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Characterisation of Cassava Cyanide on Heat Treated Ductile Cast Iron

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Authors' contributions

This work was carried out in collaboration between all authors. Author TAT designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors OSS and JKA managed the analyses of the study. Author RAA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The present study explored the feasibility of using cassava leaves (CL) cyanide for surface strengthening of ductile cast irons through heat treatment. Dried cassava leaves were pulverized and sieved to 500 µm particle size, the pulverised mass was mixed with $BaCl_2$ (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 cyanided 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. All analyses are carried out to ascertaining the formation of a case within the microstructure and phase formation

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owing to the heat treatment. The results revealed graphite nodules surrounded by ferritic-pearlitic matrix for the as-cast samples while the Pack Cyanided Cassava Leaves (PCCL) samples revealed dark structures (visible diffusion zone) at the edges of the samples containing carbides and appreciable amount of nitrides precipitation in the matrix (case) while the center reveals a ferritic/pearlite matrix (core).

Keywords: Cassava; cyanide; ductile cast iron; surface strengthening.

1. 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 components and modification of properties such as mechanical properties (hardness, wear resistance, toughness, ductility, etc) and cost savings [1]. Cast iron is widely used in the manufacturing of components such as machine tool beds, cylinders, cams, and pistons. Ductile cast iron can be use as a good replacement for steels in applications that has comparable properties such as good machinability, good strength to toughness ratio, low cost of production, a high fatigue resistance, good fluidity, and good wear resistance [2].

Heat treatments are often applied to ductile iron to create or alter microstructures that improve some mechanical properties such as stress relieving annealing to achieve ferritic matrix structures, normalising heat treatment for a pearlitic matrix structure, hardening to achieve martensitic structures, and surface strengthening produces a hardened case with a tougher core matrix. Cyaniding heat treatment are carried out in fused mixtures of know weighted salts containing sodium cyanide, sodium carbonate and varying amounts of sodium or barium chloride melted in a salt bath furnace at temperature ranging from 750-950°C [3].

This study aims to explore the feasibility of using cassava leave for the surface strengthening of ductile iron by the thermochemical method of diffusion using cassava leaf as a 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 — l000 ppm depending on the variety of the cassava, planting period and age, the condition of soil, fertilizer application, weather and other factors [4 and 5]. In Nigeria, cassava is at present predominantly used for food and production of cassava remains low regarding yield per hectare compared to its potential [6]. 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 [7]. The cellulosic and lignocellulosic content in cassava is also used as feedstocks in the production of bio-ethanol [8].

When cassava leaves are crushed, glucose and acetone cyanohydrin is 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 Fig. 1.

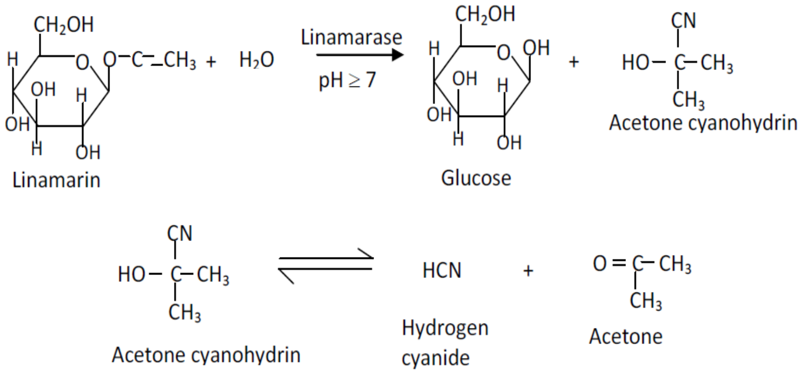


Fig. 1. Enzymatic hydrolysis of linamarin [9 and 10]

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

$$BaCl_2 + 2HCN \rightarrow Ba(CN)_2 + 2HCl \quad (1)$$

$$Ba(CN)_2 + Fe \rightarrow FeC + BaCN_2 \quad (2)$$

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

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

$$2HCN + O_2 \longrightarrow 2HCNO \quad (3)$$

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

$$8HCNO \rightarrow 4HCN + 2H_2CO_3 + 2CO + 4N \quad (4)$$

The nitrogen (4N) formed diffuses interstitially into the iron surface during the pack cyaniding process, similar to pack nitriding process [11].

2. 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 (FeSi) containing 75% Si was added to the melt to improve fluidity, and the ejection of the metal during the dissolution of magnesium was prevented by means of special enclosed reaction vessels for desulphurization and deoxidation treatment [12]. After tapping, inoculation with 0.6 wt.% ferrosilicon containing 75% Si was carried out in the ladle and 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 [13].

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.

