

CHARACTERIZATION OF CASSAVA CYANIDE ON HEAT TREATED DUCTILE CAST IRON

Abstract

The present study explored the feasibility of using cassava leave (CL) cyanide for surface strengthening of ductile cast irons through heat treatment. Dried cassava leaves were pulverized and sieved to 500 μ m particle size, the pulverized mass was mixed with BaCl₂ (energizer) at a ratio of 4:1 by weight. Standard ductile iron samples were produced using sand casting technique and the samples were heat treated at temperatures ranging from 750 to 900 °C in steps of 50 °C for the period of 3—5 hours. Characterization of the cynided ductile iron was carried out using JEOL 7600F Field Emission Scanning Electron Microscope (SEM), Oxford X-Man (EDS), PANALYTICAL Empyrian X-Ray Diffractometer (XRD) and LECO ASTM E384 hardness tester. These were with a view to ascertaining the formation of a case within the microstructure and phase formation owing to the heat treatment. The results revealed a graphite nodules surrounded by ferrite in a pearlitic matrix for the as-cast samples while the PCCL-treated samples revealed dark circumfrenical structures (visible difusion zone) containing carbides and appreciable amount of nitrides precipitation in a pearlitic matrix (case) while the center reveals a ferritic/pearlite matrix (core).

keywords: *Cassava, cyanide, ductile cast iron, surface strengthening*

1.0 INTRODUCTION

Ductile cast iron is a versatile engineering material which has formed the subject of leading international research. Cast iron is finding increasing application through materials combination for engineering applications and modification of properties such as mechanical properties (hardness, wear resistance, toughness, ductility, etc) and cost savings (Imasogie and Afonja, 2003). Cast iron is widely used in the manufacturing of components such as machine tool beds, cylinders, cams, and pistons. Ductile cast iron is a grade of cast iron that is regarded as a suitable replacement for steels because it has a relatively low cost, good machinability, a good combination of strength and toughness, a high fatigue resistance, good fluidity, and good wear resistance (Gulzar *et al.*, 2009)

Heat treatments are often applied to ductile iron to create or alter microstructures that improve some mechanical properties such as stress relieving annealing to produce a ferritic matrix, normalizing to produce a pearlitic matrix, hardening to produce martensitic structures, and surface strengthening to produce a hardened case with a tougher core matrix.

The aim of this study is to explore the feasibility of using cassava leave for surface strengthening of ductile iron by thermochemical method of diffusion using cassava leaf as source of cyanide. However, the choice of cassava leaves is based on the amount of cyanoglucoside content present in the leaves which generally ranges from 140 — 1000 ppm depending on the variety, plant age, soil condition, fertilizer application, weather and other factors (Falade and Akingbala, 2011; Komolafe and Arawande 2011). In Nigeria, cassava is at present predominantly used for food and production of cassava remains low in terms of yield per hectare compared to its potential (AIIT 2008). Cassava may play a very significant role in surface strengthening since it produces relatively high amounts of Hydrogen cyanide, is easily hydrolysed and has a high content of dry matter (Kosugi *et al.*, 2009). The cellulosic and lignocellulosic content in cassava are also used as feed stocks in production of bio-ethanol (Londo *et al.*, 2009).

2.0 METHODOLOGY

2.1 Production of ductile cast iron

The ductile iron used was cast by charging cast iron scraps, ductile iron returns, engine sleeves, ferro-silicon alloy and ferro-silicon-magnesium, FeSiMg (5% Mg) alloy into a rotary furnace. After melting was achieved between 1350 -1450 °C, inoculation with 2.4 wt. % of ferro-silicon containing 75% Si was done to improve fluidity. Ejection of the metal during dissolution of magnesium was prevented by means of special enclosed reaction vessels for desulphurization and deoxidation treatment (Imasogie *et al.*, 2000). After tapping, inoculation with 0.6 wt.% ferro-silicon containing 75% Si was carried out in the ladle. A reaction chamber which holds the inoculants material in the running system was used to ensure the uniform pouring of inoculants over the whole casting, to achieve a satisfying distribution of spherical graphite and to maximize the efficiency of the inoculant material (Imasogie, 2002).

The melts were tapped and poured into a Y-block shaped mold, according to the ASTM A897M-90 standard, followed by shakeout and appropriate sample preparation.

