Archives of Current Research International

14(4): 1-11, 2018; Article no.ACRI.42632
ISSN: 2454-7077

Characterization of Mild Steel Case-hardened in Processed Cassava Leaves

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Authors' contributions

This work was carried out in collaboration between all authors. Author DAI designed the study, performed literature review and heat treatment, wrote the protocol and first draft of the manuscript. Author KJA supervised the heat treatment and reviewed the study while authors KMO and OSA managed the analyses of the study. Authors ARA and MOA supervised the study and interpreted results. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/ACRI/2018/42632
Editor(s):
(1) M. A. Elbagermi, Chemistry Department, Misurata University, Libya.
Reviewers:
(1) Glauber Cruz, Federal University of Maranhão, Brazil.
(2) J. R. Premjith, Karunya University, India.
Complete Peer review History: http://www.sciencedomain.org/review-history/25940

Original Research Article

Received 15th May 2018
Accepted 20th July 2018
Published 18th August 2018

ABSTRACT

This study characterized 1018 steel case-hardened in processed cassava leaves. The microstructures, phases and case depths of treated samples were characterized and the effect of soaking time on case depth was determined. Standard specimens machined from 1018 steel were pack-cyanided at 950°C using pulverized cassava leaves combined with barium trioxocarbonate IV, $BaCO_3$ energizer. The treated samples were characterized with Advanced Optical Microscope, Scanning Electron Microscope and X-Ray Diffractometer. Results from these tests formed the basis of conclusion. The results showed formation of appreciable cases whose case depths increased with soaking time. The XRD result revealed that the cases contained cementite (Fe_3C), silicon carbide (SiC), iron-silicon-carbon (FeSiC) and iron silicide (FeSi) phases which are responsible for surface hardness.

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Keywords: Characterization; cassava leaves; pack-cyaniding; microstructure; phases; 1018 steel.

1. INTRODUCTION

Mild steel is a plain carbon steel with carbon content up to 0.25% by weight [1]. Among the different grades of steel available, those produced in the greatest quantities are the low-carbon steels because they are the least expensive to produce and therefore deployed for structural applications. They are usually selected due to properties such as weldability, ease of fabrication, availability and lower cost. Unfortunately, they are not responsive to hardening heat treatment intended to form martensite [1,2]. To produce a hard wear-resistant surface while still maintaining the soft tough core in the low-carbon steel, the surface is often modified by augmenting the level of hardening species such as carbon and/or nitrogen content at the surface through diffusion [3]. A typical example of low carbon steel is AISI 1018 steel, which is the most common of the cold-rolled steels and has carbon content of about 0.18% suitable for case hardening. It is a general purpose carbon steel most commonly used in high volume screw machine parts including self drilling screws, shafts, spindles, pins and rods, in a surface-hardened condition [4].

In the quest for ferrous components of satisfactory strength, toughness, hard and wear resistant surface, a number of methods have come to be used. Prominent among these is case hardening — a process used to improve the wear resistance of parts without affecting the soft but tough core of the part. Usually, what is required of an engineering component is a combination of a hard surface to resist wear and a tough interior to resist any impact loading during operations [5].

