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ABRASIVE WEAR STUDIES OF PACK CYANIDED MILD STEEL (PCMS)

A THESIS SUBMITTED TO THE ACADEMIC AFFAIRS AND OTHER ADMINISTRATIVE UNITS

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BY

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(Materials Science and Engineering)

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DEDICATION

This project is dedicated to Vivian Robinson, my mother and my grand-parents who inspired me towards hard work and achievement; and to my uncles who are always an integral part of my life.

CERTIFICATION

This is to certify that the thesis entitled, ‘’**ABRASIVE WEAR STUDIES OF PACK CYANIDED MILD STEEL**’’ was carried out by Emmanuel Kwesi Arthur under my guidance and supervision for the partial fulfilment of the requirements for the award of Masters of Science (Honours) in Materials Science and Engineering at the African University of Science and Technology, Abuja-Nigeria.

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LIST OF ABREVIATIONS

NASENI ……. National Agency for Science and Engineering Infrastructure
EMDI ………... Engineering Materials Development Institute
PEDI ………….Prototype Engineering Development Institute
MS …………….Mild Steel
PC ……………..Pack Cyaniding
PCMS …………Pack Cyanided Mild Steel
HCN …………..Hydrogen Cyanide
HTPC ………….High Temperature Pack Cyaniding
VHN …………..Vickers Hardness Number
PCL ……………Processed Cassava Leaves

ABSTRACT

This work aimed at using processed cassava leaves to pack cyanide mild steel (MS) under different treatment conditions and investigating the wear properties of the pack cyanided mild steel (PCMS). Pack cyaniding (PC) of a MS was achieved using processed cassava leaves powder with $BaCO_3$ as energizer in the heat treatment process. Four different powder particle sizes were utilized at four different temperatures (750^oC, 800^oC, 850^oC and 900^oC) and soaked for 3 hours.

In this present work, the microstructures of the un-treated sample and PCMS were characterized to know the cases formed. The abrasive wear tests of the PCMS were carried out using a pin-on-disk wear tester against untreated mild steel pin having a hardness of 197.5 VHN. The PMSs wear properties were evaluated, using abrasive velocity of 0.26 m/s, normal load of 20 N, total abrasive distance of 156 m and controlled room temperature of 25 ◦C.

The effect of particle size (212, 300, 600 and 850 µm) on the hardness and wear properties of a series of PCMS treated at different temperatures has been studied in this work. Case hardness was observed to decrease with a decrease in particle size and decreasing pack cyaniding temperature (PCT). Results revealed that the case hardness of the heat treated steels is related to the pack cyaniding temperature and the particle size used. The PCT of mild steel in cyaniding boat has a significant effect on the case hardness of the steel. Also, the wear test results indicated that the wear rate of treated mild steel increases with increasing PCT and particle size.

The study concluded that case hardness and wear resistance of mild steel parts could be improved by pack-cyaniding in pulverized dry cassava leaves.

CHAPTER ONE

1.0 INTRODUCTION

It is an undisputable fact that iron and steel are the most widely used engineering materials in industries. MS possesses the unique combinations of good mechanical properties and toughness but poor resistance to wear [1]. When the contact surfaces of these materials are subjected to relative motion, they undergo material removal known as wear. Thus their surface modification is necessary to improve their tribological behaviour. Therefore, there is the need to minimise friction and wear in order to extend the lifespan of these components. Although, several methods have been used to engineer the surface of these engineering components, they are more expensive and cumbersome. For example, diamond deposition [2, 3] on various non-diamond substrates has been well achieved and established. The problem this has is the difficulty in depositing the diamond on ferrous materials due to that; it has not yet been commercialized.

Intensive research work has been carried out on surface modification of engineering components by various research groups [4-12]. It has been shown that cyaniding [13], carbonitriding [14], nitriding [4], and nitrocarburizing improve the wear resistance of steels [15]. The process used in cyaniding, nitriding and carbonitriding is a thermochemical treatment that involves diffusion of nitrogen and or carbon into the surface of the part. Diffusion of carbon and or nitrogen form nitride or carbide with substrate material to enhance its surface hardness and wear resistance. Conventional cyaniding is carried out at 800–960^{o}C in a salt bath and involves the diffusion of C and N atoms into the steel, giving a thin wear resistant layer of the carbonitride $\in$ -phase [16]. Instead of using poisonous salt cyanate, cyanide content present in the cassava plant has been utilized in several research works such as cyanidation of gold [17] and recently for PC of mild steel [16].

Recently, Adetunji et al [16] performed microstructural examination on the case-hardened mild steel. In their work, they investigated the effect of cyanide on PC of MS for case-hardening using $BaCO_3$ and $BaCl_2$ as energizers. The study revealed that, at high temperature there is C diffusion into the case of MS from cassava leaf powder. Similarly, it was showed that at low temperatures, there is a diffusion of N [16] and that diffusion proceeds from the case to the core of the mild steel with increasing treatment temperature and increasing treatment time. The authors found that, the optimum hardness of the pack cyanided mild steel (PCMS) was achieved at a high temperature of 900^oC.

In the present work, processed cassava leaves (PCL) rich in hydrogen cyanide (HCN) were employed in the PC process to achieve the coating on MS. Researches [16, 18 and 19] have shown that, this HCN released from the cassava plant improves the surface modification of steels. This is as a result of decomposition of cyanogenic glycosides linamarin and lotaustralin by β-glucosidase-catalyse [20]. High temperature pack cyaniding (HTPC) was utilized in this work. This is non-pollutant method and is appropriate to increase the surface hardness and wear resistance of the MS. The aim of this work is to investigate the influence of pack cyaniding and microstructure on case hardness and abrasive wear behaviour of mild steel. The present work utilized combination of the two important PC variables: pack cyaniding temperature and PCLs particle size for PC of MS and characterizing the wear properties of the cases formed. It is a well established fact that, the mechanical and wear properties of a material vary significantly based on the microstructures obtained. The microstructure and wear properties of the pack cyanided coatings were investigated through micro-hardness measurement, wear testing, optical microscopy and SEM with EDS.

1.1 Motivation for Current Work

The usage of steels has been limited due to its low wear resistance and surface hardness [21]. In major industrial plants, the increasing deterioration caused by wear of metallic surfaces in contact profoundly leads to loss of plant efficiency and also can lead to plant shutdown [22]. It has been estimated that, in United States, corrosion and wear damages to materials (both directly and indirectly) cost hundreds of billions of dollars annually [22]. As of 2001, corrosion of metals alone costs the US economy almost $300 billion. Also, similar estimation on wear damages alone shows that about $20 billion is spent on wear of materials per year compared to $80 billion annually for corrosion cases during the same period [22].

MS has several engineering applications such as in machine parts and construction industries. During service, numerous industries encounter the problem of wear on parts made with mild steel. Almost any two relative moving parts in service will be subject to wear at the contact point. The consequence of this wear is that parts need to be replaced, which costs money and causes downtime on the equipment. The ongoing challenge of engineers in these fields is to find, or design, materials that are the most wear resistant, in order to extend the life of the parts and reduce the frequency of part replacement [23].

Attempts have been made by researchers [16, 18 and 19] to improve the case hardness of mild steel by pack cyaniding. The results obtained from this approach seem very promising; however, no attention has been paid to investigating how the pack cyanided coating affect the abrasive wear properties of the mild steel. There is, therefore, a need to study abrasive wear properties of pack cyanided mild steel to optimize their wear performance. This was explored in the current work using a combination of pin-on-disk experiments.

1.2 Aim and Objectives of Present Work

The aim of this work is to investigate the influence of pack cyaniding and microstructure on case hardness and abrasive wear behaviour of mild steel.

The objectives of present work are:

- To pack cyanide mild steel components and characterize its microstructures
- To study the effects of PCT and particle size of PCLs on the case hardness of treated samples
- To determine the wear properties of the pack cyanided mild steel samples
- To study the effects of PCT and particle size of PCLs on the wear properties of the treated samples

1.3 Outline of work

The work was carried out in the following steps:

- Microstructural and chemical characterisation of as-received mild steel
- Pack cyaniding of mild steel; and microstructural characterisation of the pack cyanided samples
- Microhardness measurement
- Pin-on-disk wear testing of both treated and untreated samples

1.4 Scope

The scope of this work is limited to the study of abrasive wear behaviour of high temperature pack-cyanided mild steel components.

1.5 Justification

Previous works done on pack cyaniding of mild steel only focused on the case depth studies (Ibironke *et al*, 2004) and metallographic studies (Adetunji, *et al*., 2008). The present work introduces abrasive wear behaviour of high temperature pack-cyanided mild steel components. This seeks to probe into the effect of heat treatment temperature on the pack cyanided coatings and its abrasive wear properties and also to determine the effects of particle size of cassava leaf powder on the microstructure and pack cyanided coating on the abrasive wear properties.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Background

‘’Mild steel’’ refers to low-carbon steel typically with maximum carbon content of 0.25%. It is the most common form of different grades of steel available, because they are the least expensive to produce. These materials are relatively soft and weak due to the fact that they have relatively low carbon content and they are not responsive to heat treatments intended to form martensite. There are several types of heat-treatment process used to change the surface properties of these steel components. Carbonitriding stands out unique among many surface modification (hardening) processes. This is because, carbonitriding has short hardening time which is achieved by fast hardened layer formation as compared with other processes, and it has been used widely for surface hardening of automobile parts. Also, carbonitriding has been utilized due to its non-significant dimensional deformation of the treated parts [24].

Carbonitriding is a diffusion process that is different from carburizing and nitriding. In carburizing, the cases normally contain no nitrogen, and nitrided cases contain nitrogen primarily, whereas carbonitrided cases contain both nitrogen and carbon [1]. The case structures achieved from these diffusion processes are suitable in applications where wear resistance is paramount, and for conventional approach, large amount of ammonia is needed to achieve such case compound. The process in this study is pack cyaniding at high temperatures, which is different from the conventional treatment of liquid cyaniding, where the nitrogen and carbon source is salts of the cyanides and the cyanates which is toxic. Utilizing processed cassava leaf with the intention of harnessing the C and N content of cyanide in cassava leaf with a view to increasing their strength as a consequence of increasing C and N limits the toxic impact of cyaniding on the personnel as well as the environment. This approach has both economic and ecological benefits in that it is potentially an inexpensive and environmentally friendly source of carbo-nitriding.

According to Adewusi et al (1999), it was shown that the cyanide content of the cassava leaf is between 3% and 4%, which is 100 times more than in tubers [25]. Therefore, using the cassava leaf to pack cyanide mild steel is in the right direction. The cyanided case obtained for low C steels contains both C and N, having hardness ranging between 800 and 900 VHN. The case structure surface formed in pack cyaniding contains a thin high N containing ε-phase and is analogous to that of a carburized case. At the surface, martensite which is rich in dissolved C and N is obtained after hardening. These surfaces increase hardness and it is also of the view that, wear resistance; the fatigue limit and corrosion resistance are improved [25].

Few reports [22, 25, and 26] have been published on the pack cyaniding study of mild steel using PCL. However, no investigation has been reported on wear properties of cassava leaf pack cyaniding process of mild steels. The mechanical and wear properties of iron and steels components investigations under different case hardening conditions have been studied by a number of researchers. From literature, Luo et al [26] worked on the effect of microstructure on the abrasive wear behaviour of spheroidal cast iron. In their studies, they reported that, spheroidal grey cast iron has a wear resistance which is inferior to that of steel with a similar matrix. Also, they reported that, austempered structures were less resistance to abrasion wear than quenched structures. In addition, Luo et al (1995) revealed that the wear performance of steel and quenched iron samples were better than austenized at higher temperature. The abrasive wear behaviour of mild, medium carbon, leaf and high carbon, low chromium steel by means of a dry stand rubber wheel abrasion apparatus was studied by Kuma and Gupta (1990). It was found that the heat treated high carbon low Cr. Steel and mild steel carburized by their technique had the best abrasive resistance. The abrasive wear resistance values of the two materials wear found to be very much comparable with each other. The study also included abrasive wear of carburized mild steel. The influence of carburization conditions (e.g., temperature, time, properties of carbonaceous material etc.) on the abrasive wear loss was investigated. Eventually, Kumar (1990) developed a cheaper method of carburizing with better wear resistance.

The case-depth of pack cyanided mild steel using cassava leaves has been studied [18]. The study showed variation of case depth with soaking time using cassava leaves powder for pack cyaniding. Experimental data of hardness at different depths from steel surface obtained from pack cyanided bar steel ST44 using cassava leaves at 860 ^{o}C soaked for 2, 3, and 4 hrs were collated and analyzed to obtain a model described by eqn 1:

$$y\,(x,t) = g(t)\,h(x,t) + K \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{eqn (1)}$$

where $y\,(x,t)$ is hardness as a function of case depth (x) and soaking time (t), $g\,(t)$ is a power function of time, $h\,(x,t)$ is an exponential function of the form $(1–e^{1/x})$ and K is a constant representing hardness at zero cyaniding time.

In further work at Engineering Materials Development Institute, Akure, Nigeria, [16] microstructural examination on the case-hardened mild steel was performed. In the work, the effect of cyanide on pack cyaniding of mild steel for case-hardening using $BaCO_3$ and $BaCl_2$ as energizer was investigated. The study revealed that, at high temperature there is C diffusion into the case of mild steel from cassava leaf powder. It was also revealed that there was a case formation resulting from carbon diffusion into the specimen. Similarly, they also showed that at low temperatures, there is a diffusion of N [16]. They further explained that, the diffusion proceeds from the case to the core of the mild steel with increasing treatment temperature and increasing treatment time. The optimum hardness of the pack cyanided mild steel was achieved at a high temperature of 900 °C. They also investigated the cutting time of the case-hardened steels and correlated these with pack cyaniding heat treatment [16].

A recent study [19] introduced cassava leaves particle size as another cyaniding variable. As part of the work, the effect of particle size on the case depth of a mild steel component was also studied. He found out that the case hardness of the samples generally increases with cassava leaves particle size. It was further explained that case hardness increased with particle size because the larger particle sizes release their nascent C gradually over time whereas the smaller particle sizes being very fine burn off more quickly. It was also seen that case depth and hardness relate proportionally in that the deeper the case depth, the harder it is to penetrate the material by indentation [19]. The gentle wavy nature obtained from a plot of case hardness as a function of particle size for high temperature pack cyaniding (Fig 2.1) was believed to be due to the impure organic nature of the cassava leaves powder used. The study concluded that case depths and hardness generally increased with the heat treatment variables i.e., cassava leaves particle size, soaking time and treatment temperature. This present work also utilized cassava leaves particle size as a high temperature pack cyaniding variable to study its effect on the wear behaviour of mild steel.