59 2.2 Pack cyaniding Process

60 The cassava leaves were harvested fresh, oven-dried at 70 °C (Famurewa and Emuekele,
61 2014) and pulverized to 500 µm using ball mills. Ductile iron samples were machined to a
62 cylindrical shape of 20mm X 20mm, immersed in a mixed of pulverized cassava leaves
63 (cyanide source) and Barium chloride BaCl₂ (energizer) at a ratio 4:2 by weight sealed in 50
64 mm × 500 mm × 500 mm mild steel boxes. The samples were subjected to heat-treatment
65 process by varying the temperature from 750 °C to 900 °C in steps of 50 °C with holding time of
66 3 to 5 hrs in steps of 1 hr, total number of 64 samples was produced in all.

67 3.0 Results Discussion

68 3.1 Chemical Analysis

69 The chemical composition of ductile iron in the as-cast condition and alloying element was
70 determined by Optical Emission spectroscopy and is provided in Tables 1 and 2.

71 Table 1: chemical composition of the produced ductile cast iron

Materials	Fe	C	Si	Mn	P	Mg	S	Cr	Ni
Ductile Cast iron	92.8	3.80	2.60	0.30	0.06	0.05	0.02	0.10	0.07

72

73 Table 2: Commercial Standard Grade Inoculants (Ferro-silicon, 75%) Composition

Elements	Si	P	S	Al	Fe
Composition (%)	75	0.02	0.05	2	Balance

74 The chemical composition of the produced ductile cast iron as presented in Table 1 revealed that
75 the cast iron has the carbon equivalent value (CEV) of 4.68 which is hyper-eutectic iron and
76 Figure 1 shows the micrograph of the casted ductile iron.

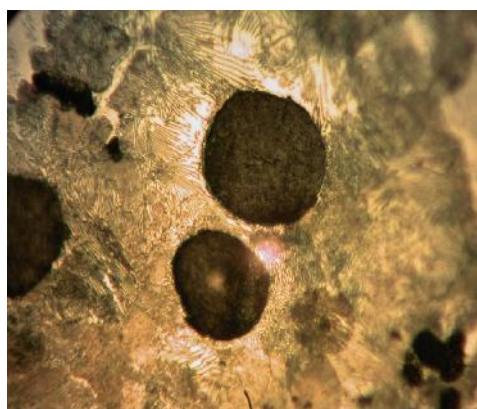


Figure 1: Micrograph of as-cast ductile iron showing graphite nodules in a pearlitic matrix with free carbide (light irregular particles), 2% nital etched x 500.

3.2 Intermediate-temperature Pack Cyaniding Decomposition Reactions

When cassava leaves are crushed, glucose and acetone cyanohydrin are hydrolysed in the presence of the enzyme *linamarase*, the acetone cyanohydrin decomposes rapidly in neutral or alkaline conditions liberating hydrogen cyanide and acetone as in Figure 2.

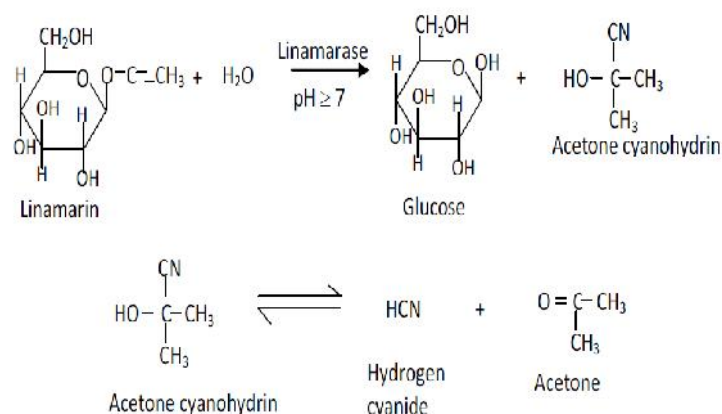
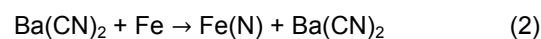


Figure 2: Enzymatic hydrolysis of linamarin (Orjiekwe *et al.*, 2013; Mburu *et al.*, 2012)

The following decomposition reactions are proposed for the intermediate-temperature pack cyaniding process:



Where BaCl_2 is the energizer that is used in the intermediate-temperature treatment, the energizer is added to increase the diffusion rate and case depth.