To mitigate the hazardous effect of cyanide salts handling on personnel and environment, researchers have beamed their searchlight on how some naturally-occurring cyanide-containing organic matters can be utilized for case hardening via pack-cyaniding. Prominent among these in the literature, is the use of cassava leaves powder for surface strengthening of low carbon steels. Ibironke et al. [6] investigated case-depths of mild steel pack-cyanided in cassava leaves. The study reported feasibility of improving the strength and hardness of low carbon steels with nascent carbon and nitrogen released *in situ* from the cyanide content of cassava leaves and a mathematical model for the estimation of hardness with depth as a function of time was also developed. Adetunji et al. [7] carried out metallographic studies of pack-cyanided mild steel using cassava leaves to ascertain the possibility of pack cyaniding low carbon steel with a mixture of cassava powder and energizers. The research further examined the microstructures of the treated specimens with optical microscope which revealed case formation resulting from the diffusion of carbon into the specimen. Akinluwade et al. [8] developed an environmentally friendly *in-situ* pack-cyaniding technique for mild steel. The research investigated the influence of cassava leaves powder size on the hardness and case-depth of pack cyanided mild steel samples. Results from the study showed that surface hardness of steel components substantially increased and that the waste product was a harmless biodegradable organic compound that posed no disposal threats. Gordon et al. [9] reported case hardening of mild steel using biomass in cassava processing. The study investigated effects of grain size refinement via severe plastic deformation on carbon/nitrogen diffusion during case hardening using cassava leaves. The result showed that the grain size of the starting material had a significant effect on the diffusion of hardening species. Arthur et al. [10] further studied indentation size effects on pack carbo-nitrided AISI 8620 steels. The surfaces of the steel samples were pack carbo-nitrided at 900°C using cyanide-containing dried cassava leaves which was achieved by quenching austenitized steel at different pH values of cyanide-based bio-processed solution. Nanoindentation was carried out with a Berkovich tip indenter to determine the hardness and elastic moduli of the quenched carbonitrided and as-received steel surfaces. The case-hardened steel was shown to have higher hardness than the as-received steel. The research revealed that the indentation size depends strongly on the hardness. Akinluwade et al. [11] made a submission on the alternative use of cassava leaves for pack cyaniding in the Encyclopedia of Iron, Steel, and their Alloys; and also reported a comparative study of low and high-temperature pack-cyaniding of 1018 steel using cassava leaves [12]. The use of cassava leaves for pack-cyaniding of low carbon steels has been widely reported and it has a future hope of replacing the toxic synthetic cyanide salts hitherto being used for cyaniding.

While the suitability of cassava leaves for case hardening of low carbon steels has been widely reported, there is dearth of information on the phases that constitute the case formed in cassava leaves case-hardened low carbon steels, hence the present research.

2. EXPERIMENTAL PROCEDURE

Fresh matured cassava leaves of *Tropical Manihot* specie (TMS–30572) were harvested, sun-dried [10] and sieved with an Octagon Sieve Shaker to 250 μm. AISI 1018 steel samples with the chemical composition given in Table 1 were subjected to pack-cyaniding heat treatment in pulverized cassava leaves in accordance with the method developed by Adetunji and Akinluwade [5,7]. Suitably dimensioned 1018 steel samples were pack cyanided at 950°C in 250 μm pulverized cassava leaves for 1 hr, 2, 3, 4 and 5 hrs. Small sections of each sample were taken for mounting in compression mount epoxy media, ground with silicon carbide from 400 grit size to 1200 and polished to a final stage of 0.04 μm particle size alumina suspension. Samples for micro-examination were prepared in accordance with ASTM E3-01 [12]. Some of the images of experimental set up and raw materials used were presented in the Appendix.

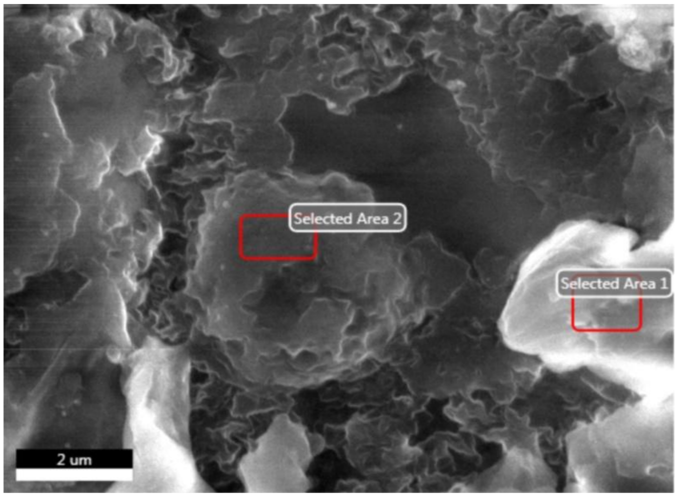
The case and core microstructure were captured on the light microscope while case depths were measured with the aid of an advanced Leica optical microscope equipped with Clemex Vision^{TM} 3.0 image analyzer at magnification of x10. Scanning electron microscopic imaging/energy dispersive spectroscopy of the cassava leaves powder used was conducted using JEOL 7000 FEGSEM scanning electron microscope. The cases were analyzed with a PANalytical Empyrean diffractometer equipped with PIXcel detector and fixed slits with Fe filtered Co-Kα radiation. These phases were identified using Philip Analytical X'Pert High Score plus software with an in-built International Centre for Diffraction Data (ICDD) database [13]. Table 1 is the chemical composition of the AISI 1018 as-received steel material.