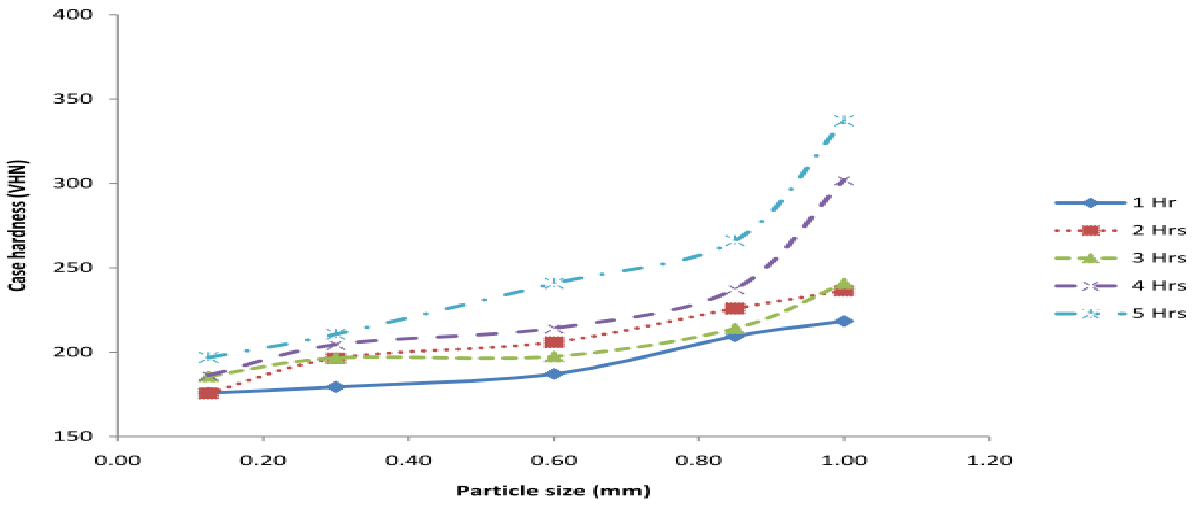


Fig 2.1: A plot of case hardness as a function of particle size for high temperature pack cyaniding (Akinluwade, MSc. Thesis 2010)

2.2.1 Cassava Leaves as a Source of both Carbon and Nitrogen

Cyanogenic glucoside has been found in cassava, which during cassava processing hydrolyzes to cyanide as a waste product. Cassava however, contains some amount of cyanide which is often removed as waste during cassava processing. The cyanide content present in the cassava varies in the various parts of the cassava plant [20]. These cyanogenic glycosides are group of naturally occurring organic compounds found in cassava plants and other edible parts of some plants. This chemical compound alone is non-toxic but as a result of hydrolysis process caused by enzyme beta-glucosidase following maceration of plant tissues as they are eaten up. Cyanogenic glycosides are decomposed to release hydrogen cyanide. This hydrogen cyanide is toxic to both humans and animals. The capacity of cyanogenic plants to release hydrogen cyanide determines the potential toxicity.

Researchers [16, 18, and 19] have shown that, this hydrogen cyanide released from the cassava plant helps in the improvement of case hardness of mild steel. Cassava leaves are used to prepare food in some countries after boiling, but in this present work, the cassava leaves were utilized for the pack cyaniding on mild steel. Research [20] has shown that, applying heat to intact cassava leaves leads to the production of hydrogen cyanide. This is as a result of decomposition of cyanogenic glycosides linamarin and lotaustralin by β-glucosidase-catalysed [20]. Also, it has been proven that, cyanide released from intact cassava leaf by supplying heat at a temperature of 80^{o}C is more complete than liberation by homogenisation [4]. This homogenisation method is commonly used by homogenising the cassava leaf tissues with liquid nitrogen or dry ice [20].

2.1.2 Case-hardening

Cyaniding, carbonitriding, nitriding, and nitrocarburizing are case-hardening heat-treatment carried out either in the presence of gas or in salt baths. Conventional cyaniding is a process that involves diffusion of C and N atoms into the surface of steel. This process is usually carried out at 800^oC – 900^oC in a salt bath which forms a thin wear resistant layer of carbonitride ∈ -phase. The conventional cyaniding method utilizes salts of cyanides and cyanates which are toxic [20]. The new cyaniding process (pack cyaniding) minimizes the toxic impact of cyanide on the personnel during the treatment process [16]. It has been proven by Adetunji et al in their work that, the higher the process temperature, the less effective the cassava powder as a nitrogen source, because the rate of spontaneous decomposition of the nitrogen compound in the powder to molecular nitrogen increases as the temperature is raised. The cyaniding process imparts both carbon and nitrogen to the surface of steel material. It is very similar to carbo-nitriding in that both are generally used for thin cases of about 0.15mm-1.8mm [27]. In typical steel, the atoms of these elements migrate into the steel by the diffusion process. The rate of diffusion depends on the concentration gradient and diffusion coefficient of the material.

2.1.3 Diffusion Methods

Hutchings (1992) [28] identified two thermochemical classes of solid state processes in which atomic transport by thermally-enhanced diffusion leads to surface modification. The first class results in the formation of an interstitial solid solution in the substrate material due to diffusion of small atoms into the surface. Sometimes the diffusion also lead to the formation of compounds as very fine precipitates in the substrate material with the modified region having similar chemistry to that of the bulk. Carburizing and carbonitriding are examples. In the second type, there is a chemical reaction between the diffusing atoms and constituents of the substrate. This causes the formation of a distinct layer of a new compound at the surface. Nitriding, nitrocarburizing, boronizing and chromizing are examples of this type.

Table 2.1: Typical characteristics of diffusion treatments [29]

Process	**Nature of case**	**Process temperature (°C)**	**Typical case depth**	**Case hardness (HRC)**	**Typical base metals**
Carburizing (Pack)	Diffused carbon	815-1090	125µm-1.5mm	50-63*	Low carbon steels, low carbon alloy steel
Gas	Diffused carbon	815-980	75 µm-1.5mm	50-63*	Low-carbon steels, low-carbon alloy steels
Liquid	Diffused carbon and possibly nitrogen	815-980	50 µm-1.5mm	50-65*	Low-carbon steels, low-carbon alloy steels
vacuum	Diffused carbon	815-1090	75 µm-1.5mm	50-63*	Low-carbon steels, low-carbon alloy steels
Nitriding Gas	Diffused nitrogen, nitrogen compounds	480-590	12µm-0.75mm	50-70	Alloy steels, nitriding steels, stainless steels
Salt	Diffused nitrogen, nitrogen compounds	510-565	2.5µm-0.75mm	50-70	Most ferrous metals. Including cast irons
Ion	Diffused nitrogen, nitrogen compound	340-565	75µm-0.75mm	50-70	Alloy steels, nitriding steels, stainless steels
Carbonitriding Gas	Diffused nitrogen, nitrogen compound	760-870	75µm-0.75mm	50-65*	Low-carbon steels, low-carbon alloy steels, stainless steels
Liquid (cyaniding)	Diffused carbon and nitrogen	760-870	2.5-125µm	50-65*	Low-carbon steels
Ferritic	Diffused	565-675	2.5-	40-60*	Low-carbon

Table 2.1: (Cont'd)

nitrocarburizing	carbon and nitrogen		25µm		steels
Other Aluminizing (pack)	Diffused aluminum	870-980	25µm-1mm	< 20	Low-carbon steel
Siliconizing by chemical vapor deposition	Diffused silicon	925-1040	25µm-1mm	30-50	Low-carbon steels
Chromizing by chemical vapor deposition	Diffused chromium	980-1090	25-50µm	Low-carbon steel < 30; High-carbon 50-60	High- and low carbon steels
Titanium Carbide	Diffused carbon and titanium, TiC compound	900-1010	2,5-12.5µm	> 70*	Alloy steels, tool steels
Boronizing	Diffused boron. boron compounds	400-1150	12,5-50µm	40- > 70	

* Requires quench from austenitizing temperature

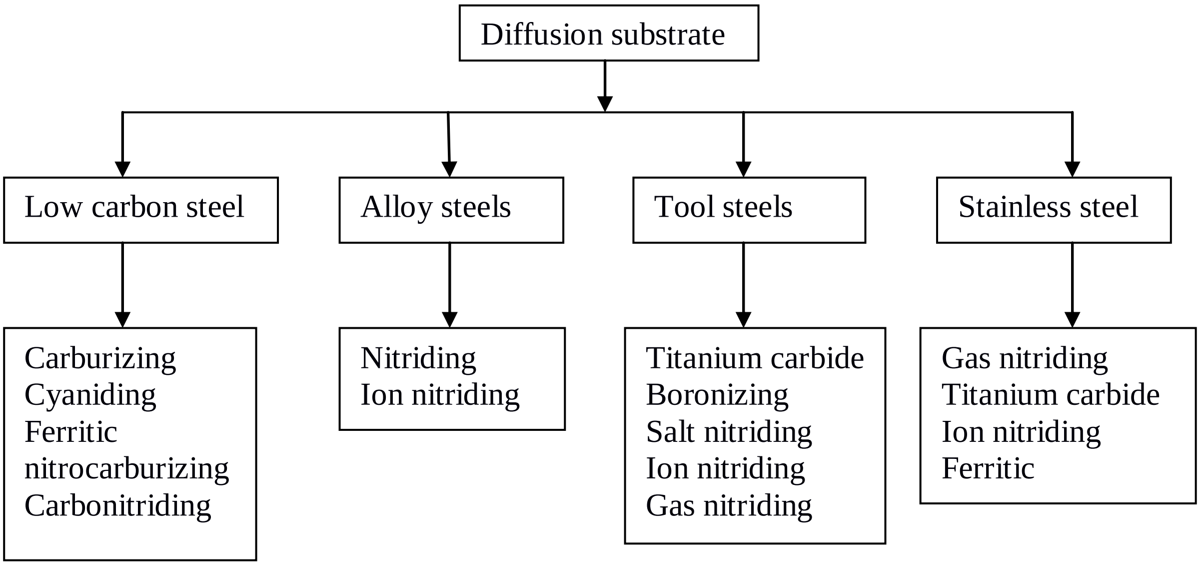


Fig. 2.2: Types of steels used for various diffusion processes [30]

2.2 Cyaniding

This process is a type of case hardening that is fast and efficient. Preheated steel is dipped into a heated cyanide bath and allowed to soak. Upon removal, it is quenched and then rinsed to remove any residual cyanide. This process produces a thin, hard shell that is harder than the one produced by carburizing and can be completed in 20 to 30 minutes vice several hours. The major drawback is that cyanide salts are a deadly poison [31].

2.3 Pack Cyaniding

In this process, the part that is to be cyanided is packed in a steel container (cyaniding boat), so that it is completely surrounded by powders of processed bitter cassava leaves **fig.2.3 .** The processing of the cassava leaves involves sun or oven drying, pulverizing to various particle sizes and addition of energizers. Pack cyaniding is divided into two categories, namely: low temperature and high temperature pack cyaniding.

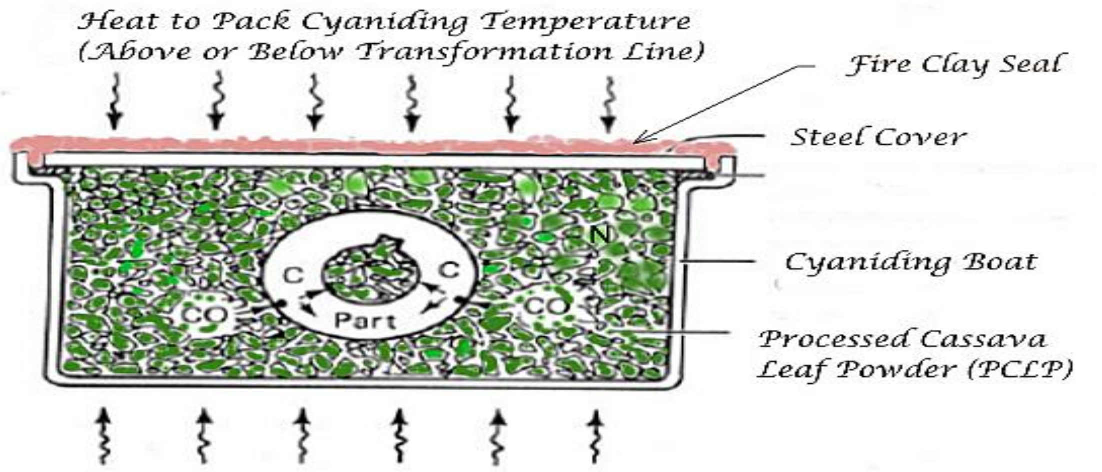


Fig. 2.3: Pack Cyaniding Setup

2.3.1 Mechanism of Reaction

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:

Cassava Leaves Powder:

$2C(s) + O_2(g) \rightarrow 2CO(g)$ ……………………………………………………………… rxn 1

$2CO\ (g) \rightarrow CO_2\ (g) + C\ (g)$ …………………………………………………………….. rxn 2

$2HCN + O_2 \rightarrow 2HCNO$ ………………………………………………………………… rxn 3

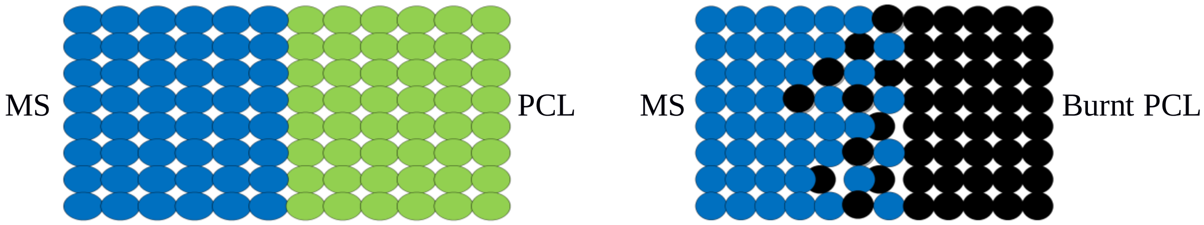
$8HCNO \rightarrow 4HCN + 2H_2CO_3 + 2CO + 4N$ .... rxn 4

Energizer:

$BaCO_3\ (s) \rightarrow BaO(s) + CO_2\ (g)$ ………………………………………………………… rxn 5

$CO_2\ (g) + C(s) \leftrightarrow 2CO(g)$ .... rxn 6

$CO\ (g) \leftrightarrow CO_2\ (g) + C(s)$ ……………………………………………………………… rxn 7



(a) (b)

Fig. 2.4: (a) initially (diffusion couple). (b) After heating to austenite temperature range

$2CO + 3Fe \rightarrow Fe_3C + CO_2$ ……………………………………………………………… rxn (8)

The oxygen of the entrapped air (in the cyaniding boat) initially reacts with the carbon of the pack cyaniding medium as follows:

$C+O_2 \rightarrow CO_2$ ………………………………………………………………………….rxn (9)

As the temperature rises the following reactions take place and the equilibrium shifts towards right that is gas becomes progressively richer in CO. At temperatures greater than 800 ^oC (> 800 °c) the boudoirs reaction occurs as shown in reaction 6.

The decomposition of CO gas occurs at the steel surface as follows:

$2C + O_2 \rightarrow CO_2 + C$ (atomic) …………………………………………………… rxn (10)

$Fe + C$ (atomic) $\rightarrow Fe(C)$ ………………………………………………………….. rxn (11)

Where Fe(C) is carbon dissolved in austenite.

There is a radial absorption of atomic and nascent carbon by the steel surface, and consequently it diffuses towards the centre of steel sample. The CO_2 formed react with the carbon (C) of the cyaniding medium (reaction 6) to produce CO, and thus, the cycle of the reaction continues. HCN, $BaCO_3$ and the burnt cassava leaves are the basic source of carbon during pack cyaniding. Whilst nitrogen source is from protein and HCN present in the leaves. As entrapped air inside the box may be less to produce enough CO_2 (reaction 9) particularly in the beginning of the pack cyaniding, it is common practice to add energizer (usually $BaCO_3$) which decomposes during the heating up period as shown from reaction 5 to 7.

The CO_2 thus formed then react with the carbon of the cyaniding medium to produce CO gas. Thus $BaCO_3$ makes CO_2 available at an early stage of pack cyaniding and hence it is called energizer.

2.3.2 Low Temperature Pack Cyaniding

It is usually carried out between 400 to 550°C with $BaCl_2$ as energizer. Adetunji et al previous work revealed that there is a diffusion of N at low temperatures [16]. The diffusion proceeds from the case into the core of the material with increasing treatment temperature and increasing treatment time. The low temperature pack cyaniding process is quite simple, and can achieve the surface hardening of simple ferrous components at temperatures of 450°C and 500°C. At 550°C, the potential of nitrogen is very high while that of carbon is very low so only nitrogen diffuses appreciably into the steel resulting in nitriding. During nitriding, a white layer of Fe_4N (γ' nitride) and Fe_2N ($\in$ nitride) forms near the outer layer of surface caused by high nitrogen potential [27], the problem of which can be avoided by keeping nitrogen potential at desired level.