2.2 Pack Cyaniding Process

The cassava leaves were harvested fresh, oven-dried at 70°C [14], pulverised using ball mills and sieved to 500 µm. Ductile iron samples were machined to a cylindrical shape of 20 mm X 20 mm, immersed in a mixture of pulverised cassava leaves (cyanide source) and Barium chloride $BaCl_2$ (energiser) at a ratio 4:2 by weight sealed in 500 mm × 500 mm × 500 mm mild steel boxes. The samples were subjected to a heat-treatment process by varying the temperature from 750°C to 900°C in steps of 50°C with holding time of 3 to 5 hrs in steps of 1 hr, a total number of 64 samples was produced in all.

2.3 Heat Treatment of Ductile Iron

Heat treatments are applied to cause desired changes in the metallurgical structure and properties of metallic and alloy parts [15].

a) Stress-relief heat treatment is the uniform heating of the material to a suitable temperature below the (Ac_1) transformation range, holding at this temperature for a predetermined period and followed by uniform cooling [3]. Treatment is used to relieve stresses (removal of residual stresses in iron) that remain locked in a structure as a consequence of manufacturing processes.
b) Annealing is a softening process in which ferrous materials are heated to a temperature above the transformation range (Ac_3) and, after being held for a sufficient time at this temperature, is cooled slowly in the furnace to a temperature below the transformation range (Ac_1).
c) Hardening is the process of heating materials above the Ac_3 transformation, holding long enough to ensure the attainment of uniform temperature and solution of carbon in the austenite, and the cooling rapidly in water (quenching).
d) Austempering Heat Treatment is an isothermal transformation of ferrous materials by heating to austenitizing temperature above 800°C with holding time long enough for the formation of fine grain austenite followed by quenching in a salt bath at temperature ranging from 260 to 400°C for bainite transformation and finally cooling to room temperature [16].

e) Surface hardening is a technique used to improve the wear resistance of engineering parts without affecting the materials interior properties [17]. There are two different approaches of surface hardening, namely Layer addition by the use of thin films, coatings, or hard-facings process and Surface modification attain by diffusion methods and selective hardening methods such as cyaniding, carbonitriding, nitriding, and nitrocarburizing processes.

2.4 Sample Preparation

The microstructures of pack cyanided samples were studied using the *Olympus BH-2* microscope with a digital camera. In preparing the samples 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 0.5 µm, respectively, etched with 2% nital.

3. RESULTS AND DISCUSSION

3.1 Chemical Analysis

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

The chemical composition of the produced ductile cast iron as presented in Table 1 revealed that the cast iron has the carbon equivalent value (CEV) of 4.68 which is hyper-eutectic iron and Fig. 2 shows the micrograph of the as-cast ductile iron.

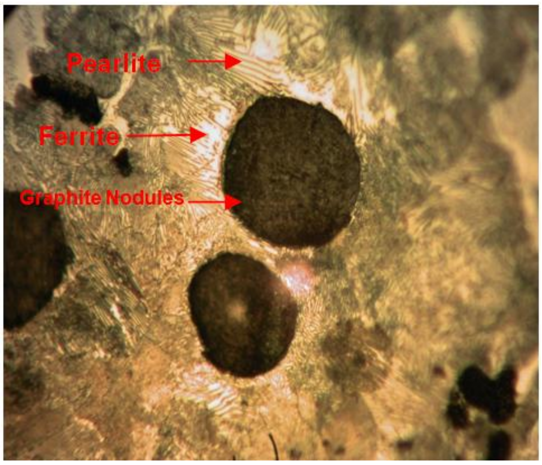
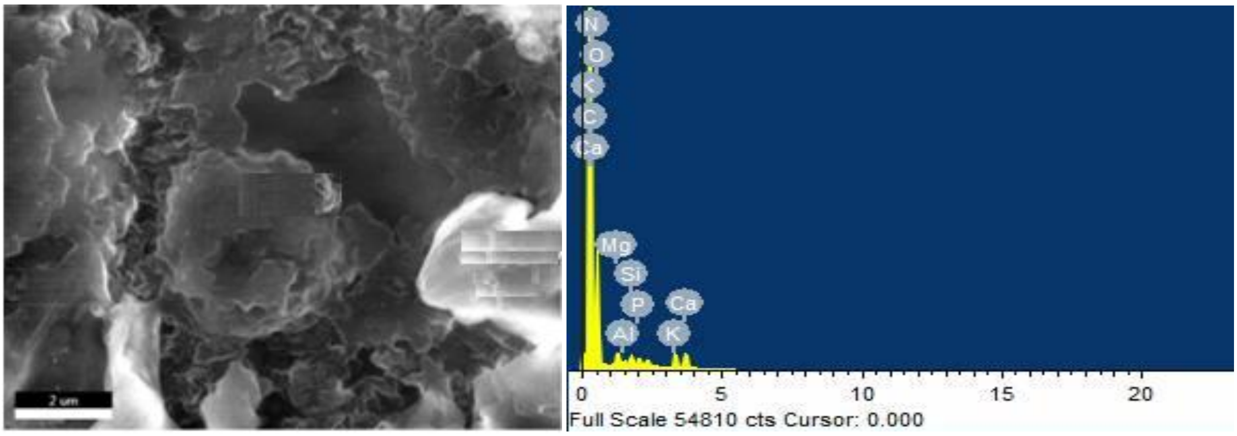