Table 1. Chemical composition of AISI 1018 steel

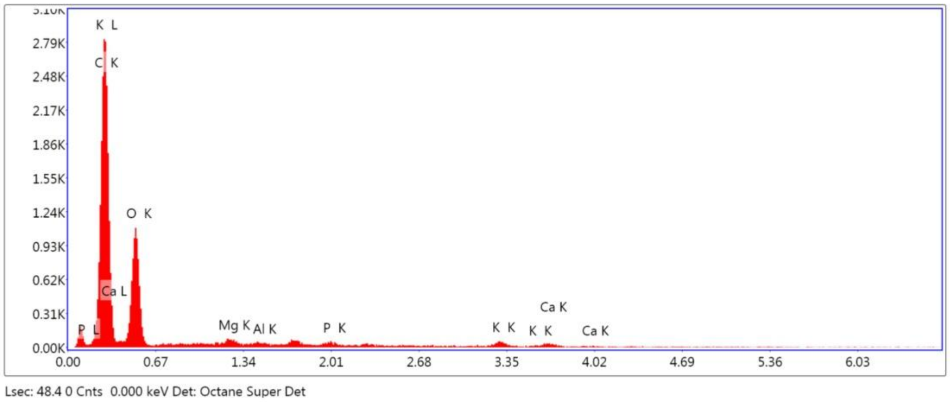
Element	Content, wt. %
Carbon	0.152
Silicon	0.049
Manganese	0.450
Phosphorous	0.009
Sulphur	0.006
Chromium	0.029
Nickel	0.023
Aluminium	0.047
Copper	0.013
Iron	99.222

3. RESULTS AND DISCUSSION

Fig. 1 shows the SEM/EDS spectra of the cassava leaves powder pellet. The EDS pattern indicates the various elements present in the cassava leaves powder and their composition. The elemental compositions are: 56.99%C, 1.33%Mg, 2.33%Ca, 0.77%Si, 0.75%Al, 34.56%O, 1.25%P, 2.82%K, etc.



(a)



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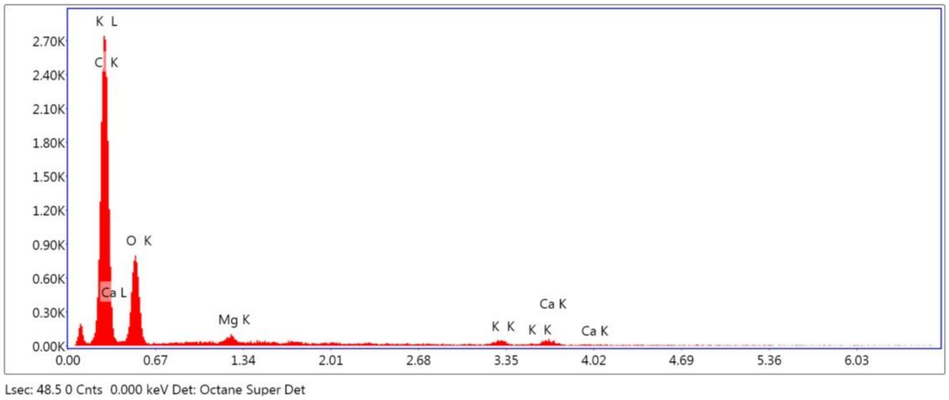

(c)

Fig. 1. a) SEM Image, b) EDS Spectra of Selected Area 1 and c) EDS Spectra of Selected Area 2 of the Cassava Leave Powder Used for the Research

3.1 Microstructure

The micrograph of as-received 1018 steel material has a microstructure that contains mostly ferrite and pearlite at ambient temperature (Fig. 2).

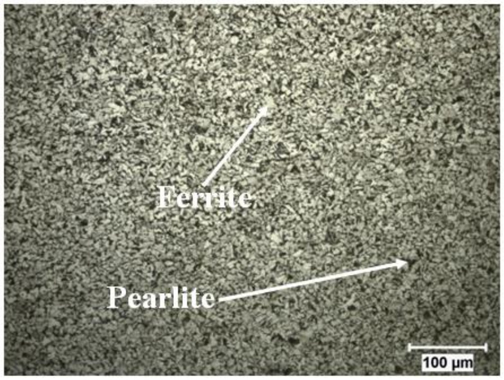

Fig. 2. Optical micrograph of as-received 1018 steel (2% NITAL) X200

In all the treated samples, cases were observed at the edges as a result of diffusion of nascent hardening species mainly carbon and nitrogen (Figs. 3-7).