2.3.3 High Temperature Pack Cyaniding

This is carried out at the temperature from 700 ^oC to 950 ^oC with an alternating chemical such as barium carbonate ($BaCO_3$) that promotes the formation of carbon dioxide (CO_2) for high temperature pack cyaniding. The $BaCO_3$ serves as energizer to facilitate the decomposition of CN present in the processed cassava leaves to liberate both nitrogen and carbon. It also augments the carbon content present in the leaves. At higher temperatures, this gas in turns reacts with the excess carbon decomposed from HCN present in the cassava leaves to produce carbon monoxide (CO). Carbon monoxide reacts with low carbon steel surface to form atomic carbon which diffuses into the steel. Carbon monoxide supplies the carbon gradient that is necessary for diffusion. This pack cyaniding process is entirely a surface modification by diffusion. At high temperatures, the optimum hardness has been achieved at 900^oC. At higher temperatures, it is believed that the reactions involved are similarly to pack carburizing.

2.4 Carburizing

Carburizing is defined as a case-hardening process by which carbon is introduced to the surface of low-carbon steel part, so that the part has a high-carbon surface and a low-carbon interior. This implies that the heat treated carburized steel will have hardened case while the core still remains soft and tough [32]. Generally, there are two methods that are used for carburizing steel. One of which consists of providing carbon monoxide atmosphere in a furnace and heating the steel. The other method has the steel placed in a container packed with charcoal or some other carbon-rich material and then heated in a furnace [32].

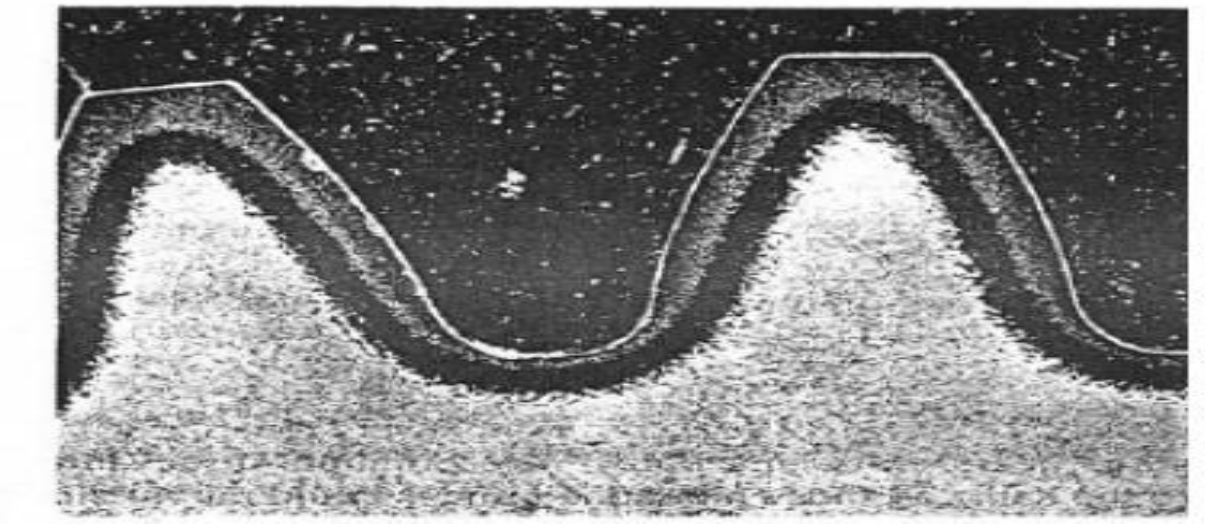


Fig 2.5: A property carburized, hardened, and tempered gear. Etched in 2% natal. 7X [33]

2.5 Nitriding

This is a type of case-hardening method that produces the hardest surface of any of the case hardening processes. It is different from other methods in that the parts ussed have been heat-treated and tempered before nitriding process. The parts are then exposed ammonia gas atmosphere in a heat treatment furnace. This process does not require quenching so it eliminates the problem of warping or distortion. Examples of parts that are nitride to be wear resistant and operate in high temperatures are gears, cylinder sleeves, camshafts and other engine parts [32].

2.6 Carbonitriding

This is a metallurgical surface modification of metals that improves the surface hardness of the metal, thereby assisting in minimizing wear. Atoms of carbon and nitrogen diffuse interstitially into the metal surface during the process of carbonitriding, forming barriers to slip thereby enhancing the modulus and hardness near the surface [34]. The conventional carbonitriding process involves applying ammonia into the gas carburizing atmosphere to introduce nitrogen to the carburized case. This happens when ammonia dissociates in the furnace atmosphere to form nascent nitrogen at the surface of the metal. Simultaneously, nitrogen interstitially diffuses into the steel with carbon [35]. The carbon and nitrogen atoms introduced into the martensitic steel impart wear resistance and improvement in strength. The nitrogen in carbonitrided steel enhances hardenability and makes it possible to form martensite in plain carbon and low-alloy steels that initially have low hardenability [36]. However, excess of nitrogen in the processed part can cause high levels of retained austenite and porosity, which are undesirable in producing a part of high hardness [34].

Carbonitriding is similar to liquid cyaniding, but it is preferable to liquid cyaniding because of the issues in disposing cyanide-bearing wastes [35]. The primary purpose of carbonitriding is to impart a hard, wear resistant case, generally from 0.075 to 0.75mm [36] deep to improve case hardenability. In the process environment, carbon is provided by introducing methane and nitrogen is also provided by introducing ammonia [36] to the furnace under controlled carrier gas. Thin skin of carbon and nitrogen rich steel (fig. 2.6) is obtained when proper ratios of the working gases are maintained. To achieve a full case hardness, the processed work piece is quenched after carbonitriding followed by low-temperature tempering (stress relief). This method does not allow hardening in the core of the metal but only allow hardening on the surface since the high carbon content is only on the surface.

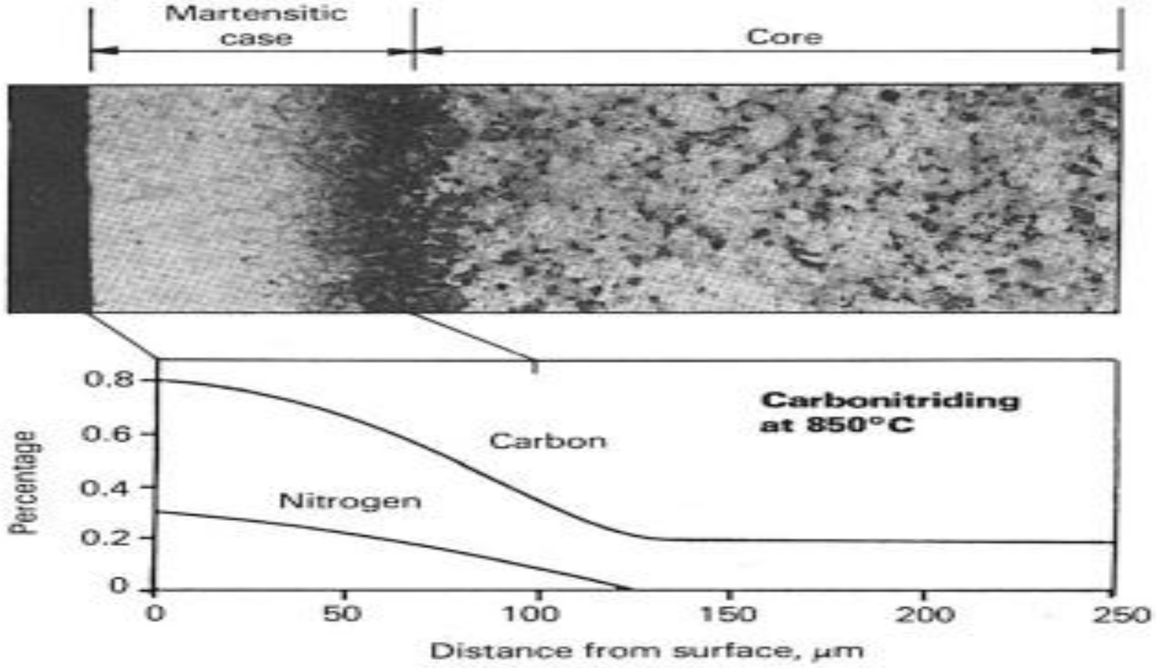
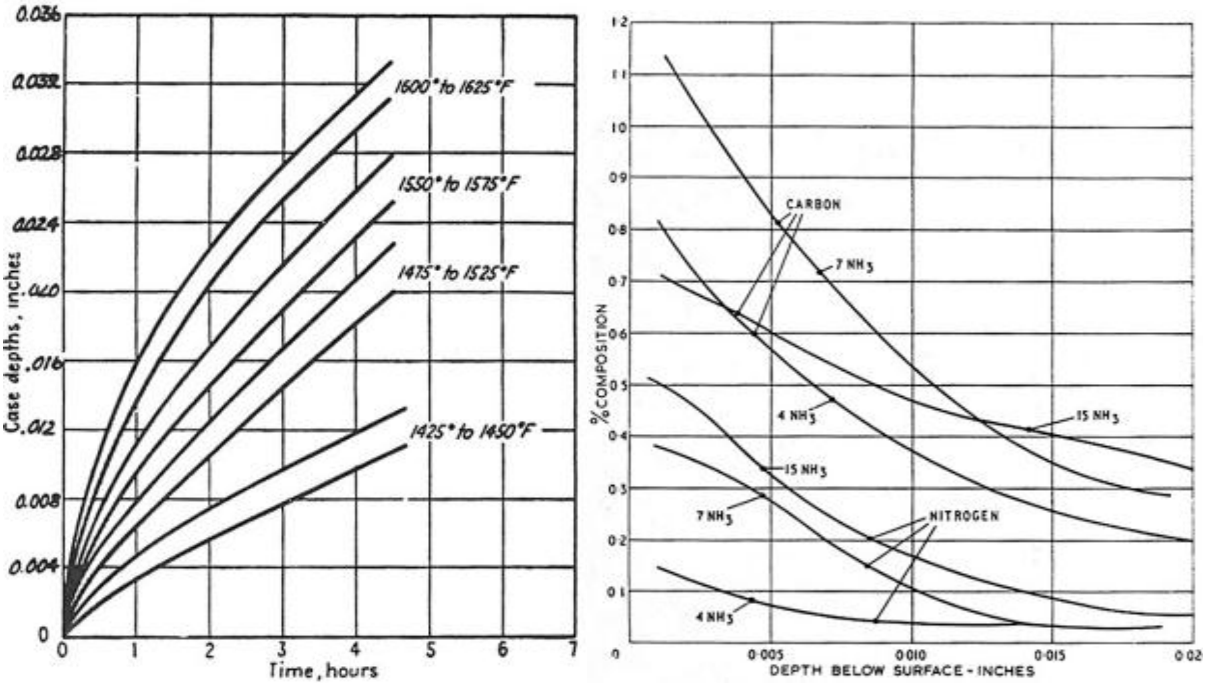
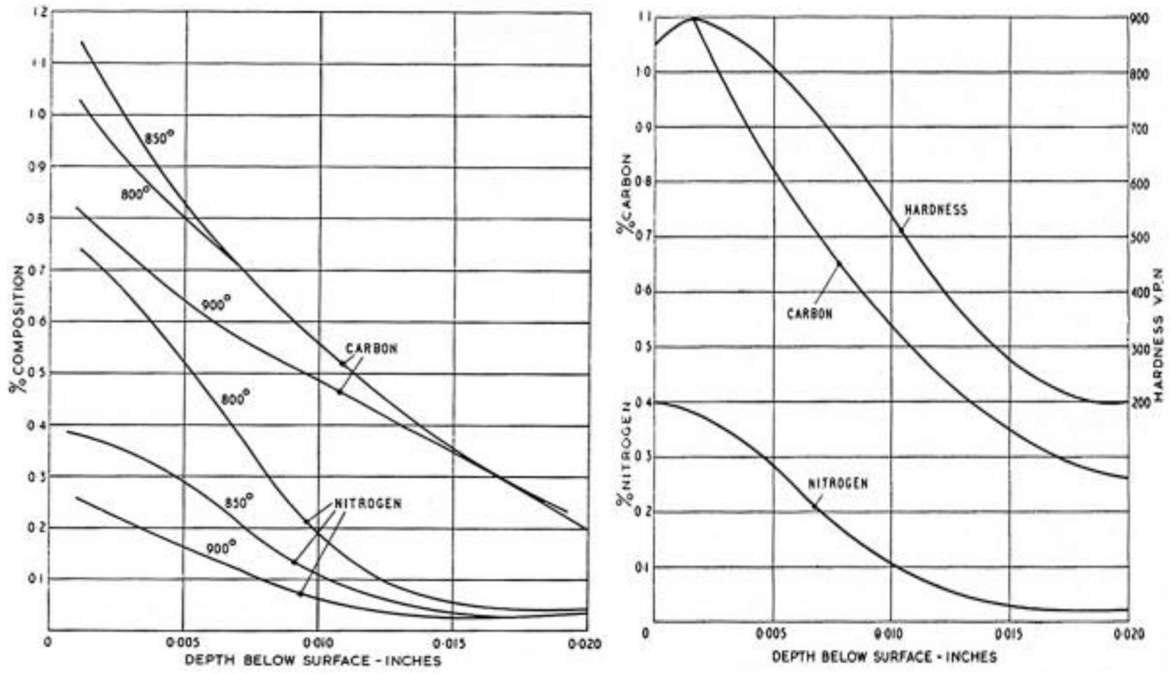


Fig 2.6: Surface layers produced by carbonitriding of steel at 1560°F (850°C) where carbon predominates in the formation of a martensitic layer [37]



(a) (b)

Fig. 2.7: (a) Case depth plotted against time for various temperatures (data based on information from about 30 plants) [38]. (b) Effect of ammonia concentration on case composition [39].



(a) (b)

Fig. 2.8: (a) Effect of temperature on case composition [39]. (b) Hardness, carbon and nitrogen profiles of a typical case [39].

2.7 Tribological Properties of Metals

Tribology deals with the study of interacting of surfaces in relative motion. It includes study and application of the principles of friction, wear and lubrication. Two common objectives in the use of surface engineering for tribological applications are: to increase the wear resistance of the surface material, and to modify its frictional behaviour [28]. In surface engineering, surface hardening is one of the numerous methods applied. Surface hardening basically involves a modification in both the microstructure and composition through thermally-enhanced diffusion of a different chemical species into the surface [28]. Fig 2.9 summarizes the range of methods used in surface engineering.

