and AISI 1070 steel were given in Figures 4.7 and 4.8. The pins were tested using the SiC paper that is rough and hard. The observation of the worn surfaces suggest that the wear mechanism involved abrasive wear and also, some clear evidence of plastic deformation in wear was shown on the image, which can be related to the abrasive wear mechanism. Also, from the images presented, it can be seen that the worn surface for the treated pins was smooth and there was a little plastic deformation compared to the untreated pin. This may be as a result of the contribution of nitrogen and carbon diffusion into the steel surface during the heat-treatment process.



(a) AISI 1065 – Untreated (b) AISI 1065 – Heat treated at 550°C

Figure 4.8: SEM image of worn surface of untreated and treated AISI 1065 steel pin



(c) AISI 1070 – Untreated (d) AISI 1070 – Heat treated at 550°C

Figure 4.9: SEM image of worn surface of untreated and treated AISI 1070 steel pin

CHAPTER FIVE CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

In this study, pack biocyanide of low-alloy AISI 1065 and AISI 1070 steel for mining tools were investigated for hardness and abrasive wear properties at 400°C, 450°C, 500°C and 550°C. Deductions can be made as the following:

1. The mechanical properties such as hardness of low-alloy steels were found to be influenced by the process of cassava leaf carbonitriding. Though this showed a little variation in microstructural view, this may be due to the as received AISI 1065 and AISI 1070 steel used for the mining operations has already been heat treated with another method before the pack bio-cyaniding process.
2. The result obtained from the cassava leaf carbonitriding showed an increment in hardness value of the heat treated AISI 1070 and AISI 1065 steels which are 327HV and 295HV, respectively, compared to the as received sample.
3. As compared for different carbonitriding temperature; the AISI 1070 and AISI 1065 steels carbonitrided at a temperature of 550°C, the highest value for hardness and wear resistance. This was due to an increase in diffusivity of nitrogen and carbon into the surface.
4. Wear experiments using a pin-on-disc machine showed that cassava leaf carbonitriding considerably improved the wear properties of AISI 1070 and AISI 1065 steels. The wear rate was reduced by $2.56 \times 10^{-3} \text{ mm}^3/\text{m}$.
5. The use of waste cassava leaves for improving hardness of steel mining tools saves cost and is environmentally friendly.
6. These estimates can be used to guide the surface engineering to improved hardness and wear of a steel using cassava leaf carbonitriding technique and for the mining process.

5.2 Recommendations for Further Research

1. This work can be extended to other variables such as soaking time and higher temperature, which might have a significant effect on wear behaviour.
2. Studies prove that hydrocyanic acid (HCN) is a volatile compound, it evaporates rapidly in the air at temperatures over 28°C. Other processing routes such as wet milling or pulverising for getting a higher cyanide content from the cassava leaf should be carried out.
3. Develop a computational model to determine the nitrogen and carbon concentration profiles in the steel in terms of temperature, atmosphere composition, steel surface condition, alloy composition and the pre-carbonitriding steel microstructure.
4. Other mechanical properties like fatigue and fracture toughness of pack biocyanide low-alloy steel should be investigated.
5. Corrosion behaviour of pack biocyanide low-alloy steel for mining activities should be studied.

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