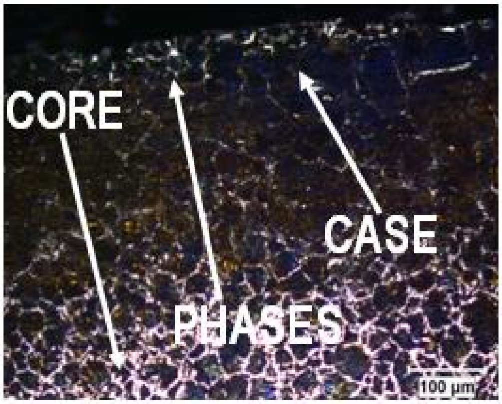

Fig. 3. Optical micrographs of the 1018 steel sample cyanided at 950°C with $BaCO_3$ for 1 hr (2% NITAL) X200

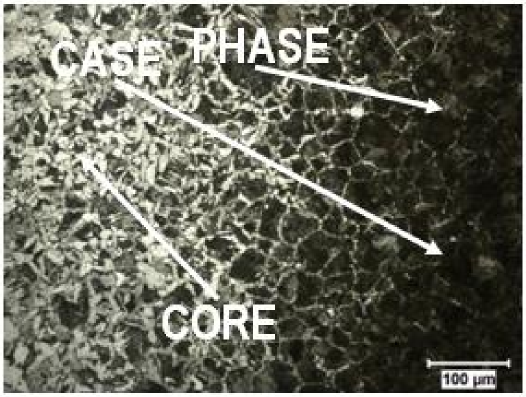

Fig. 4. Optical micrographs of the 1018 steel sample cyanided at 950°C with $BaCO_3$ for 2 hrs (2% NITAL) X200

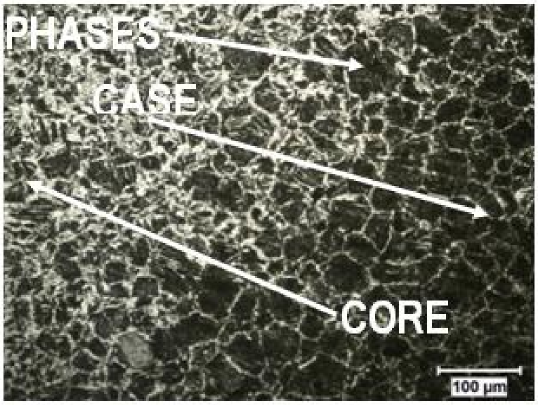

Fig. 5. Optical micrographs of the 1018 steel sample cyanided at 950°C with $BaCO_3$ for 3 hrs (2% NITAL) X200

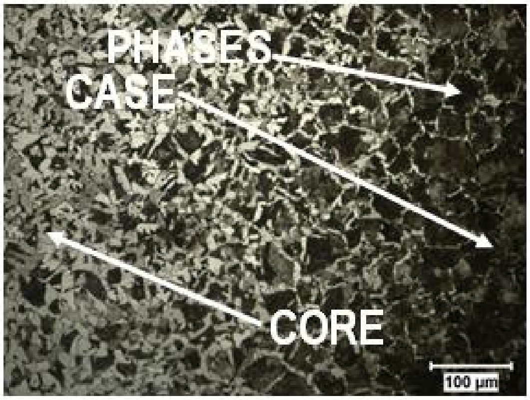

Fig. 6. Optical micrographs of the 1018 steel sample cyanided at 950°C with $BaCO_3$ for 4 hrs (2% NITAL) X200

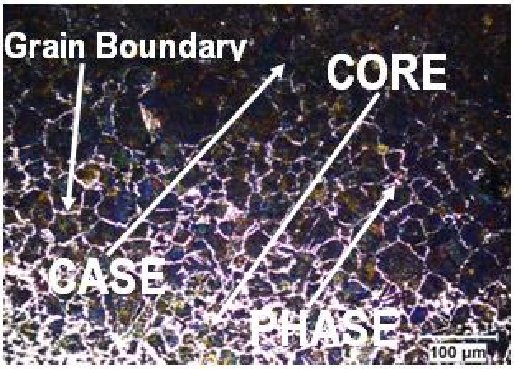

Fig. 7. Optical micrographs of the 1018 steel sample cyanided at 950°C with $BaCO_3$ for 5 hrs (2% NITAL) X200