Fig. 2. Micrograph of as-cast ductile iron showing graphite nodules and pearlite in a ferrite matrix with free carbide (light irregular particles), 2% nital etched x500

The cyanide concentration analysis was carried out using the alkaline titration method [14]. Cyanide concentration, morphology and elemental composition results are presented in Table 3 and Fig. 3.


SEM micrograph of the pulverised cassava leaf powder

EDX Spectra of Cassava Leave Powder showing Elemental composition of 21.17%N, 53.14%C, 0.77%Mg, 1.42%Ca, 0.77%Si, 0.75%Al, 20.11%O, 0.47%P, and 1.40% K

Fig. 3. SEM and EDX of the cassava leaf powder

Table 1. Chemical composition of the produced ductile cast iron

Elements	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

Table 2. Commercial standard grade inoculants (Ferro-silicon, 75%) composition

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

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

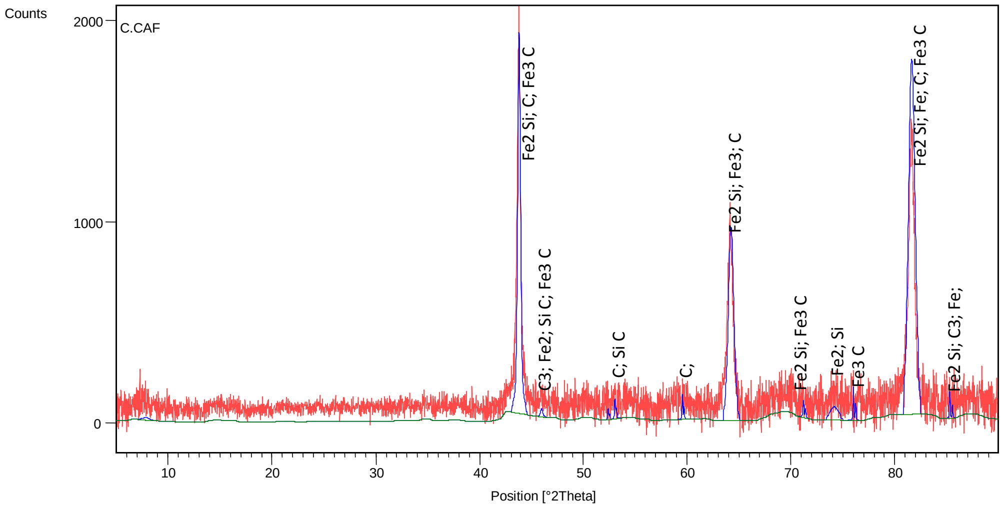


Fig. 4a. XRD Pattern of PCCL ductile iron at 850°C for 5 hrs showing an intense peak of Fe_3C, Fe_2Si, C phases at the core