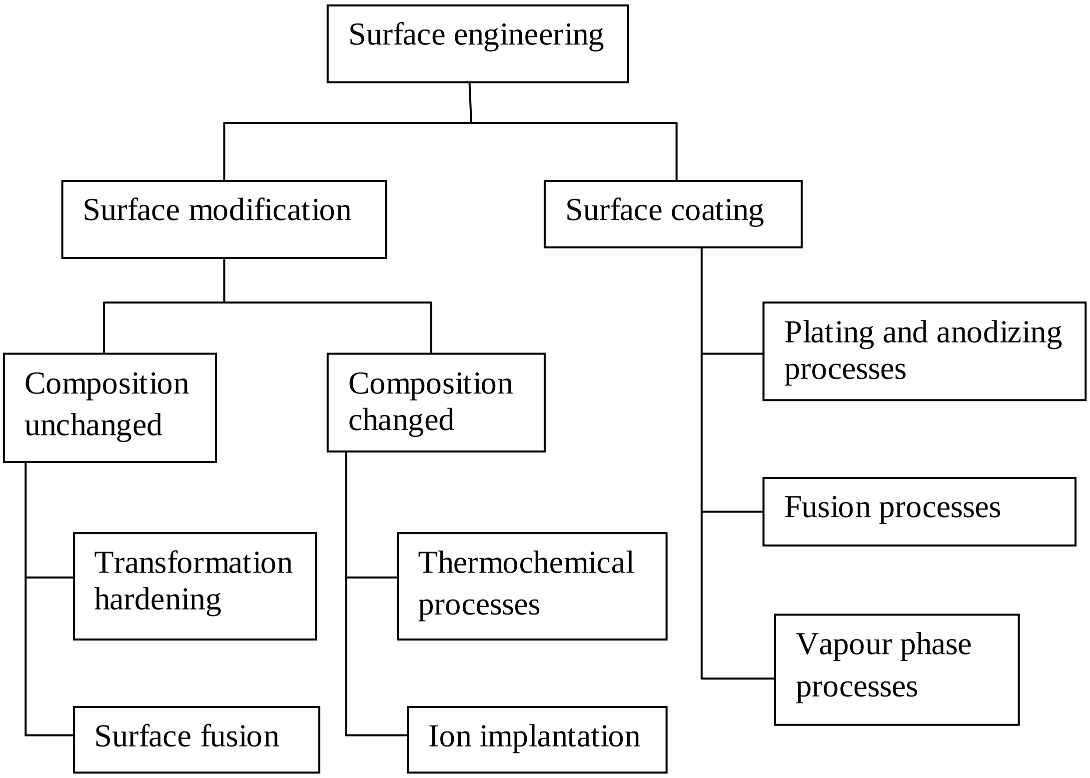


Fig 2.9: A summary of the methods available for surface engineering [42]

2.7.1 Wear

Wear in materials science is defined as the removal and deformation of materials from original position on a solid material surface due to the action of another surface [40]. Loads such as rolling, unidirectional abrasive, speed temperature and impact loads are working factors that can affect industrial wear of materials [40]. In industrials applications true values of material deterioration are obtained by performing wear testing that simulate the exact wear process. Wear can be separated into six main catergories (Bhushan and Gupta, 1991), namely: abrasion, adhesion, erosion, fatigue, corrosion and electric arc. However, in 1984, Godet argued that these wear mechanisms are only detachement mechanisms whilst both particle deachement and ejection are essential factors in the actual wear process. He further explained that,t during the period between detachement and ejection, the particle becomes entrained which he referred to it as ‘’third body’’. Essentially, Godet’s theory gives an informative view into the wear process.

The classic wear prediction model was proposed by Archard, (1953) [41] which is referred to as Archard Equation or Archard wear law. This equation was then validated against a wide variety of materials subjected to abrasive wear by Archard and Hirst (1956) [42]. Later, Rabinowicz (1965) [43] extended the law to abrasion wear. The most common wear model is the Archard wear law. This wear model relates the rate of wear (V) for a given material to the contact pressure (P), slid distance (S) and inversely to the hardness (H):

$$V = K\frac{PS}{H} \qquad \text{……………………………………………………………………eq (2)}$$

Where, K is a dimensionless constant of proportionality known as wear coefficient.

The Archard wear law can also be interpreted as indirectly relating the wear to the energy dissipation at the surface by assuming that the friction force is proportional to the normal load P, through coulomb friction. In 1999, Fouvry et al came out with a modified wear law whereby the wear coefficient is based on the dissipated energy.

Smith et al, 2005 showed that, abrasive surfaces interact; demonstrating mixing, wear particle formation and dislocation movement by molecular dynamics simulations of abrasive wear. They also enable the investigation of the tribological behaviour of a contact at atomic scale interactions. Their model was able to provide vital information on both friction and wear behaviourbased on molecular behaviour. However, these simulations are currently limited to the nanoscale, which makes it no feasible to be applied to real engineering assemblies.

2.7.2 Wear Classifications

Wear can be classified in three apparent ways. One way is in terms of the appearance of the wear scar. Examples are scratched, polished, fretted, pitted and scuffed. The second way involves physical mechanism which removes the material or causes the damage. Delamination, adhesion, oxidative and abrasion are examples of this type of classification. The third classification deals with the conditions surrounding the wear situation. Examples are metal-to-metal abrasive wear, unlubricated wear, lubricated wear, high stress abrasive wear, high temperature metallic wear and rolling wear. These three methods of classification are very useful to the engineer but in different ways. When appearance is used to classify wear, it helps in easier comparison of one wear situation with another. This also helps the engineer predict one wear situation to a newer one due to experience [44].

2.7.3 Wear Measures

Earlier, wear was defined as the removal and deformation of materials from original position on a solid material surface due to the action of another surface. Loss of material and volume of material removed which is the most common damage, can be used as a measure of wear.

Scientifically, it is generally used to measure wear. Mostly for material investigations, mass loss is commonly used to measure wear instead of volume. This is done as a result of the relative ease of performing a weight loss measurement. While mass and volume are often compatible, there are three problems related with the use of mass as the measure of wear. One of these comparisons of materials can only be done if their densities are the same. For bulk materials, this is not a major obstacle, since the density is either known or easily determined. In the case of coatings, however, this can be a major problem, since their densities may not be known or as easily determined. The other two problems are more intrinsic ones. A mass measurement does not measure displaced material, only material removed. In addition, the measured mass loss can be reduced by wear debris and transferred material that becomes attached to the surface and cannot be removed. It is not an uncommon experience in wear tests, utilizing mass or weight loss technique, to have a specimen ‘‘grow’’, that is, have a mass increase, as a result of transfer or debris accumulation [44].

2.7.4 Pin-on-Disk Wear Test

The pin-on-disk test is generally 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 materials [44]. To evaluate the abrasive wear behaviour of material pairs this test has been generally noticed to apply. The volume lost allows calculating the wear rate of the material. Since the action performed on all samples is identical, the wear rate can be used as a quantitative comparative value for wear resistance [45].

The basic configuration is shown in Fig. 2.9. A radius-tipped or flat-ended pin is pressed against a flat disk. The relative motion between the two is such that a circumferential wear path on the disk surface is generated. Either the pin or the disk can be moving. The ASTM standard for this test, ASTM G99, which does specify the use of a rounded pin, does not specify specific values for the parameters, but 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. The test can also be done in a controlled atmosphere and with lubrication [44].

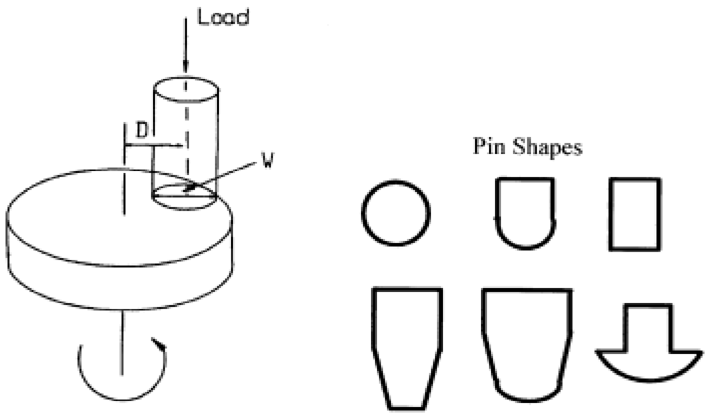


Fig. 2.10: Diagram of pin-on-disk test and cross-sections of pin shapes. With curved surfaces wear is generally confined to the curved region [44].

2.4.5 Wear Tests for Coatings

Generally, to evaluate the wear resistance of coatings, the same tests that are used with bulk materials are applied. In the case of coatings, different test parameters are usually used to evaluate the wear resistance. The test parameters normally used are lower in that the wear evaluated can be limited to the coating. Typical geometrical methods for evaluating wear can be adopted based on the thickness of the coating. If the coatings are thin, then special techniques might be required for the evaluation. For known densities of the coatings, mass loss methods are also doable. Ranking and comparing the life of the coating in the test is often used as an alternative way to measure wear or wear rate behaviour of the coatings. This is identified by examination of the surface for presence of the coating after tests of different exposure or duration. Most often, by monitoring the friction during the test is used to determine the life of the coating. With wear-through, there is often a change in the coefficient friction that can be detected by such measurements [44].

2.4.6 Adhesive Dry Rubbing Wear Factors for Surface Treatments and Coatings

Table 2.2 shows typical wear rate values for some base materials determined from a pin-on-disk abrasive test using a polished hardened steel pin rubbing against the treated disk surface [47]. Wear rate is defined as volume of material removed/unit distance of abrasive/unit loading.

Table 2.2: Typical Wear Rate Values for some Base Materials [47]

Material or Coating	**Typical Wear Rate (**m^3/Nm)
Lubricated hardened steel	10^{-17}
Sprayed Tungsten Carbide/Co	10^{-16}
Plasma Electrolytic Oxidation	10^{-16}
Sprayed Chrome Oxide	10^{-16}
PVD TiN	10^{-16}
Hard Chrome Plate	10^{-15}
Nitrided Alloy Steel	10^{-15}
Nitrided Stainless Steel	10^{-15}
Thermochemically formed Ceramic	10^{-15}
Carburised Steel	10^{-14}
Nitrided Low Alloy Steel	10^{-14}
Glass-Filled PTFE	10^{-14}
Anodised Aluminum	10^{-13}
Hardened Electroless Nickel	10^{-13}
Electroless Nickel, as Plated	10^{-12}
Normalised, unlubricated Steel	10^{-12}
Austenitic Stainless Steel	10^{-11}
Copper Plate	10^{-11}
Electrolytic Nickel Steel	10^{-11}

Aluminium Alloy	10^{-10}
Unfilled PTFE Coating	10^{-10}
Cadmium or Zinc Plate	10^{-9}
Unfilled PFA or FEP Polymer Coatings	10^{-9}
Silver Plate	10^{-8}

CHAPTER THREE

3.0 METHODOLOGY

3.1 Sample Preparation

The first and foremost job for the experiment was the sample preparation. The specimen size should be compatible to the machine specifications: A 50mm diameter rod with length 600 mm was got from mild steel trader. A chemical composition of the MS for both the disk and the pin is given in Table 4.1.

3.1.1 Disk Preparation

In order to carry out the wear test (pin-on-disk) experiment with ease, the heat treatment samples of the as-received mild steel were prepared in a disk form. The counter face or disk, Fig. 3.3, was obtained by cutting a slice from a mild steel rod. Seventeen (17) disks were all machined to 44 mm diameter and 6 mm thickness from a mild steel rod of 50 mm diameter and a length of 300 mm. Sixteen (16) disks of the above dimensions were utilized in both the pack cyaniding heat treatment and the wear experiment. An additional disk was used as a control experiment (untreated). Also, the entire 17 disks were grinded and polished on 60,120,180,240,320,400, and 600 SiC grit papers to reach a value of 0.09 µm for the roughness parameter Ra of the surface.

3.1.2 Pin Preparation

The pins were machined by the conventional methods, i.e., turning and grinding to obtain the desired pin shape with a rounded tip with radius approximately 10 mm as seen in Fig. 3.1. Five (5) cylindrical test pins (fig. 3.2b) with dimensions shown below were fabricated from a different mild steel rod with 300 mm length and diameter of 15 mm. The pin material used was harder than the disk material. These pins were used in the wear experiment.

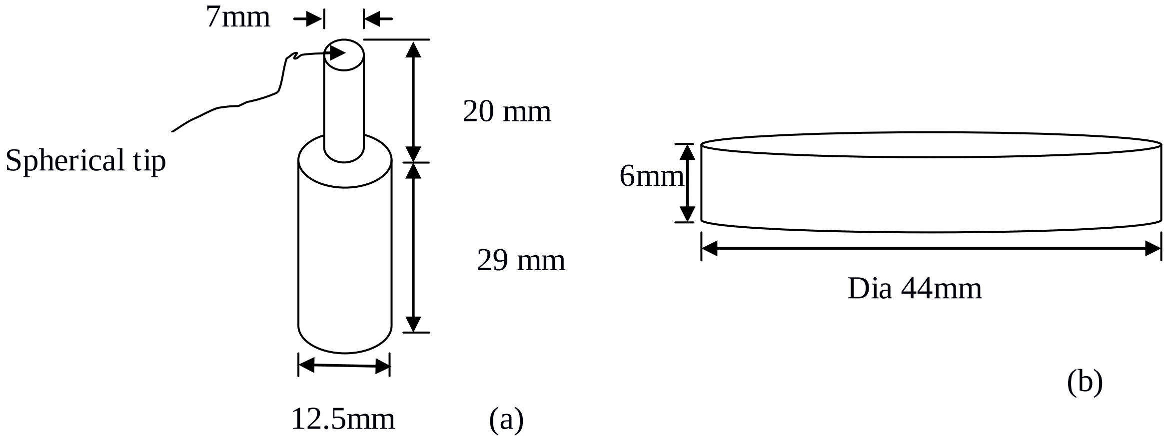


Fig. 3.1: (a) Test Pin dimension (b) Test Disk dimension

(a)

(b)

Fig. 3.2: (a) the Prepared Test Disk. (b) The Prepared Test Pin

3.1.3 Metallographic Sample:

Seventeen (17) rectangular shaped samples (20x20x10 mm^3) were cut from the same mild steel rod which was used to fabricate the disk. Each of the 16 rectangular samples was heat treated along side with the 16 disk samples. The rectangular sample treated under the same condition as the disk was used for the metallographic specimen preparation to determine both the microstructure of the cases formed.

3.1.4 Cyaniding Boat

Sixteen (16) heat-treatment boxes (cyaniding boats) of 70 mm × 100 mm × 80 mm (fig. 3.6b) were constructed using mild steel plates of 3 mm thickness. The space contained in each boat was able to accommodate the heat treatment powder mixture, one standard mild steel disk specimen and one rectangular test specimen.

3.2 Cassava Leaves Powder Preparation

The specie of the cassava used is manihot esculenta (bitter variety) which was gotten from a farm near EMDI, Akure-Nigeria. Two (2) 50 kg rice bag of cassava leaves were freshly harvested from eight month old cassava plant. The leaves were then oven-dried at about 72 ^{o}C to liberate the moisture content of the leaves without turning the leaves brown (Fig 3.4a). Oven dried is preferred to sun dried, because sun-drying eliminate more cyanide than oven-drying (82 to 94% vs 68 to 76%, respectively) [45]. The oven drying process reduces the rate of liberation of HCN which is the component to be utilized in the heat treatment. Drying of the leaves was stopped only after constant weights reading on the scale was obtained and were collected in a sack for pulverizing.

(a) (b)

Fig. 3.3: Cassava Plant (a) Bitter Variety with Yellowish Leaf Stalk. (b) Sweet Variety with Reddish Leaf Stalk


(a) (b)

Fig. 3.4: (a) Oven-Drying of Cassava leaves at 72oC. (b) Dried Cassava Leaves after Oven Drying at 72^{o}C

3.2.1 Sieve Analysis

To obtain different particle sizes, the oven-dried cassava leaves were pulverized in a hammer milling machine. The powder obtained was subjected to sizing in an octagon sieve shaker machine as shown in fig. 3.9. Four particle sizes (fig. 3.5b) were needed for this work and so four aperture sizes of 850, 600, 300 and 212µm were selected and arranged in descending order. The milled powder was put in 850µm aperture size and the sieve shaker was subjected to vigorous vibration. Four different sizes were then collected and the procedure was repeated till all the milled powders were sieved. The various particle sizes were then gathered separately and preserved for use in the heat treatment stage.

(a) (b)

Fig. 3.5: (a) Octagon Sieve Shaker Machine for Sieve Analysis. (b) Four Particle Sizes of PCLs Used

3.3 High-Temperature Pack Cyaniding Treatment Procedure

16 disk-shaped samples were utilized for the pack cyaniding process. Eight (8) disk samples were used in the heat treatment process to investigate the effect of pack cyaniding temperature on the case hardness and abrasive wear properties of the PCMS. The pack cyaniding processes were performed at four different temperatures at 750°C, 800°C, 850°C and 900°C in an Omszov heat-treatment furnace (fig. 3.6a) of 1200 °C capacity. Also, the other 8 disk-shaped samples were used to study the effect of the particle size of the PCL on the case hardness and abrasive wear property of the treated samples.

For the high-temperature pack cyaniding, each particle size obtained was divided into four equal parts and mixed with $BaCO_3$ using volume ratio of cassava leaf powder to $BaCO_3$ proportion of 4:1. The $BaCO_3$ was added as an energizer. Four batches (Batch 1, 2, 3 and 4) were used for the high temperature pack cyaniding. The standard mild steel disk specimens and the rectangular specimen were completely embedded in the processed cassava leaves powder mixture contained in the boats. Each of the boats were covered with mild steel lid and sealed with fire clay to entrap the gases generated and to also provide a reducing atmosphere in the boat.