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



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



The nitrogen (4N) formed diffuses interstitially into the iron surface during the pack cyaniding process, similar to pack nitriding process (Li and Xiang, 2010).

The cyanide concentration analysis was carried out using the alkaline titration method (Famurewa and Emuekele, 2014). Cyanide concentration, morphology and elemental composition results are presented in Tables 3 and figure 3, while the EDX analyses of the cyanided heat treated sample surface (case) were listed in Table 4.

Table 3: Cyanide value present in the Experimental cassava leaf

S/N	Sample	Titre Value	Cyanide Content HCN (mg/kg)
1	TMS30572	6.038	20.38

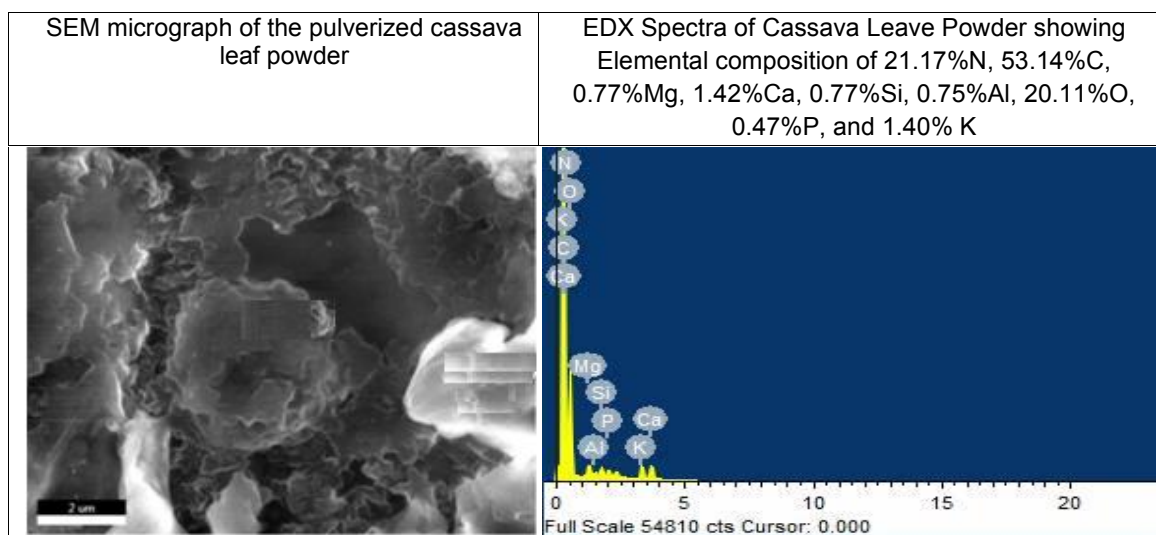
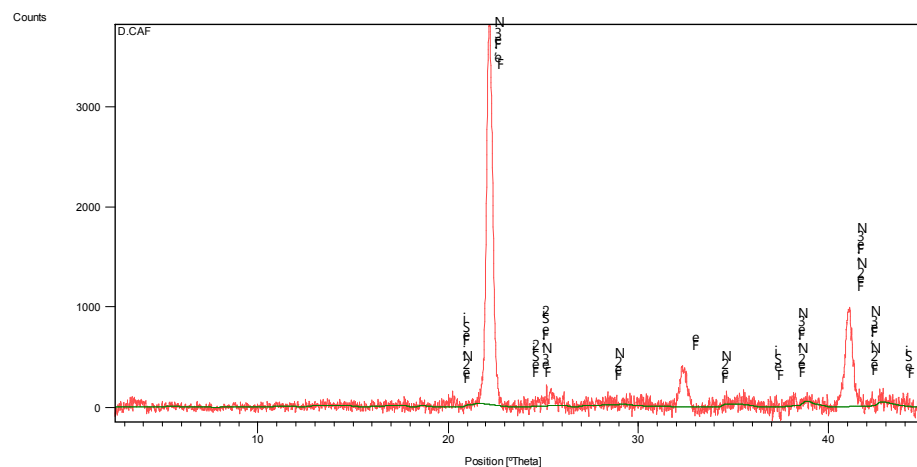
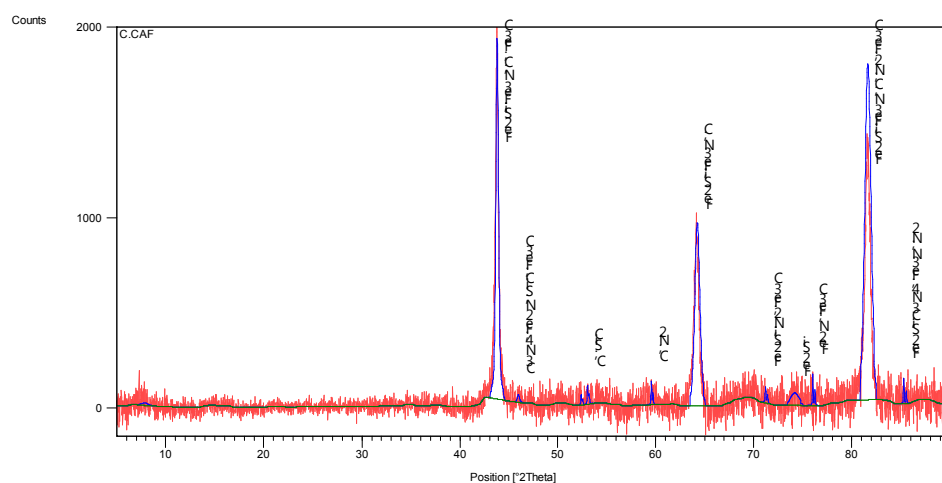