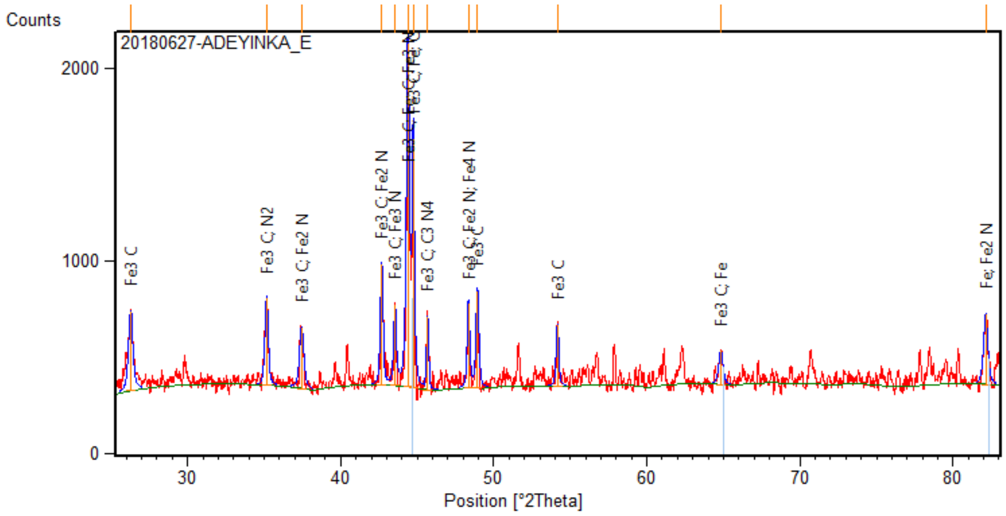


Fig. 4b. XRD Pattern of the Pack cyanided Ductile Iron samples at 850°C for 5 hrs showing intense peaks of carbides (Fe_3C, C) and nitrides (Fe_2N, Fe_4N, N_2) at the case

3.2 Light Microscopy

Fig. 5, Plate 1 reveals a microstructure of graphite nodules in a pearlitic matrix and 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 3 hrs. 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 samples reveal a case formation containing a diminutive structure (compound layer) with a fading structure of the diffusion zone (DZ) beneath. The progressive changes in the diffusion zone are ascribed to the good wear resistance of ductile iron [18]. 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 sample simultaneously [19].

3.3 SEM Observation

The micrographs of the cyanided samples were studied using Scanning Electron Microscopy (SEM). Results obtained after heat treatments revealed a thin hard case with an enhanced hardness at the surface and from the surface inward, the hardness decreases toward the centre core which denotes the diffusion zone as illustrated in Fig. 6(a,b). During the cyaniding treatment process, the diffusion of carbon and nitrogen produced precipitates of carbide (FeC_3) and nitrides (ε-Fe_2N and γ'-Fe_4N) within the matrix of the sample as illustrated in Fig. 4. The microstructure of the core reveals a predominantly carbide phases (Fig. 4a) while the cases reveals a combination of carbides, nitrides and an appreciable amount of cementite at the circumference of the sample (Fig. 4b). The morphological changes in the SEM micrographs of the untreated and treated samples against the hardness profile as illustrated in Fig. 6, this reveals a decrease in hardness value from the edge (surface) toward the centre (core) of sample B, C and D respectively.

3.4 Compound Layer Thickness and Diffusion Zone Depth

The compound layer thicknesses and diffusion zone depths of ductile iron were studied using the SEM micrographs cross-sectional structures as presented in Fig. 6. Fig. 7 illustrates the relationship between the thickness of the compound layer and the diffusion zone respectively, the figure reveals a progressive increase in the compound layer thickness of samples treated at 750°C with holding time of 3hrs to a thickness value of 9.2 µm while samples 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 (Fe3C), free carbon (C) and an appreciable amounts of ε-nitride, γ^{I}-nitride (Fig. 4) at the surface (case) of the treated samples (Sample C, Fig. 6,) follow by decreases in compound layer thickness at 900°C the owing to decrease in saturated effect of the carbon and nitrogen diffusivity at high temperature.

3.5 Hardness Test Result

The hardness results illustrated in Fig. 8 explains the hardness value of 198.4 HV at the case, and 197.2 HV at the core was obtained for sample A (as-cast), sample B at 750°C held for 3hrs reveals a hardness value of 207 HV at the case and 198 HV at the core, Sample C has a hardness value of 235.3HV at the case and 197.6 HV at the core, while sample D reveals a hardness value of 242.6 HV was observed at the circumference (case) and 208.4 HV at the core at 850°C held for 5 hrs and a decrease to hardness value of 223.4 HV at the case and 209.6 HV at the core of sample D at 900°C held for 5hrs as illustrated in Fig. 6b. The increase in hardness is as a result of the presence of ε-nitrides at the compound layer consisting of Fe_2N and Fe_4N in Fig. 4b with reduction in hardness value at the core for the treated cassava cyanided samples respectively, This may be expected because, at temperatures above the eutectic temperature, the ferrite iron will transform to austenite which encourages appreciable diffusion of carbon (C) and diminutive 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 (Fig. 1), the degree of C diffusion is much higher than that of N; this is because carbon has high diffusivity at high temperature than nitrogen [17 and 20]. 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 sample the increase in the hardness was due to the presence of carbides, significant nitrides and retained austenite within the matrix.