The micrographs above indicate formation of substantive cases as a result of effective diffusion of nascent carbon into the austenitic phase of steel. The micrograph of the as-received sample in Fig. 2 showed fine-grained steels characterized with small grains and numerous grain boundaries. Although carbon tends to be attached to dislocation centers, a large network of grain boundaries may possibly act as constraints inhibiting the drift of carbon into the steel [9,12]. Consequently, diffusing carbon atoms will not travel far before being locked in the subsurface. This is feasible since the grain boundaries can be regarded as regions of discontinuity occurring in the regular repetitive arrangement of atoms [1]. At 950°C, both substitutional and interstitial diffusion of nascent carbon occur; since diffusion increases exponentially with rise in temperature [3]. A larger proportion of the diffusion of carbon into steel takes place through the matrix and not through the grain boundary [12]. Another reason that could adduce to the effective diffusion of carbon despite the inhibitive nature of the numerous grain boundaries observed is the use of an energizer which enhances the diffusion process by accelerating the mechanism of pack cyaniding reactions. According to Singh et al. [4], an energizer or activator speeds up cyaniding mechanism by reducing the melting/decomposition temperature of cyanate and the viscosity of the melt, depending on the cyaniding media. Fig. 7 indicates higher density of grain boundaries as compared to others, this is because at 5 hrs soaking time, more nascent carbon were able to diffuse into the steel surface since the process involves diffusion and growth both of which are time dependent [14].

3.2 Case Depth Measurement

The case depths were measured with the aid of a Leica optical microscope equipped with Clemex Vision^{TM} 3.0 image analyzer. Each sample was placed in turn on the lens of a top-loading microscope. The magnification of the microscope was set to 10X because this has been found suitable to reveal the case depth and macrostructure [15]. A careful adjustment of the intensity of admitted light rays as well as its focus on the surface of the specimen and proper alignment of the specimen assisted in capturing good macrographs for case depth determination. The image analyzing software attached to the equipment paved way for digital measurement of case depths. Identified cases are indicated by arrows with depth values inscribed on the arrows. Identified cases are quite different from the core of the material.

The variation of case depth with soaking time is provided in Figs. 8 to 12. In general, case depth increases with soaking time. This is because a longer soaking time allows more time for the reaction to proceed resulting in more carbon atoms present in the reaction atmosphere diffusing and migrating deeper into the sample surface. The mechanism of case hardening essentially involves diffusion, which are nucleation and growth processes. These processes are temperature and time dependent and therefore the general trend of increase in case depth with soaking time at a particular temperature agrees with the literature [15].

The general trend obtained agrees with the results of previous research on pack cyaniding of mild steel using cassava leaves powder [6].

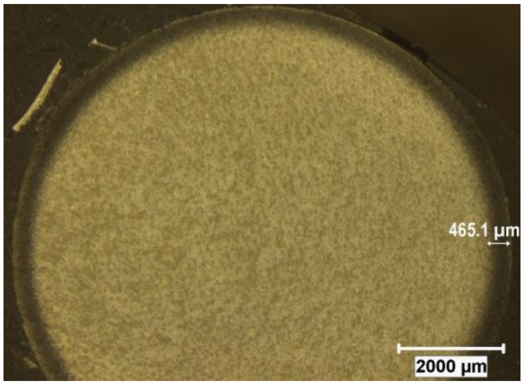

Fig. 8. Optical Macrograph of Case Depth Measurement for 1018 Steel Sample Cyanided at 950°C with $BaCO_3$ for 1 hr (Indicating the case depth to be 465.1 µm) X10