Figure 3: SEM and EDX of the cassava leaf powder



a



b

Figure 4: XRD Results of the cyanided samples of Ductile Iron samples showing compound of nitrides in (a) and compound of carbides and nitrides in (b)

Table 4: EDX Analysis of the cyanided heat treated surface (case) samples (A, B, C, D, and E)

Element Symbol	control	750 °C	800 °C	850 °C	900 °C	Error
Fe	92.6	92.5	92.5	92.5	92.5	91.28-94.10
Si	2.7	2.6	2.6	2.7	2.7	2.25-3.00
C	3.4	3.52	3.49	3.5	3.45	3.50-3.90
S	0.02	0.02	0.02	0.02	0.01	0.025-0.15
Cr	0.03	0.03	0.03	0.03	0.02	

	N	0	0.98	0.92	1.1	0.94	<0.02-1.20
Mg		0.03	0.02	0.02	0.02	0.02	-
P		0.03	0.02	0.01	0.01	0.01	0.01 - 0.23
Ni		0.03	0.02	0.02	0.02	0.02	0.02 - 2.50
Mn		0.26	0.25	0.24	0.1	0.21	0.15-0.35

3.2 Light microscopy

The microstructures of pack cyanided samples were studied using the *Olympus BH-2* microscope with a digital camera. In preparing the specimens for microstructural studies, rough polishing was carried out on 240, 320, 400, and 600, 800 and 1200 SiC grit papers while final polishing was accomplished with alumina pastes of 1µm, and 0.5µm, respectively, etched with 2% nital and thereafter observed with the microscope.

Figure 5, plate 1 reveals a microstructure of graphite nodules in a pearlitic matrix. In Plate 2, a visible diffusion zone was identified revealing a visually dark portion around the circumference of the sample heat treated at 750 °C with holding time of 3hrs. This zone represents a region of elemental diffusion on the sub-surface to form a case; where the darker morphology of the diffusion zone increases in intensity as the holding time increases. Over the temperature range of 750 — 900 °C, the treated specimens show a case formation containing a thin compound layer (CL) with a diffusion zone (DZ) underneath. The progressive changes in the diffusion zone are ascribed to good wear resistance of ductile iron (Zaidoa, 2013). In plates 2 and 3, the effect of cassava cyanidation is similar to the carbonitriding process involving the diffusion of Carbon (C) and Nitrogen (N) on the surface of the specimen simultaneously (Wang *et al.*, 2015).