3.3.1 Labelling of Samples

The cyaniding boats containing the specimens and the processed powder mixture were labelled with the following codes:

- A750, B750, C750 and D750 for Batch 1
- A800, B800, C800 and D800 for Batch 2
- A850, B850, C850 and D850 for Batch 3
- A900, B900, C900 and D900 for Batch 4

Where, A, B, C and D represent powder of sizes 212, 300, 600 and 850µm respectively and the numbers representing the respective temperature used.

(a) (b)

Fig. 3.6: (a) High-Temperature Pack Cyaniding Treatment. (b) Four Cyaniding Boats removed from the furnace for air cooling

3.3.2 Pack Cyaniding Procedure

- The pack cyaniding was done in four (4) batches
- Each batch contains four cyaniding boats placed on a 130 x 180 mm^2 base plate
- Batch 1, 2, 3 and 4 were austenitised at a temperature of 750°C, 800°C, 850°C and 900°C for 3 hours each, respectively
- All the batches were started from room temperature and after attaining the required temperature and soaking time, they were air cooled

(a) (b)

Fig. 3.7: (a) Four Burnt PCL Particle Sizes after Pack Cyaniding. (b) Four Burnt PCL Particle Sizes after Pack Cyaniding with their corresponding initial state

3.4 Metallography

In preparing the specimens for microstructural studies, each of the 20x20x10 mm^3 pack cyanided rectangular specimen was cross-sectioned about 10 mm from its tip in a direction perpendicular to the flat surface of the tip. The cross-sectioned surface was roughly ground on 60, 120, 180, 240, 320, 400, and 600 SiC grit papers of the Buehler grinding machine. Water from running tap was constantly supplied to avoid rising temperature and also to wash off chopped pieces of metallic samples that were generated as a result of abrasion. Rough polishing was carried out on 800 and 1200 SiC grit papers while final polishing was accomplished with a 0.1 µm diamond suspension paste to obtain a mirror finish.

All the samples were etched with 2% nital (2% concentarated HNO_3 acid and 98% ethanol) for few seconds, washed under a running tap of water, washed with some alcohol and then dried using hand blower. Microstructural examination was carried out on the cyanided mild steels and untreated samples and details about the microstructure of the pack cyanided samples, as a function of treatment temperature and particle size, were characterized by optical microscopy (OM). The microstructures of the specimens were studied using the Olympus BH-2 microscope with a digital camera.

3.5 Case Hardness Measurement

To determine the hardness (both at the core and at the edges) of treated steel samples, a LECO ASTM E384 Microhardness tester was used. The specimens used for hardness were the samples used for microscopy test. The hardness was measured base on three measurements using a load of 490.3 mN (49 g) for 10 s through a diamond pyramid indenter at the polished surface of each sample. The average hardness of the untreated mild steel for the disk was 121.5 VHN. The hardness of the treated samples was measured and recorded. Also, the average hardness of the pin material was measured and recorded.

3.6 Wear test and analysis method

Abrasive wear tests of the pack cyanided mild steel specimen were carried out on a pin-on-disk wear testing machine which contained a fractional transducer to record the wear data at ambient temperature (25^{o}C). Figure 3.8 shows the abrasive wear test configuration where the test disk and pin are in place. The disk is made of treated MS whose dimension is 44 mm diameter and 6 mm thickness. The pin was made from mild steel of different composition with diameter of 12.5 mm and average hardness of 197.5 VHN.

3.6.1 Cleanliness

The pins and disks were first cleaned by concurrently wiping with laboratory tissue paper and acetone to remove any trace of dirt or oxidation. Before every test, the tip of the pins was reconditioned by using 600 SiC grit abrasive papers.

3.6.2 Wear Test Procedure

The base of the machine was first levelled in the horizontal position by adjusting the rubber pads at each corner. Before the test, the initial mass of both the pin and the disk were determined separately in an analytical balance with resolution 0.1 mg. Next, the initial surface roughness of each disk was determined using surface profilometer. The test pin was then inserted in the pin-holder. The pin holder was held in the load arm and placed at a level that allow the tribometer arm to be horizontally levelled while resting on the disk to make sure that vertical load is applied. Counter weights were applied to balance the arm to ensure that the pin holder and arm initially exert no force on the disk surface. Table 3.1 shows the wear test parameters used for the test.

Table 3.1 – Parameters used for performing the wear tests

Force applied	20 N
Speed of rotation	200.0 rpm
Sliding velocity	0.26 m/s
Radius of wear track	12.2 mm
Duration of each test	10.0 minutes
Total abrasive distance	156 m

Table 3.2: Environmental conditions

Lubricant	None
Atmosphere	Air
Temperature	25°C

Deadweight of 20N was applied vertically on the arm to press against the rotating disk to corresponding to the normal load required for the test. Throughout the test, the pin was kept stationary in the wear process whiles the disk wears against the static pin. Next, the abrasive track radius and the revolutions counter were set to the operation conditions. After each wear test, the weights of the pin and the disk were determined to measure the weight loss. Surface profilometer was used to determine the depth of the wear track after the wear test which was then used to calculate the wear volume.

(a) (b)

Fig. 3.8: (a) Pin-On-Disk Wear Test Setup. (b) Test Disk and Pin inserted on the sample stage

CHAPTER FOUR

4.0 RESULTS/ DISCUSSION

4.1 Composition Analysis

The nominal composition of as received mild steel for both the disk and the pin is shown in table 4.1 and 4.2 respectively.

Table 4.1: Chemical composition of as received mild steel for the disk

C%	**Si%**	**Mn%**	**Cr%**	**Ni%**	**S%**	**P%**	**Cu%**	**Al%**	**Nb%**	**Mo%**	**Fe%**
0.216	0.199	0.71	0.01	0.02	0.039	0.018	0.019	0.030	0.0020	0.011	98.6

Table 4.2: Chemical composition of as received mild steel for the pin

C%	**Si%**	**Mn%**	**Cr%**	**Ni%**	**S%**	**P%**	**Cu%**	**Al%**	**Nb%**	**Mo%**	**Fe%**
0.322	0.192	0.62	0.060	0.035	0.012	0.023	0.029	0.0001	0.0009	0.01	98.7

4.2 Case Formation and Micrographs

The microstructure of the as received mild steel used for the present study is given in Table 4.3 and 4.4. Optical microscope images of some of the cases identified for the treated samples are shown in Table 4.5. Each paired micrograph shows microstructures of specimens' cross-section case and core that proves case formation. Visually, distinct cases were observed by optical microscope after the mild steel samples were pack cyanided at varying temperatures in different particle sizes of processed cassava leaf. Results obtained from micro-indentation of untreated samples and pack cyanided samples are presented in Table 4.6 and 4.7 respectively. These values are plotted as a function of pack cyaniding temperature in Fig. 4.1

and as a function of particle size of processed cassava leaves in Fig. 4.2. Fig. 4.3 is a bar chart of case hardness showing particle size groups.

Table 4.3: Micrograph of untreated material for the disk

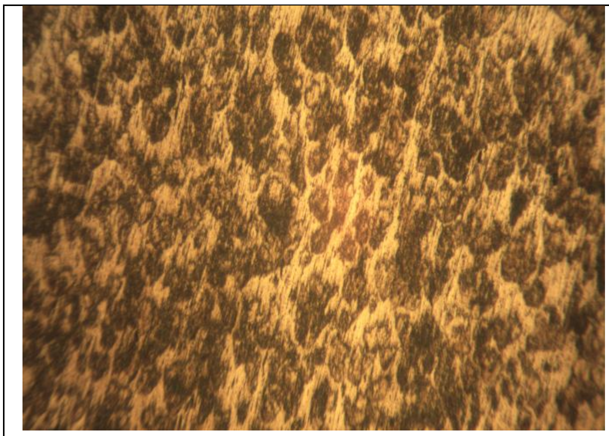
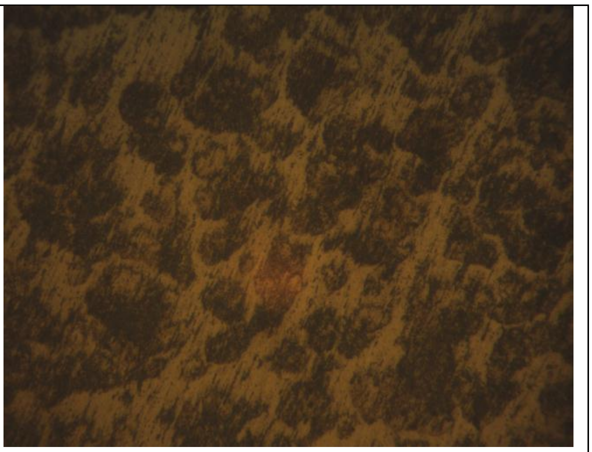
	
X200	X400

Table 4.4: Micrograph of Pin material

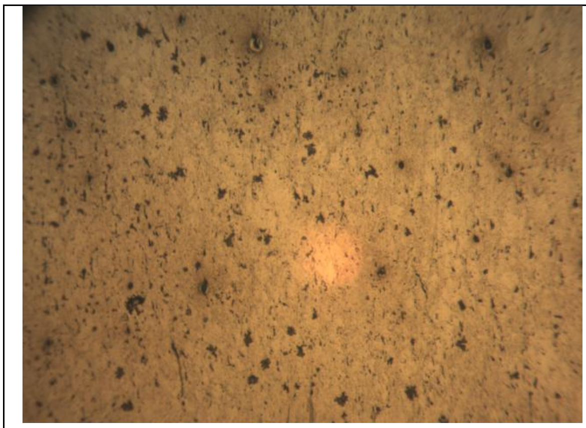
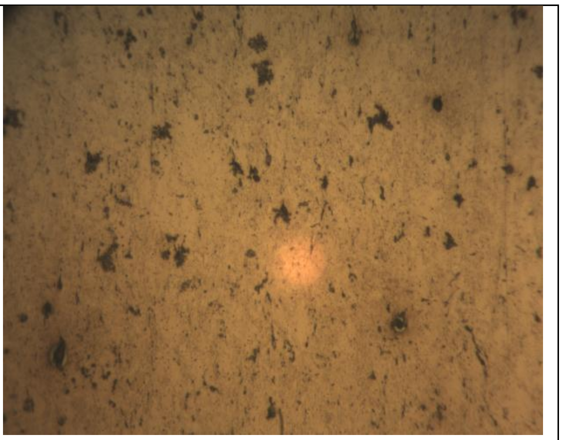
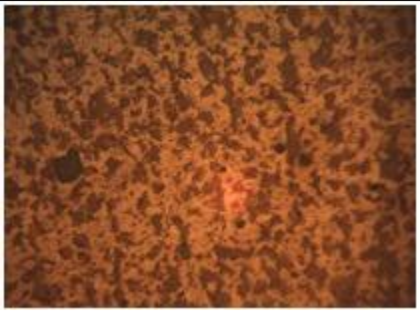
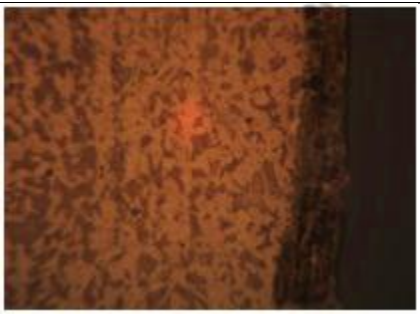
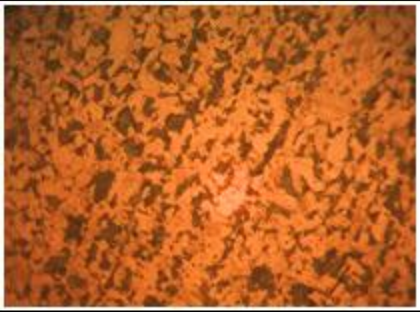
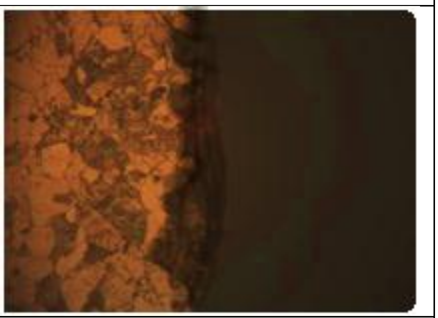
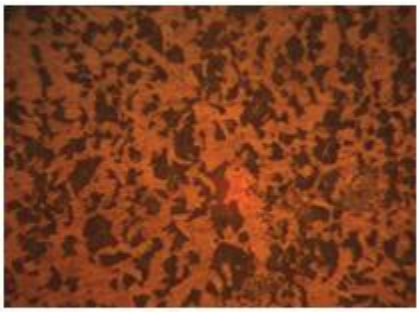
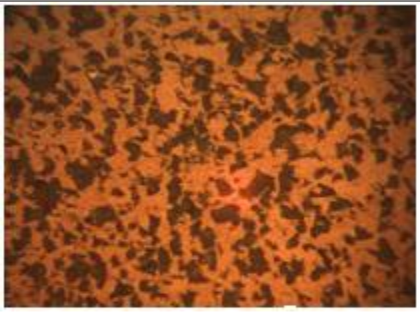
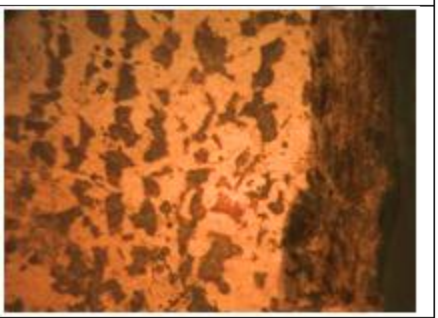
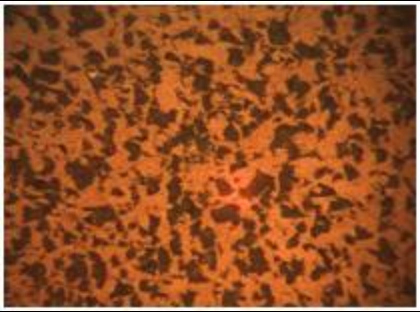
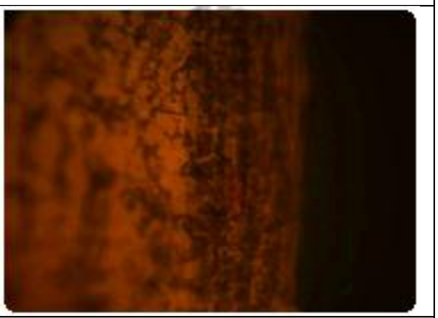
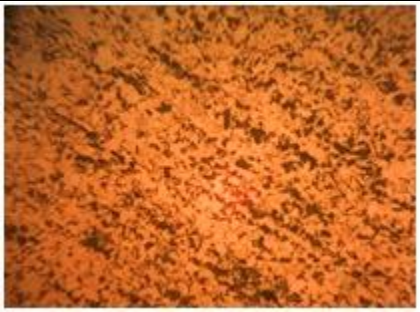
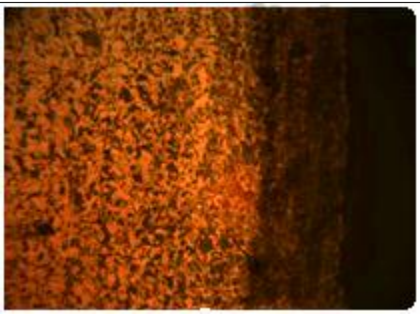
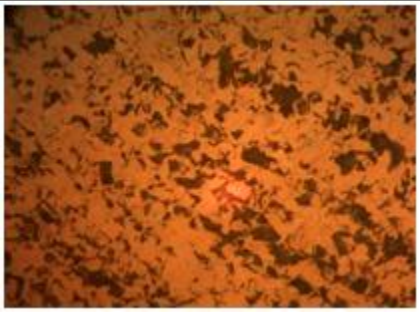
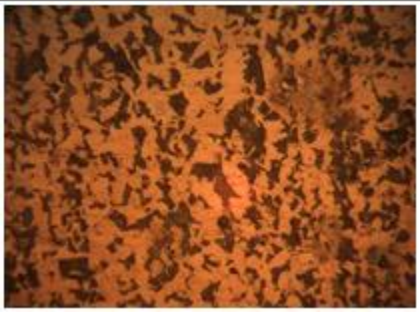
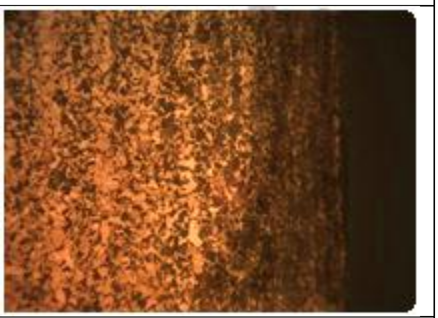
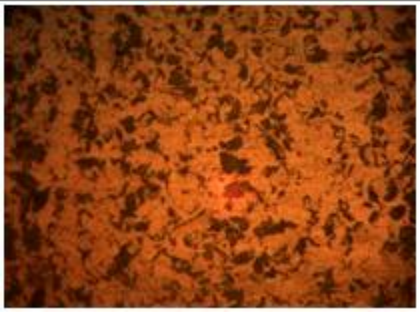
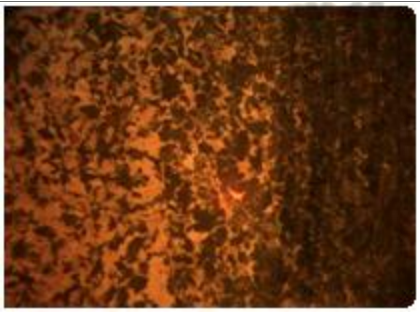
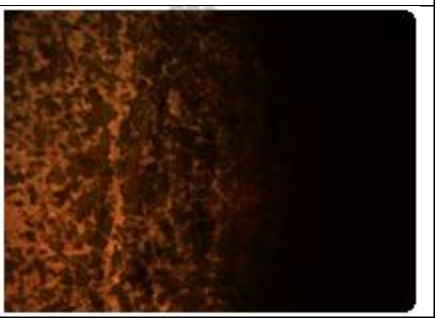
	