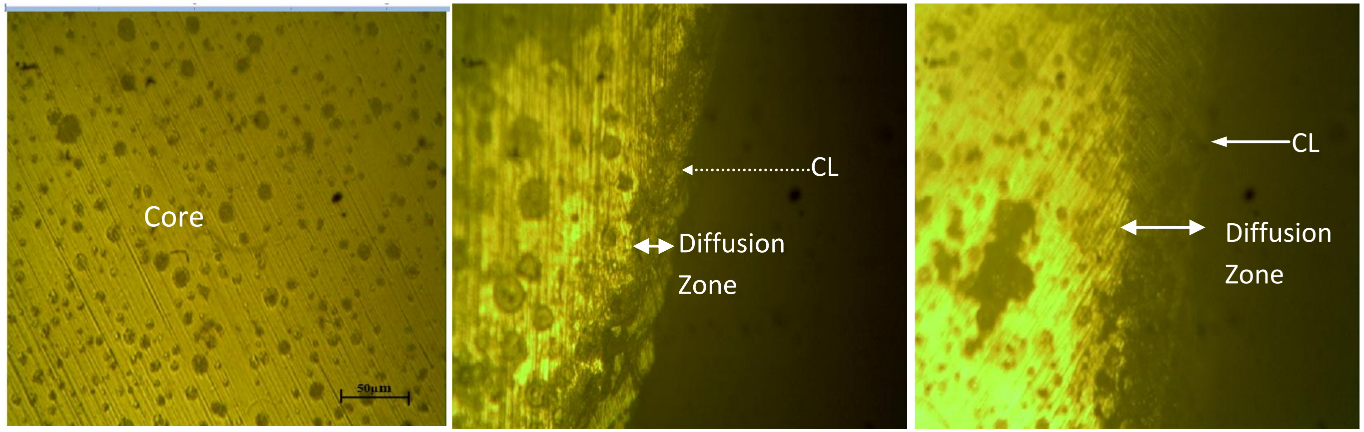


Plate 1. Microstructure of cyanide treated sample core at 850°C for 5 hrs, 2% nital etched, X200

Plate 2. Microstructure of cyanide treated sample case at 850°C for 3 hrs, 2% nital etched, X200

Plate 3. Microstructure of cyanide treated sample case at 850°C for 5 hrs, 2% nital etched, X200

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

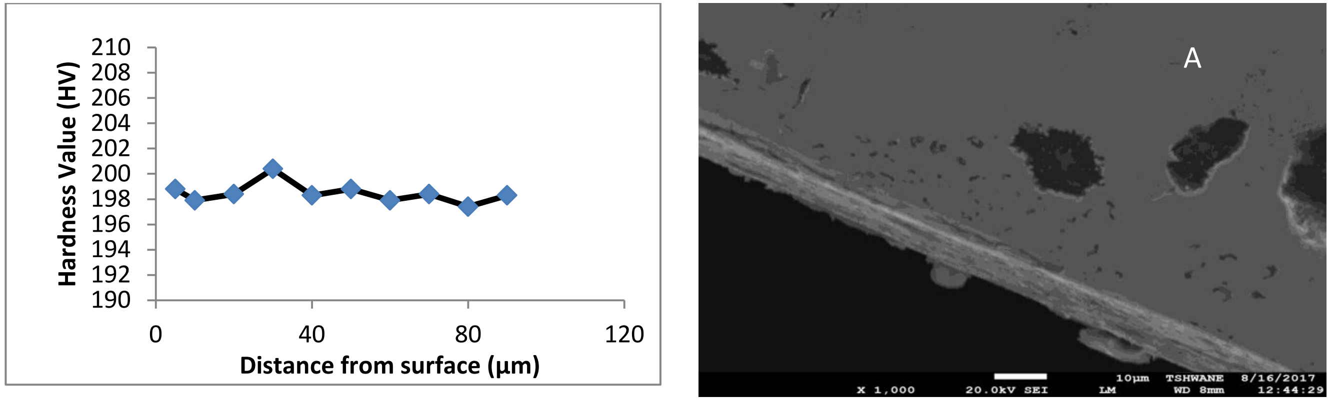
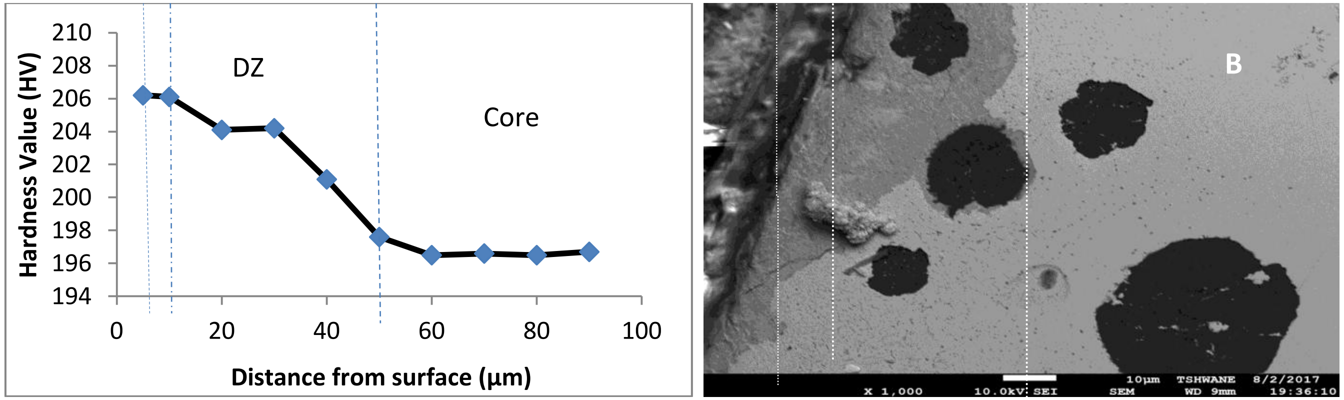