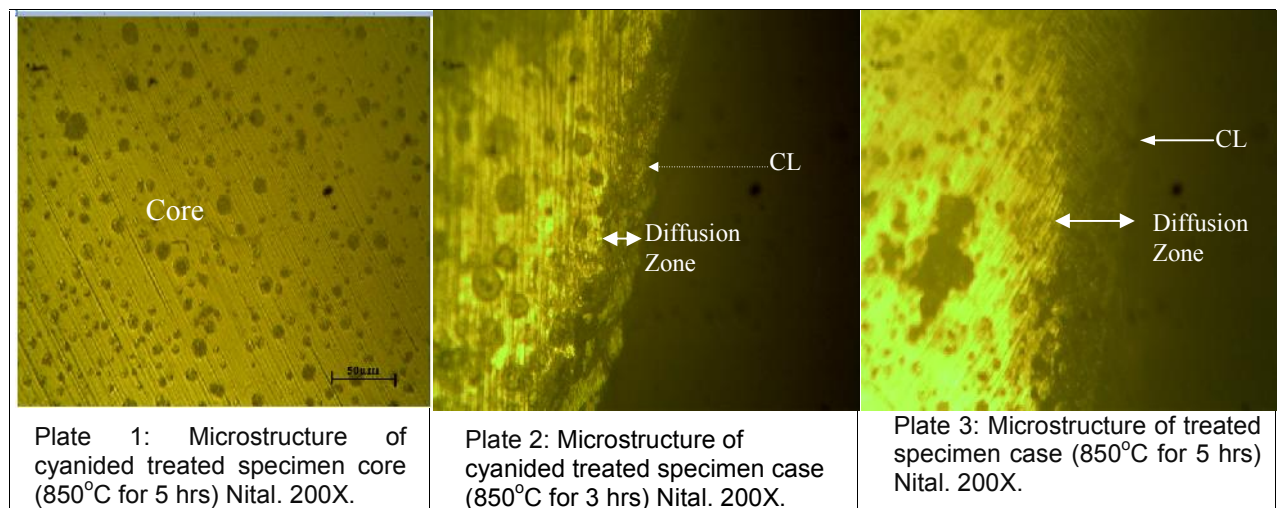
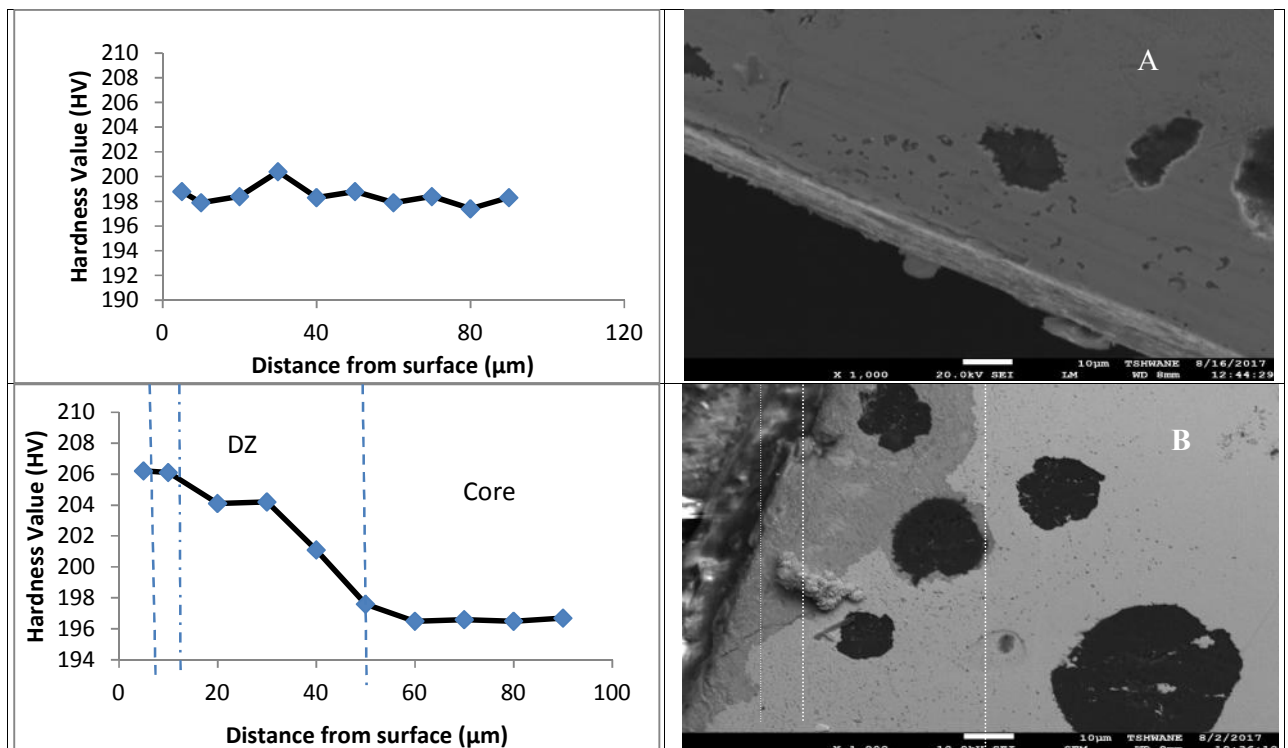