Pin X200	Pin X400

Table 4.5: Some of the cases identified using optical microscope

212µm 800°C (A800)		
	Core X200	Case X200
212µm 900°C (A900)		
	Core X200	Case X400
300 µm 850°C (B850)		
	Core X200	Case X200
300 µm 900°C (B900)		
	Core X200	Case X400

300µm 800°C (B800)		
	Core X200	Case X200
600µm 850°C (C850)		
	Core X200	Case X400
600µm 900°C (C900)		
	Core X200	Case X200
600µm 900°C		
	Core X400	Case X400
850µm 750°C (D750)		

	Core X200	Case X400
850µm 750^{o}C		
	Core X200	Case X200
850µm 900^{o}C (D900)		
	Core X200	Case X200
600µm 900^{o}C (C900)		
	Core X400	Case X400
600µm 900^{o}C (C900)		
	Core X200	Case X200

In the micrographs, dark region represents pearlite phase that shows carbon pickup from the processed cassava leaf while light region is ferrite phase. Also, looking at the case micrographs, the dark portion at the right end side of the specimen is the case formed. Due to the diffusion, this portion is very rich in carbon and is composed of predominant pearlite phase. SEM and optical images showed that, the nitrogen and carbon contents diffused into the surface during pack cyaniding were found to be pack cyaniding temperature and particle size dependent. The microstructure of the mild steel in as received condition is mostly pearlitic. After different treatments there is a change in matrix/phase structure due to the diffusion of both nitrogen and carbon. The diffusion of atoms into the steel depends on the initial microstructure of the steel. Fine-grained steels that have small grains and numerous grain boundaries do not carburize or harden as deeply as the coarse-grained steels (Samuels, 1999). Though, carbon tends to be attached to dislocation centers but the numerous grain boundaries impede the drift of carbon into the steel. Consequently, diffusing carbon atoms will not travel far before being locked in the subsurface. Coarse-grained steel possesses fewer grain boundaries. Movement of dislocation here is less constrained and the diffusion of carbon atoms is enhanced. At high temperatures, both substitutional and interstitial diffusion takes place for carbon atoms diffusing into steel. Eventually, larger proportion of the diffusion of carbon into steel occurs through the matrix and not through the grain boundary.

Aside the inherent grains that affect the diffusion of atoms, the particle size of the processed cassava leaf also affect the diffusion during the pack cyaniding process. It was seen from the experiment that, the finer the particle size, the higher the packing density. The higher the packing density, the lower the diffusion due to the fact that the particles are not loosely packed; and the atoms generated from the cyaniding medium cannot easily find their way to the surface of the steel to be diffused. The converse is also true, the larger the particle size, the higher the diffusion as evident in the micrographs shown in table 4.5. A critical look at the micrographs shows a change in the length /and sharpness of the pearlite. This brings about much difference in the matrix pattern of 16 treated samples.

From the micrographs, it could also be seen that the cases are not too thick because the samples were air cooled (Samuels, 1999). This makes the change from high to low carbon to be abrupt. Furnace cooling involves gradual penetration and the case is deeper (Samuels, 1999).

During furnace-cooling, the specimen is allowed enough time in the furnace which makes the diffusion to continue for a much longer time than air cooling until the temperature falls below A_1 (723 ^{o}C). While air-cooling allows the diffusion process occuring on the surface of the specimen to truncate- making the case relatively shallower.

4.3 Microhardness Results

The microhardness of various mild steel studied at different pack cyaniding temperatures and particle sizes is as shown in table 4.7. The pack cyaniding treatments allow increasing the surface hardness of about three times in respect to the untreated mild steel. This can be caused by the diffused carbon and nitrogen that forms carbides with carbide forming element such as molybdenum. All the treated samples show high case hardness values, which remain approximately constant through the modified layer and then steeply decrease to matrix values. The variation in hardness with respect to cyaniding temperature is graphically shown in fig. 4.1. It shows decreasing trend in hardness with increase in treatment temperature. This trend has been observed in other mild steel as well [16, 19]. Several PCMSs were investigated in the literature and the trend almost repeats for every one of them. Mild steel sample A750 exhibited the lowest microhardness while the steel sample D800 had the highest hardness for all temperature values used.

The highest surface hardness of all steels samples at all temperature values was obtained when the heat treated samples were pack cyanided with particle size of 850µm. Generally, the surface hardness of pack cyanided heat treated steels depends on the treatment time and the heat treatment temperature. Also, the particle size of the powder used in cyaniding boats has a significant effect on the hardness property of the steel.

Table 4.6: Hardness Value of Untreated Samples

Sample	**Hardness (VHN)**
Disk Material (E)	121.5
Pin Material (P)	197.5

Table 4.7: Hardness Values of Mild Steel Samples Pack-Cyanided in PCL

		Case Hardness (VHN)			
Particle size (µm)		(A) **212**	(B) **300**	(C) **600**	(D) **850**
Pack cyaniding Temp (°C)	**750**	123.2	150.5	160.9	163.9
	800	146.0	155.0	161.3	165.8
	850	134.8	140.1	147.1	147.7
	900	158.0	160.1	149.5	165.0

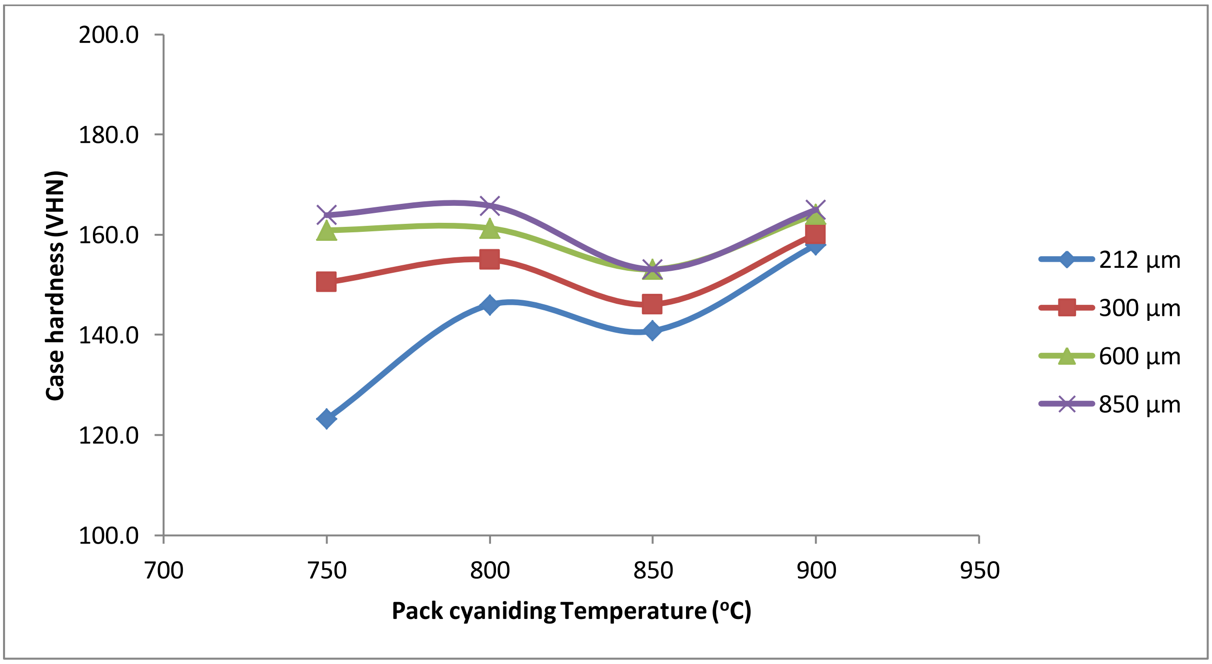


Fig. 4.1: Case Hardness as a Function of Cyaniding Temperature

4.3.1 Variation of Case Hardness with Pack Cyaniding Temperature

Fig 4.1 is a plot of case hardness as a function of cyaniding temperature for high temperature pack cyaniding. Generally, it could be seen that the case hardness increases as pack cyaniding temperature increases. However, at a temperature of 850°C there was a fall in the case hardness and it shoot up again at a temperature of 900°C. This general trend occurred for all the four particle sizes and shows a wavy nature. The reason for this gentle wavy form is partly due to the organic nature of the cassava leaves powder (Akinluwade, 2010).

Also, the reason for the increase in case hardness with increase in temperature for the particle sizes is due to the increase in rate of diffusion of nascent and atomic carbon and nitrogen as temperature is increased.

Diffusion coefficient which is the measure of mobility of diffusing species is given as:

$$D = D_o \exp\left(\frac{-Q_d}{RT}\right) \quad \text{……………………………………………………………………. eq. (9)}$$

Where, D_o is temperature-independent preexponential (m^2 /s)

Q_d is the activation energy for diffusion (J/mol or eV/atom)

R is the gas constant (8.31 J/mol-K or 8.62×10^{-5} eV/atom-K)

T is absolute temperature (K)

From eq. (9) it could be seen that, increase in temperature increases the diffusion coefficient which is a measure of mobility of diffusing species. This implies an increase in temperature increases atoms' speed (kinetic energy) to enhance the diffusion process. So the atoms move faster which means that diffusion occurs quicker. This is more easily achieved when the atoms vibrate strongly, that is, at high temperatures more energy is given to the atoms to overcome energy barriers to enhance atomic motion. In order for atoms to diffuse they must overcome the energy barrier associated with changing their position. The more kinetic energy the atoms have, the more likely it is that the energy barrier will be overcome. If the temperature of the cyaniding medium is high, the kinetic energy of the atoms is greater and the higher the diffusion. This therefore explains why temperature has a significant effect on the diffusivity of the species.

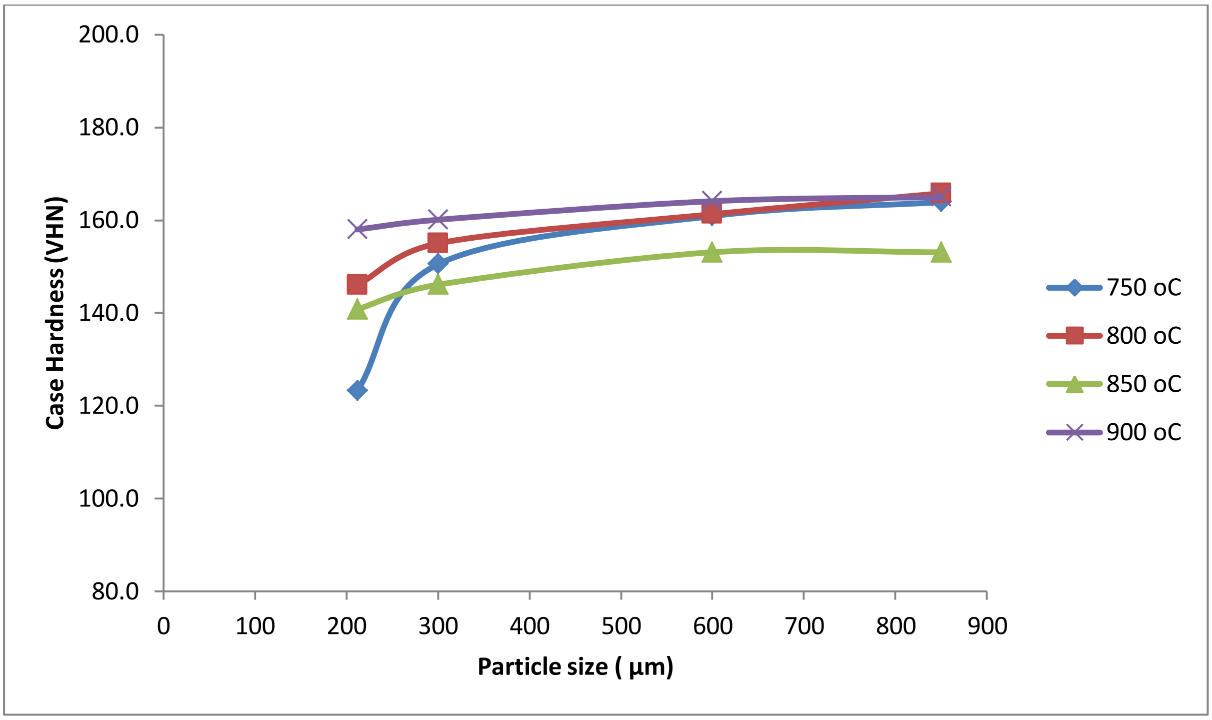


Fig. 4.2: Case hardness as a function of particle size

4.3.2 Variation of Case Hardness with Cassava Leaves Particle Size

Fig 4.2 and 4.3 show the dependence of case hardness on cassava leaves particle size for high temperature pack cyaniding. The case hardness determined for all the cyanided samples showed a dependence on particle size of processed cassava leaves powder. It was generally observed that case hardness increases with particle size at constant soaking time—this is the general trend displayed by all the pack cyaniding temperatures. This really shows that there has been significant diffusion of carbon and nitrogen from the processed cassava leaves powder into the steel. The observed variation is due to the fact that larger particle sizes release their nascent carbon gradually over time; hence more carbon atoms are allowed to diffuse thereby producing high case hardness and deeper cases [13]. However, the smaller particle sizes burn off more rapidly (due to its fine size) dissipating most of their carbon which results in shallow cases [19] and less case hardness.

Also, the trend was observed due to the variation of the packing density of the various sizes of the powder used. The smaller the particle size the higher the packing density and the larger the particle size, the lower the packing density. When the packing density is high, the particles are too close that the nascent nitrogen and carbon generated from the decomposition of HCN is hindered. Consequently, more of the nascent nitrogen and carbon do not get access to the surface of the steel to be diffused. However, when the particles are large, the atoms can easily move to the surface of the steel since the particles are loosely packed (low packing density).