Fig. 6a. Table showing the correlation between Hardness profiles against SEM micrographs of the untreated sample



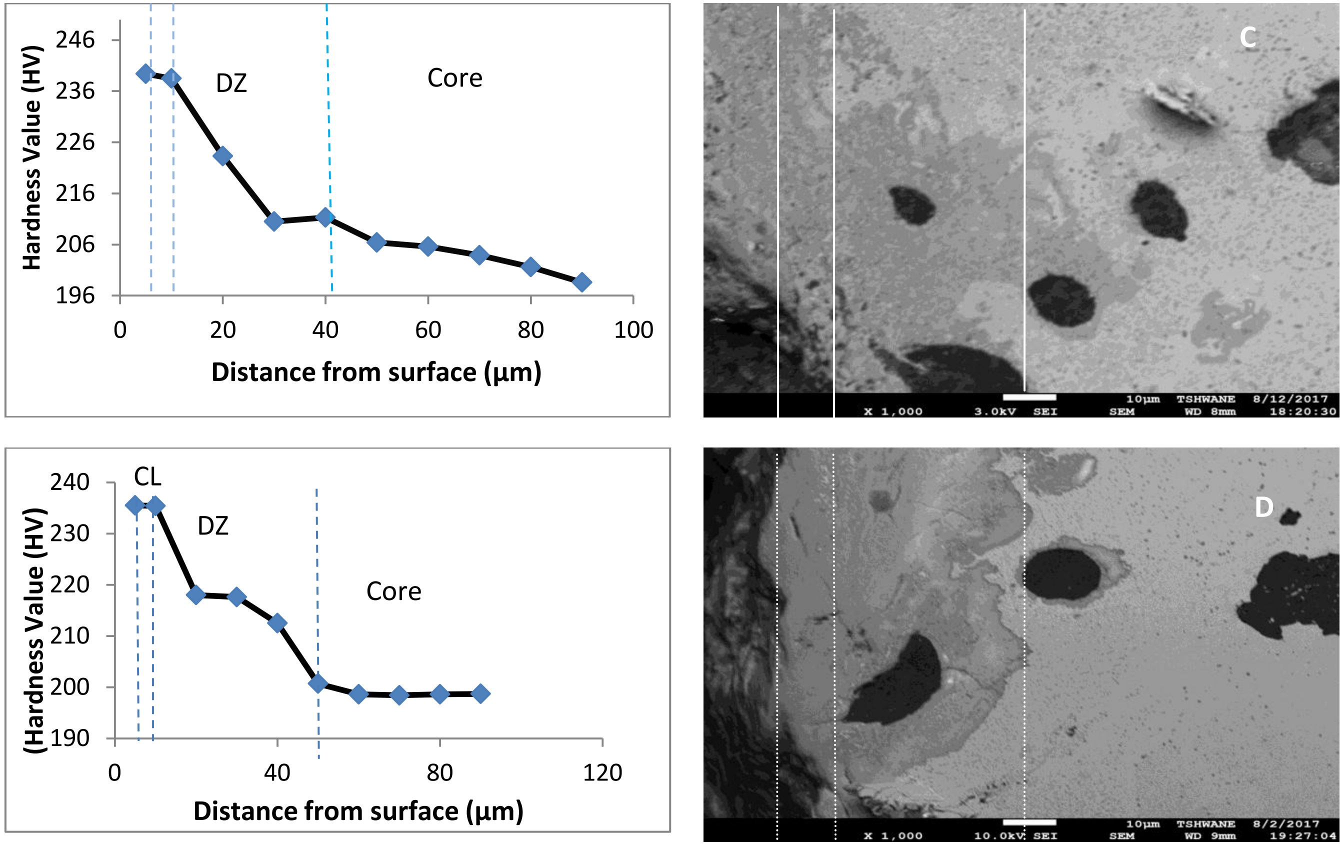


Fig. 6b. Table showing the correlation between Hardness profiles against SEM micrographs of the treated cyanided samples