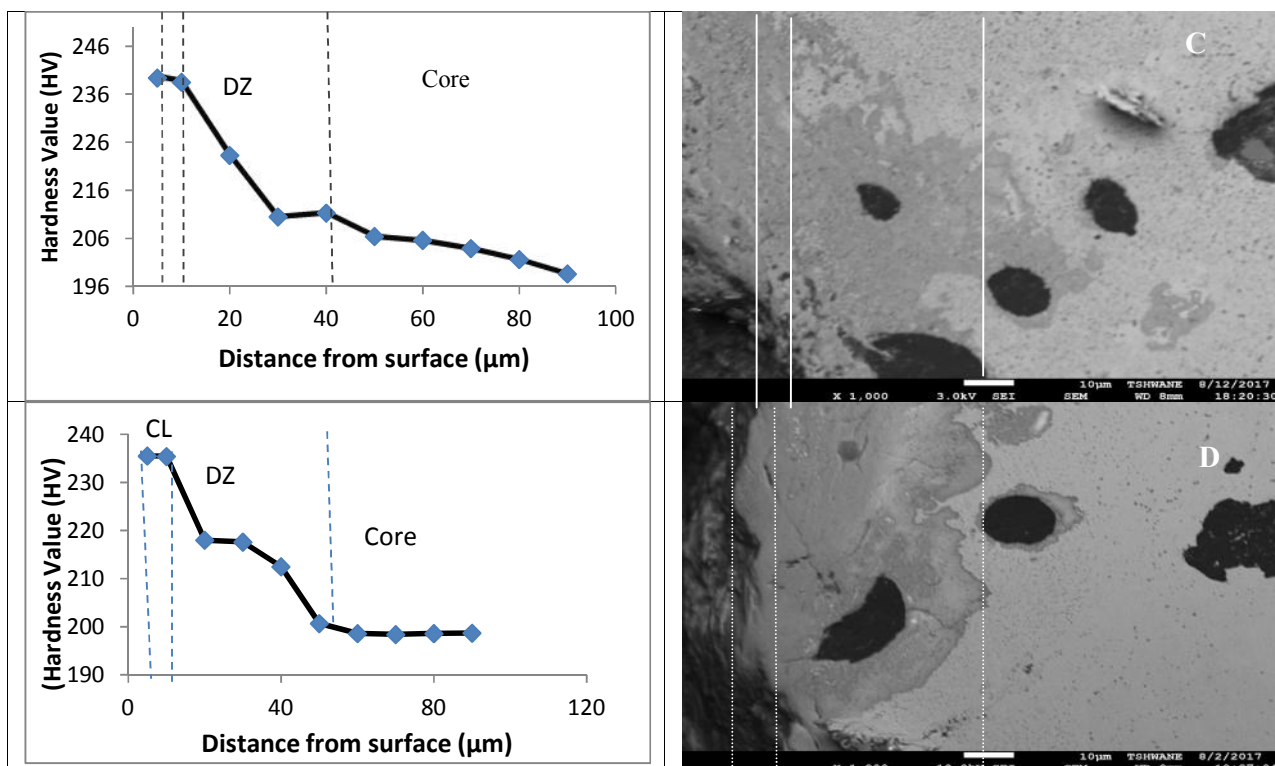
Figure 5: The microstructures of cassava leaves heat treated samples at 850°C. 200X

3.3 SEM Observation

The micrographs of the cyanided samples were studied using Scanning Electron Microscopy. Results obtained after heat treatments revealed a thin hard case with a high compressive residual stress at the surface and from the surface inward, the developed case comprises of a compound layer and a diffusion zone (DZ) in table 5. During the heat treatment process, the diffusion of carbon and nitrogen produced precipitates of carbide (FeC_3) and nitrides ($\epsilon\text{-Fe}_2\text{N}$ and $\gamma'\text{-Fe}_4\text{N}$) within the matrix of the sample as illustrated in figure 4. The microstructure of the core reveals a predominantly pearlite in a ferritic phase while the cases reveals a combination of carbides, nitrides and an appreciable amount of cementite at the circumference of the sample.