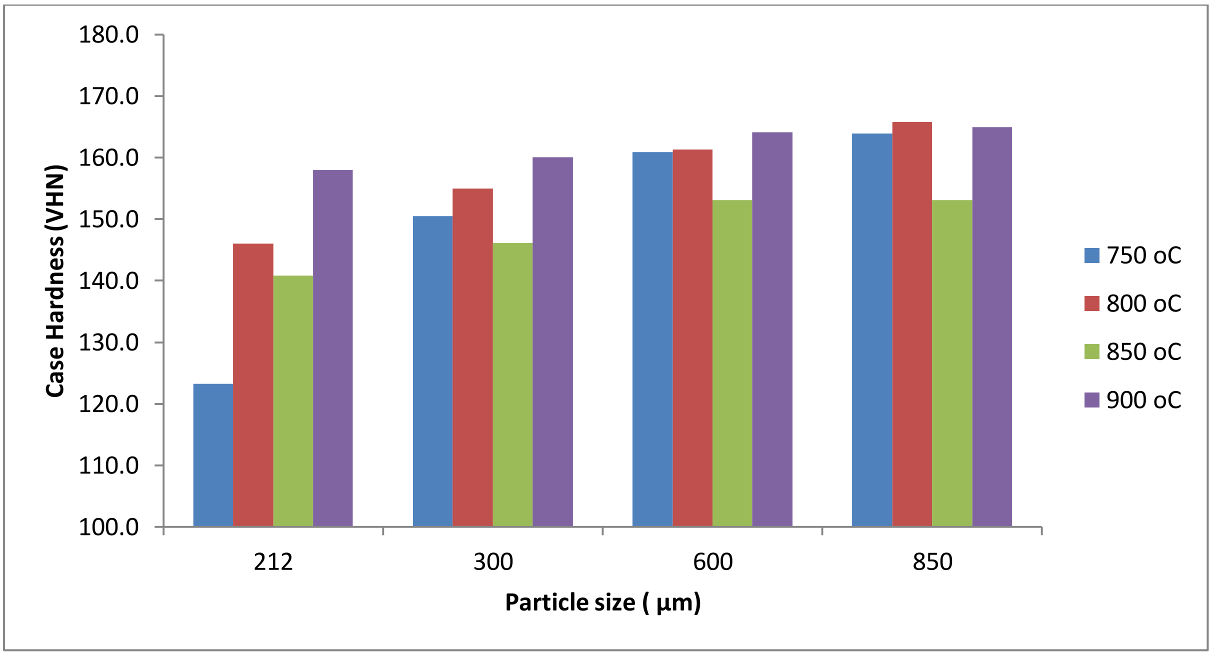


Fig. 4.3: Case hardness as a function of particle size

4.4 Deductions from Packing Cyaniding

The following deductions can be made from the results provided above.

1. Visually distinct cases were formed at the surfaces of mild steel samples pack cyanided at 750, 800, 850 and 900 ^{o}C in processed cassava leaves of particle sizes 212, 300, 600 and 850 µm at a constant soaking time of 3 hours. This finding corroborates the works of Adetunji et al, (2008) and Akinluwade (2010).
2. The Vickers hardness values obtained for the cases were consistently higher than those obtained for the core.
3. The two variables of this study (pack cyaniding temperature and particle size of processed cassava leaves) were responsible for the variation in hardness values from one sample to another.
4. With little deviations, hardness generally increases with particle size as well as with pack cyaniding temperature. In addition to reasons offered in existing literature for this hardness—particle size trend, it is proposed here that the packing density of smaller particles, being higher than that of larger sizes, occludes considerable nascent carbon and nitrogen from reaching the surface of samples for effective diffusion.

4.5 Pin-On-Disk Test Results

In Table 4.8 to 4.11, the experimental results for the pin-on-disk tests are presented. Although all the pins have the same hardness value of 197.5 VHN, the disk wear rate varied substantially due to the disk different hardness.

4.5.1 Effect of Pack Cyaniding on Wear Properties of Pack Cyanided Mild Steel

Wear test experiment was carried on the both the treated and untreated samples using pin-on-disk machine. Surface profilometry method was used to determine the wear volume of each sample, since the present work is concerned with coatings on mild steel. The wear rate of each sample was determined from the wear volume. Wear volume, wear rate and wear resistance can be calculated as follows.

1. Wear volume: - determined from surface profilometry

2. Wear rate: - It is given by wear volume per unit distance travelled [46]

$$Wear\ Rate = \frac{Wear\ Volume}{Sliding\ distance}$$

Abrasive distance is given by:

$$\text{Abrasive distance} = \text{Velocity (V) x time (t)}$$

$$= \frac{2\pi RN}{60}\ \text{x t}$$

Where, R = wear track radius of the disk (12.2 mm)

N = R.P.M (200)

Π = 3.14 (constant)

Time = 5 minute = 600 s

3. Wear resistance: - wear resistance is a reciprocal of wear rate

$$Wear\ Resistance = \frac{1}{\text{wear rate}}$$

Table 4.8: the summary of disks-wear parameters under load of 20 N

	Wear Volume (mm^3)	**Wear Rate (mm^3/m)**	**Wear Resistance (m/mm^3)**
Untreated Sample (E)	0.044529262	0.000285444	3503.314

Table 4.9: Wear Volume Values of Pack-Cyanided Mild Steel Samples under load of 20 N

Wear Volume (mm^3)					
		(A)	(B)	(C)	(D)
Particle size (μm)		**212**	**300**	**600**	**850**
Pack cyaniding Temp (°C)	**750**	3.18E-02	2.67E-02	2.42E-02	2.29E-02
	800	2.29E-02	2.04E-02	1.91E-02	2.04E-02
	850	1.65E-02	2.16E-02	1.40E-02	1.27E-02
	900	1.27E-02	1.02E-02	8.91E-03	6.36E-03

Table 4.10: Wear Rate Values of Pack-Cyanided Mild Steel Samples

Wear Rate (mm^3/m)					
		(A)	(B)	(C)	(D)
Particle size (μm)		**212**	**300**	**600**	**850**
Pack cyaniding Temp (°C)	**750**	2.04E-04	1.71E-04	1.55E-04	1.47E-04
	800	1.47E-04	1.30E-04	1.22E-04	1.30E-04
	850	1.06E-04	1.39E-04	8.97E-05	8.16E-05
	900	8.16E-05	6.52E-05	5.71E-05	4.08E-05

Table 4.11: Wear Resistance Values of Pack-Cyanided Mild Steel Samples

Wear Resistance (m/mm^3)					
		(A)	(B)	(C)	(D)
Particle size (μm)		**212**	**300**	**600**	**850**
Pack cyaniding Temp (°C)	**750**	4.90E+03	5.84E+03	6.45E+03	6.81E+03
	800	6.81E+03	7.66E+03	8.17E+03	7.66E+03
	850	9.43E+03	7.21E+03	1.11E+04	1.23E+04
	900	1.23E+04	1.53E+04	1.75E+04	2.45E+04