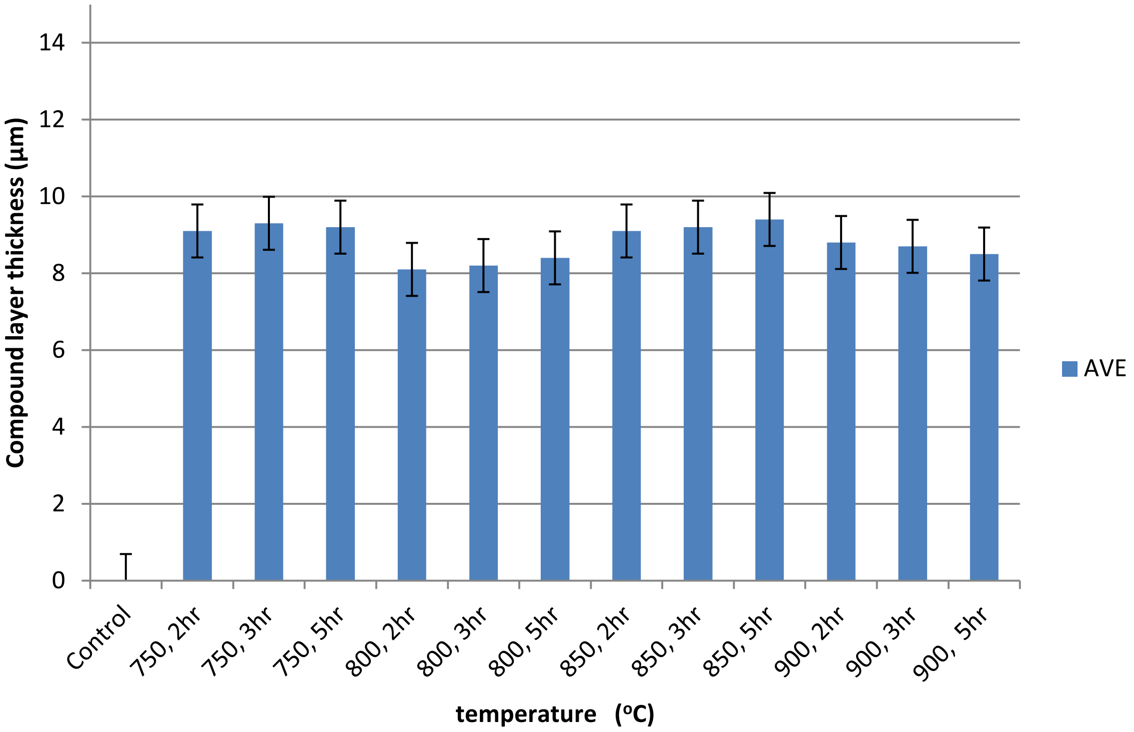


Fig. 7. Compound layer and diffusion zone thickness of the pack cyanided cassava leaves samples