Table 5: Table showing the correlation between Hardness profiles against SEM micrographs





3.4 Compound layer thickness and diffusion zone depth

The compound layer thicknesses and diffusion zone depths of ductile iron were determined using the cross-sectional of the SEM micrographs presented in table 5. Figure 5a shows the relation between the compound layer thickness and the diffusion zone depth respectively.

Figure 5a reveals a progressive increase in the compound layer thickness of sample treated at 750°C with holding time of 3hrs to a thickness value of 9.2 μm. The sample pack cyanided at 850°C with holding time of 5hrs has the highest compound layer value of 9.4 μm. This is expected due to the presence of carbides and appreciable amounts of ε-nitride, γ^I-nitride in figure 4, at the case (Table 5, sample C). At 900°C the compound layer thickness decreases owing to decrease in nitrogen diffusivity at high temperature.

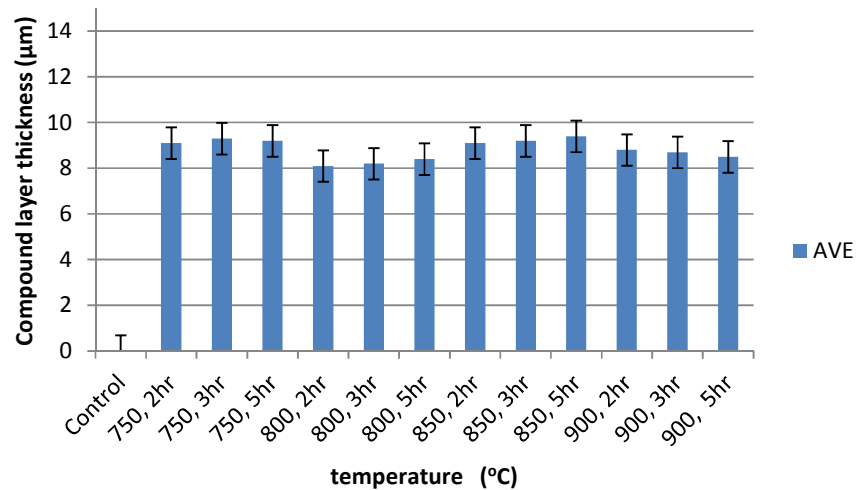


Figure 5a: Compound layer thickness and diffusion zone depth of the treated samples

3.5 Hardness Test Result

The hardness results illustrated in Table 5 show the hardness value of 198.4 HV at the case and 197.2 HV at the core obtained in sample A (as-cast), sample B (750 °C held for 3hrs) reveals a hardness value of 207 HV at the case and 198 HV at the core while a hardness value of 242.6 HV was observed at the circumference (case) of sample C (850°C held for 5 hrs) and a decrease to hardness value of 223HV at the case of sample D (900°C). The increase in hardness is as a result of the presence of ϵ -nitrides at the compound layer (CL) consisting of Fe_2N and Fe_4N in figure 4 with an average value of 198.4 HV at the core for the treated PCCL samples (b, c, and d) respectively, This may be expected because at temperatures above the eutectic temperature, the ferrite iron will transform to austenite which encourages an appreciable diffusion of carbon (C) and a little nitrogen (N) simultaneously into the matrix of the iron, depleting the 'dark' case structure and hence increasing the hardness. At temperatures above the A_{CM} line, the degree of C diffusion is much higher than that of N; this is because carbon has high diffusivity at high temperature than nitrogen (Akinluwade *et al.*, 2013; Ampaw *et al.*, 2016). Thus, the optimum treatment condition experienced in this process was observed in the treated PCCL at a temperature of 850°C held for 5 hours (sample C) and at the boundaries of the sectioned specimen the increase in the hardness was due to the presence of carbides, significant nitrides and retained austenite within the matrix.

4.0 Conclusion

The cassava pack cyaniding method inturn shows an increase in the hardness values of ductile cast iron as a result of the intersiatial diffuction of carbon as carbides (Fe_3C), retained Austenite and nitrogen as nitrides (Fe_4N , Fe_2N , and Fe_3N) at the surface of sample,this phenomenal indicate a potential use of cassava leaves for cast iron strengthening. Thus, harnessing cassava for food and as well as in cast iron strengthening production.

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