4.5.2 Effect of Pack Cyaniding Temperature on Wear Resistance of PCMS

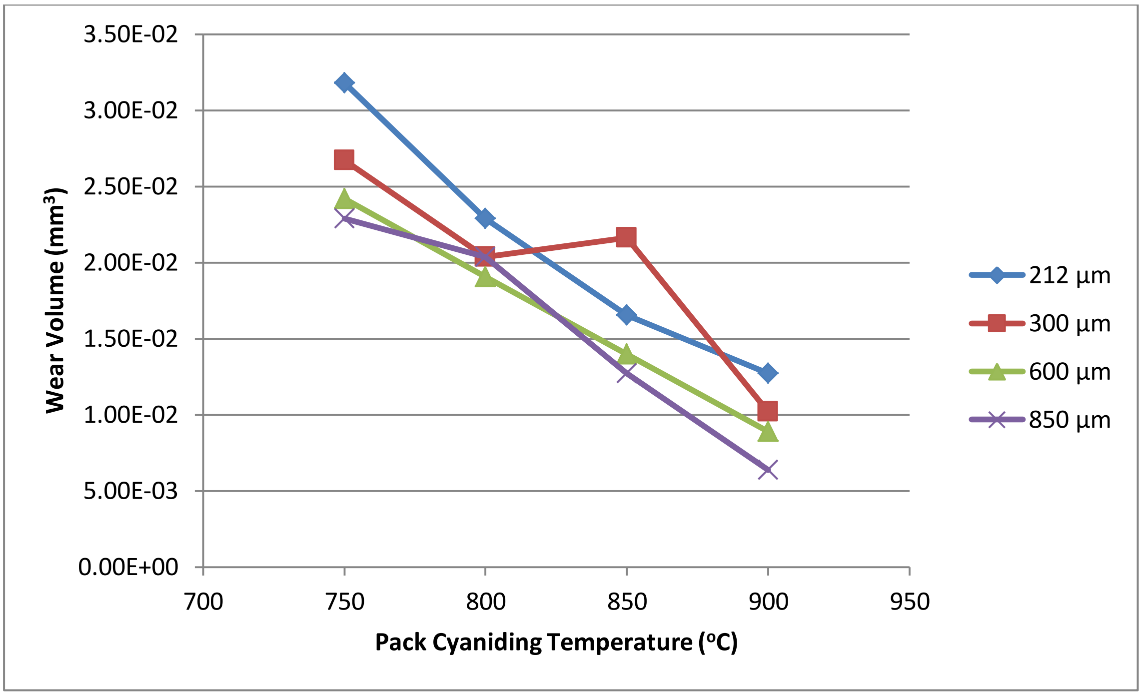


Fig. 4.4: Wear volume as a function of pack cyaniding temperature

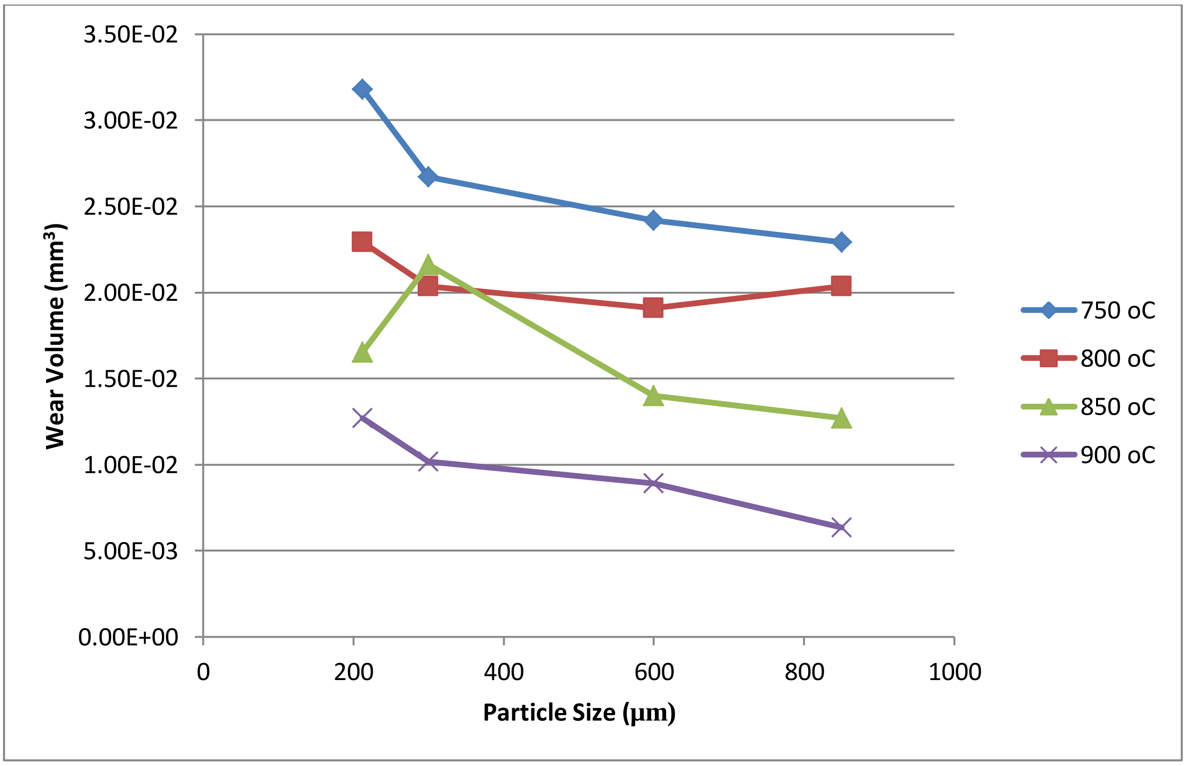


Fig. 4.5: Wear volume as a function of particle size

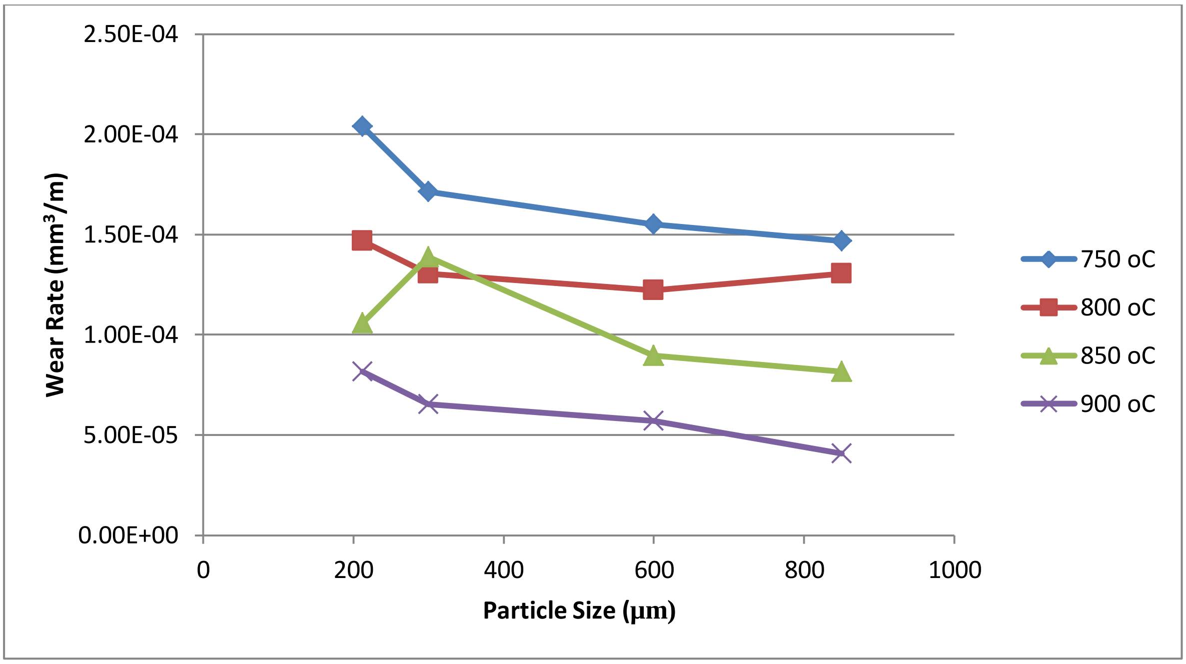


Fig. 4.6: Wear rate as a function of particle size

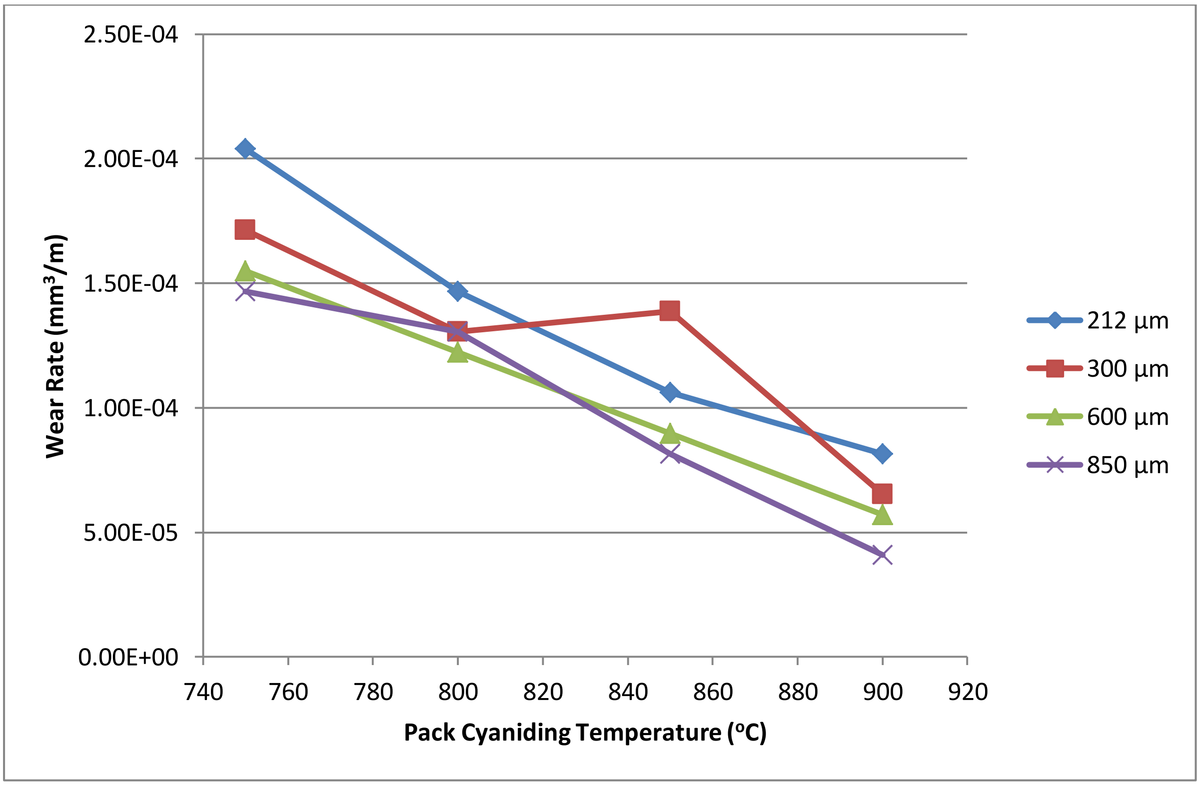


Fig. 4.7: Wear rate as a function of pack cyaniding temperature

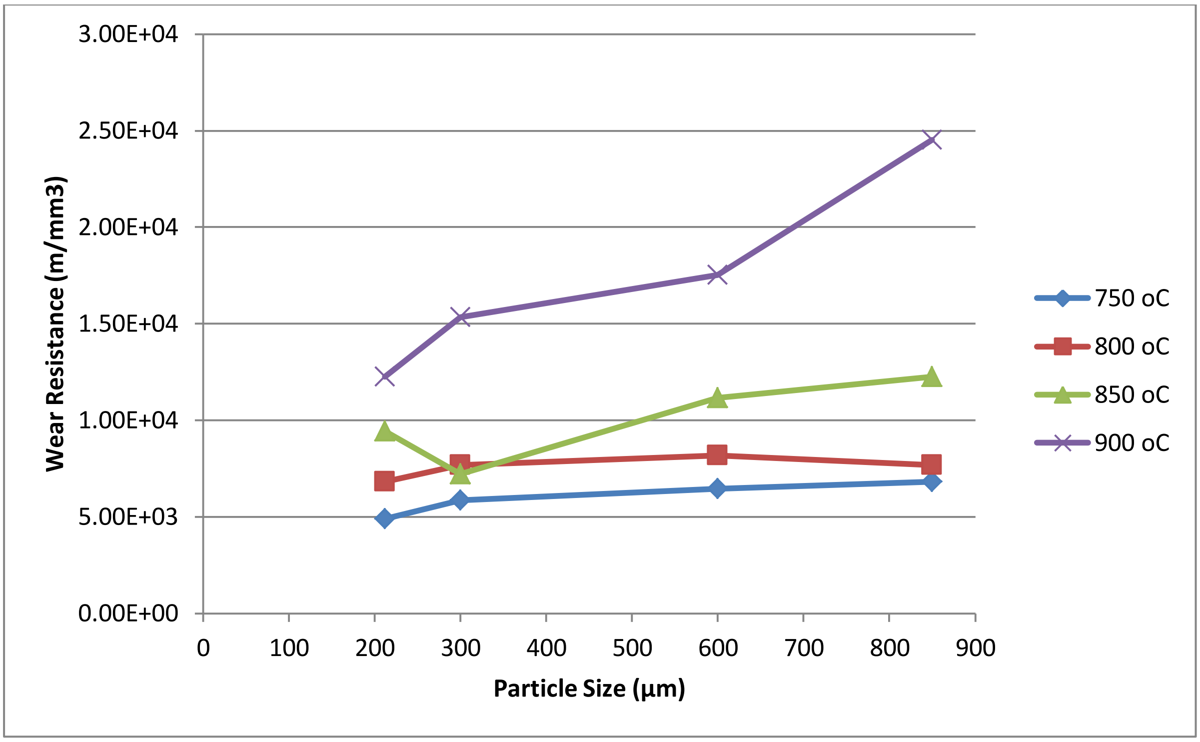


Fig. 4.8: Wear Resistance as a function of particle size

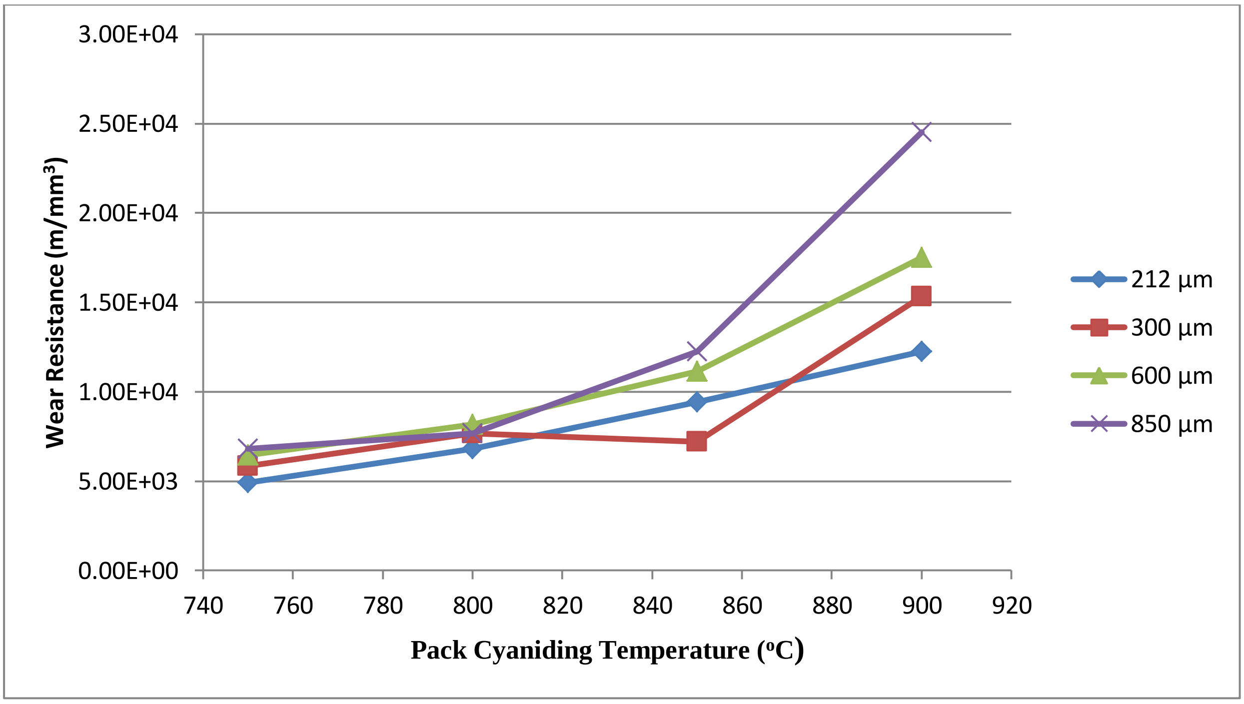


Fig. 4.9: Wear resistance as a function of particle size

The wear loss trend of the samples at varying cyaniding temperature and particle size is as shown in Fig. 4.4 to 4.9. Obviously, the untreated steel sample exhibited a very poor wear resistance as evidenced by the deep and wide wear tracks on the sample surface due to the fact that the case is not treated. In comparison, the pack cyanided samples exhibited considerably less wear which shows that there has been diffusion of carbon which has improved the surface hardness of the steel. The wear track on the cyanided surface was found to be shallow due to the effect of pack cyaniding on the case hardness. The improvement of wear resistance for pack cyanided mild steel is considered as a result of the combined effects of the microstructure and the high case hardness which can resist plastic deformation in the cyanided layer. The nitrogen that is introduced in cyanided layer generates high compressive residual stresses that tend to close the formed micro-cracks or hinder their formation during wear [41, 42].

It was seen that the wear volume gradually increases with decrease in cyaniding temperature and particle size. This could be explained as a result of diffusion which is favoured at higher temperature at larger particle size. The wear volume is lowest for the sample D900.

4.5.3 Effect of Pack Cyaniding Temperature on Wear Volume of PCMS

As shown by Fig. 4.4, the pack cyanided steel showed a decrease in its wear volume as the cyaniding temperature is raised from 750^{o}C to 900^{o}C. But the contribution of this parameter on wear volume was relatively small in comparison to the effect of particle size.

The decrease in wear volume with increase of pack cyaniding temperature from 750^{o}C to 900^{o}C is believed to be due to the increase in case hardness caused by diffusion of carbon at increasing pack cyaniding temperature.

It could be seen that mild steel, pack cyanided in particle size of 300 µm, showed a different behaviour in the variations of its wear volume with cyaniding temperature. As evident in Fig. 4.4, the wear volume decreased with increasing cyaniding temperature up to 800 ^{o}C and thereafter started increasing to 850^{o}C and then decrease again to 900^{o} C. This is most probably due to other reaction that occurs at 850 ^{o}C that hinders diffusion and so carbon pick up is less.

4.5.4 Effect of Particle Size on Wear Volume of Pack Cyanided Mild Steels

Also, it is evident in fig 4.5 that, wear volume decreases with increase in particle size from 212 µm to 850 µm. This is generally believed to be due to the dependence of case hardness on cassava leaves particle size for high temperature pack cyaniding. The observed variation is due to the fact that larger particle sizes release their nascent carbon gradually over time than smaller particle size; hence more carbon atoms are allowed to diffuse thereby producing high case hardness and deeper cases [13]. Also, the trend was observed due to the variation of the packing density of the various sizes of the powder used as explained earlier.

There is an observed abnormality in the general trend (fig. 4.5) at 850 ^{o}C for particle size of 300 µm due to the unexpected reaction that is believed to occur at cyaniding temperature of 850 ^{o}C. Fig. 4.7 shows a decrease trend in wear rate with increasing pack cyaniding temperature due to the direct relationship between wear volume and wear rate.

4.5.5 Effect of Pack Cyaniding Temperature on Wear Resistance of PCMS

The variation of pack cyaniding temperature with wear resistance due to abrasive is shown in the Table 4.11 and it is also graphically represented in the Fig.4.9. From these results it was realized that the wear resistance is highest for the mild steel pack cyanided at temperature of 900 ^{o}C and it is lowest for the mild steel pack cyanided at temperature of 750 ^{o}C.

The curves exhibit gradual increase in wear resistance with increase in the pack cyaniding temperature. This is evident in the case hardness results with increasing cyaniding temperature. As the pack cyaniding temperature increases, the case hardness of PCMS is also increased and due to increase in the case hardness the wear resistance due to abrasive is increased. This is most probably because of appreciable change in the surface morphology of pack cyanided layers with increase in cyaniding temperature.

4.5.6 Effect of Particle Size on Wear Resistance of Pack Cyanided Mild Steels

This is most probably due to the dependence of case hardness on cassava leaves particle size for high temperature pack cyaniding. The larger the particle size, the higher the case hardness and thereby the higher the wear resistance.

4.6 Deduction from Wear Test Result

From the experimental results of dry abrasive wear test (Table 4.4 – 4.7), the following regularities can be found.

- The wear volume during abrasive is highest for un-pack cyanided mild steel sample and is lowest for the mild steel pack cyanided at temperature of 900 ^{o}C with particle size of 850 µm.
- When only pack cyanided mild steels are compared, the wear volume during abrasive is highest for the mild steel pack cyanided at temperature of 750 ^{o}C with 212 µm particle size and is lowest for the mild steel pack cyanided at temperature of 900 ^{o}C with particle size of 850 µm.
- The wear rate is highest for un-pack cyanided mild steel sample and is lowest for the mild steel pack cyanided at temperature of 750 ^{o}C with 212 µm particle size and this wear rate is gradually decreases with increase in particle size

(Fig.4.5 – 4.7). This is as a result of direct relation of wear volume to the wear rate during abrasive wear, so as the particle size increases the wear volume during abrasive wear decreases due to the increase in case hardness and simultaneously there is the decrease in the wear rate.

- The wear rate is also pack cyaniding temperature dependent and the abrasive wear test results (Fig 4.6) show that the wear rate increases gradually while decreasing the cyaniding temperature, so the wear rate is highest for the cyaniding temperature of 750 ^{o}C and it is lowest for the cyaniding temperature of 900 ^{o}C.
- The wear resistance is highest for the mild steel pack cyanided at the temperature of 900 ^{o}C with particle size of 850 µm and it is lowest for the un-pack cyanided mild steel. Considering only pack cyanided mild steels, the wear resistance is highest for the mild steel pack cyanided at the temperature of 900 ^{o}C with particle size of 850 µm and is lowest for mild steels pack cyanided at temperature of 750 ^{o}C with 212 µm particle size.
- Hence the abrasive wear results explain that the wear resistance is directly proportional to the cyaniding temperature and particle size. As the both cyaniding temperature and particle size increase, the wear resistance increases (Fig 4.8)

4.7 Practical Implications

It is expected that the applications of these results will contribute to the improvement and optimization of wear properties of PCMS.

CHAPTER FIVE

5.0 CONCLUSION

This work has successfully investigated the case hardness and abrasive wear properties of the pack cyanided mild steel. The effects of the pack cyaniding treatment temperature and particle size on the surface hardness and abrasive wear behaviour of pack cyanided mild steel were fully examined following a logical experimental approach. The following conclusions were drawn from the results obtained.

1. Pack cyaniding is an effective method of increasing the case hardness and abrasive wear resistance of mild steels.

2. The abrasive wear resistance and case hardness of cyanided mild steels depends on the pack cyaniding temperature and particle size with larger particle size producing the highest hardness at all temperatures.

3. In all the experiment conducted, mild steel pack cyanided at temperature of 900^{o}C with 850µm particle size demonstrated the highest case hardness and abrasive wear resistance.

4. Within the pack cyaniding temperature range of 750^{o}C to 900^{o}C, the case hardness and abrasive wear resistance of the mild steel increases with the rise in the temperature.

5. The abrasive wear resistance and case hardness of pack cyanided mild steel increase with the particle size of processed cassava leaf powder. However, cassava leaf particle size of 850µm produced the hardest case and highest wear resistance.

5.1 RECOMMENDATION FOR FURTHER RESEARCH

From this work, it was observed that the wear rate decreases with increase of powder particle size and pack cyaniding temperature. This experiment was only carried out for high temperature pack cyaniding with two variables (i.e. cyaniding temperature and particle size).

- This work can be extended to other variables such as soaking time.
- Also, investigation of abrasive wear properties of low temperature pack cyanided mild steel should be studied.
- Also, determination of Wear Mechanism of Pack Cyanided Samples should be studied.
- Microstructural characterisation and local composition relation to hardness and wear behaviour should be studied
- Investigation of abrasive wear properties of low temperature PCMS should also be studied
- Cracking and fatigue resistance studies of PCMS should be carried out
- Corrosion behaviour of PCMS should be investigated
- Toxicity studies of cyanided parts for applications in food processing machines should also be carried out

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