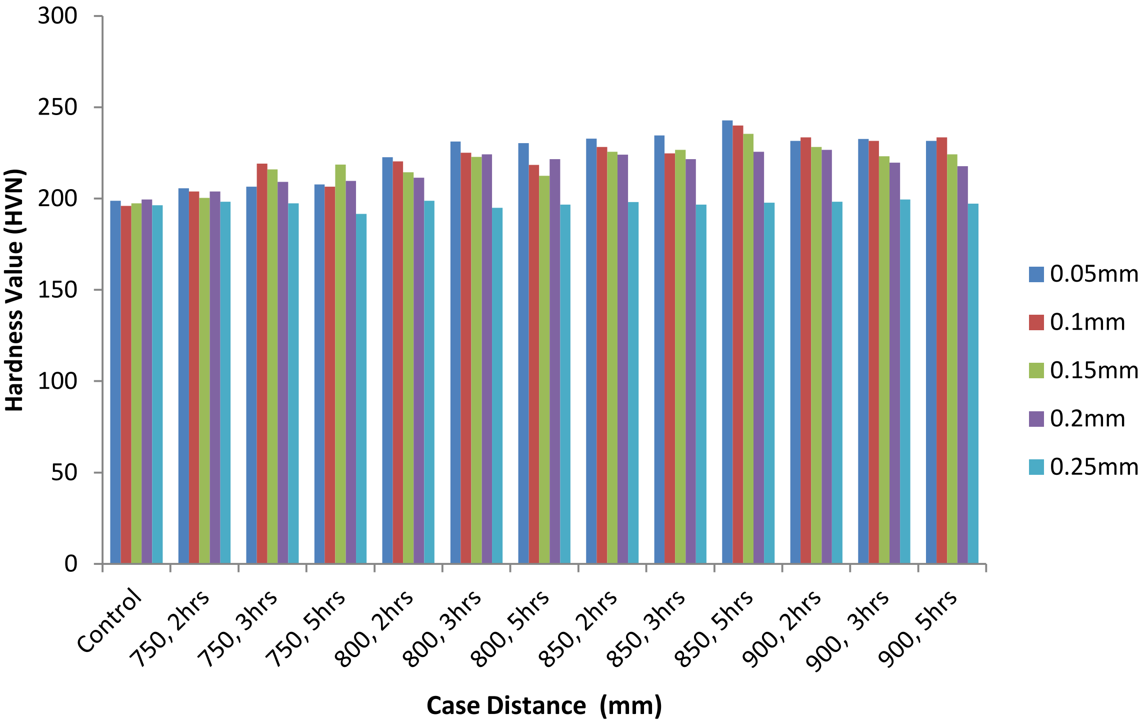


Fig. 8. Case hardness concerning the soaking time for the control and cassava cyanided samples

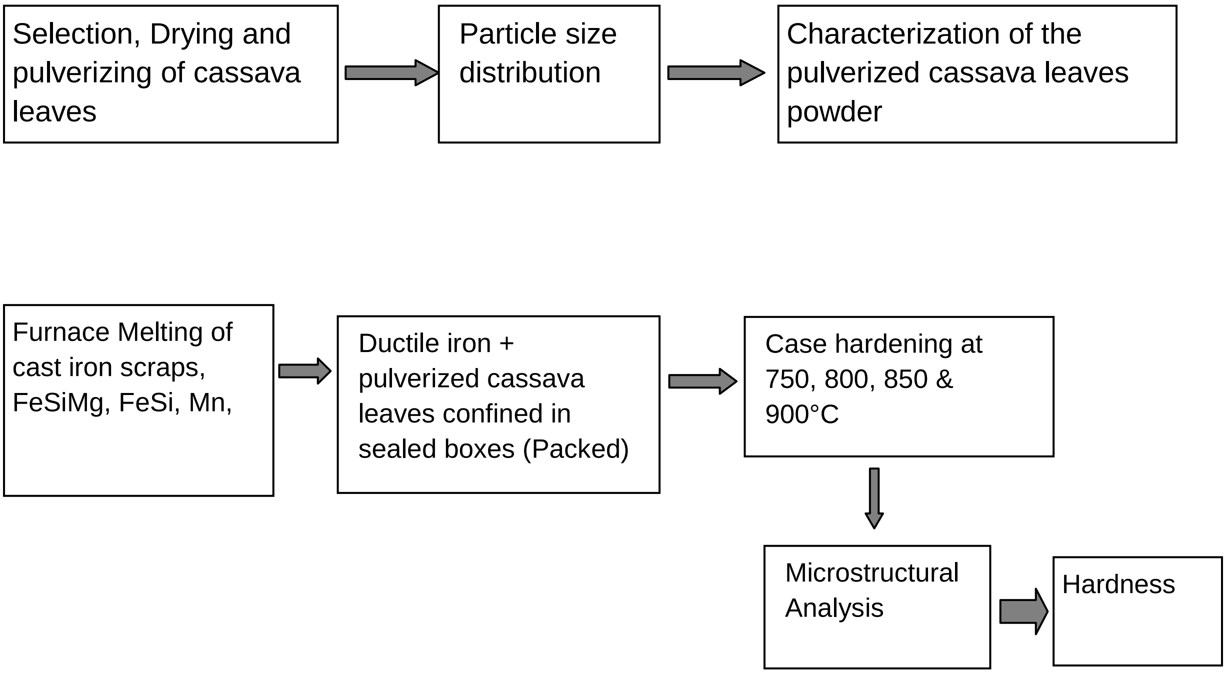


Fig. 9. Schematic representation of cassava leaves preparation and the production of cyanided ductile iron

4. CONCLUSION

The cassava pack cyaniding method in turn shows an increase in the hardness values of ductile cast iron as a result of the interstitial diffusion of carbon as carbides (Fe_3C), retained Austenite and nitrogen as nitrides (Fe_4N, Fe_2N, N, and Fe_3N) at the surface of treated samples, this phenomenal indicate a potential use of cassava leaves for cast iron surface strengthening and the method also demonstrates potentials for increasing wear resistance of ductile iron components for an extensive application service life. Thus, harnessing cassava tuber for food and leaves (waste) for engineering application such as surface strengthening of ductile cast iron components.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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