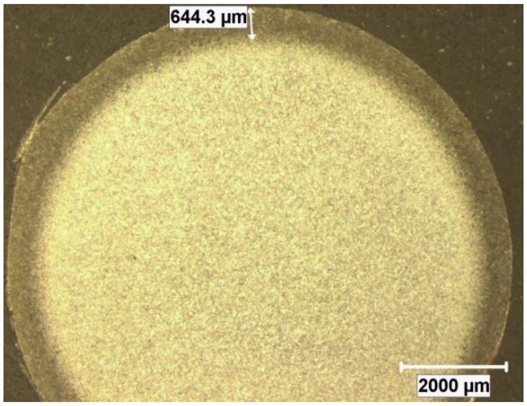

Fig. 9. Optical Macrograph of Case Depth Measurement for 1018 Steel Sample Cyanided at 950°C with $BaCO_3$ for 2 hrs (Indicating the case depth to be 644.3 µm) X10

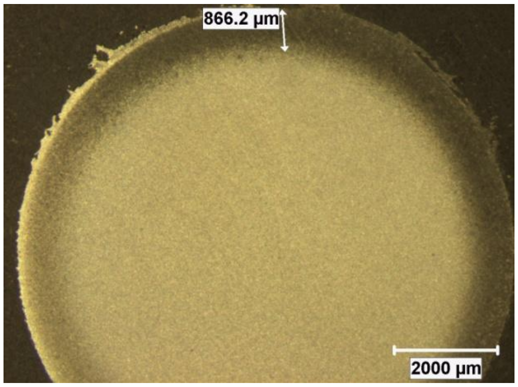

Fig. 10. Optical Macrograph of Case Depth Measurement for 1018 Steel Sample Cyanided at 950°C with $BaCO_3$ for 3 hrs (Indicating the case depth to be 866.2 µm) X10

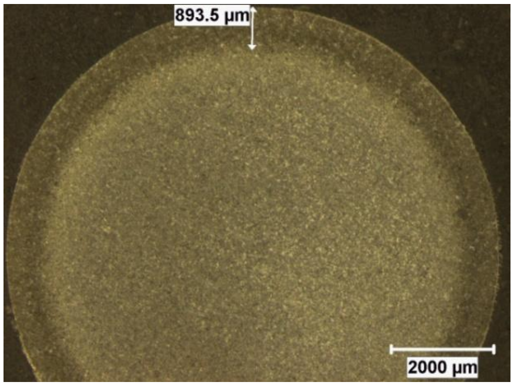

Fig. 11. Optical Macrograph of Case Depth Measurement for 1018 Steel Sample Cyanided at 950°C with $BaCO_3$ for 4 hrs (Indicating the case depth to be 892.5 µm) X10

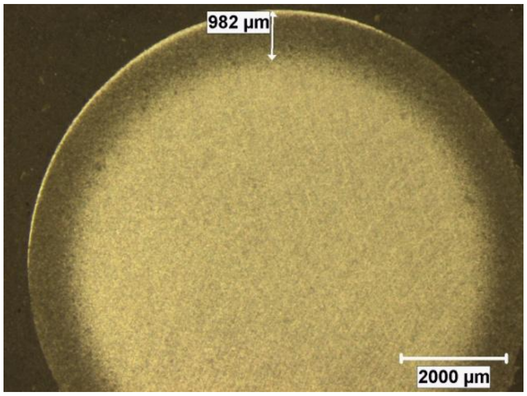

Fig. 12. Optical Macrograph of Case Depth Measurement for 1018 Steel Sample Cyanided at 950°C with $BaCO_3$ for 5 hrs (Indicating the case depth to be 982.0 µm) X10

The result also corroborates that of Adetunji et al. [7] and Akinluwade et al. [5], both of which reported increase in case depth with soaking time when cassava leaves powder was used for cyaniding mild steel in solid media.

3.3 Phase Identification

From the XRD results, phases that constituted the cases were found to be SiC, FeSiC, FeSi, Fe_3C and iron carbide ($C_{0.09}Fe_{1.91}$) as shown in Figs. 13 and 14. It proved that case-hardening of mild steel with cassava leaves powder at 950°C results in carburizing [5]. At high temperatures, steel will be in austenite phase where carbon demonstrates a higher solubility in austenite than in ferrite, therefore there was an effective diffusion of carbon into the surface of the samples with subsequent formation of various phases earlier identified [1]. Since the treated samples were not quenched, the cases formed contained mainly carbides rather than martensite such that the strengthening mechanism here could be regarded as dispersion strengthening [3]. The developed phases would act as strong barriers to the motion of dislocation leading to a strengthening effect in the treated material [4]. The peaks obtained in Figs. 12 and 13 are quite similar revealing virtually the same phases. This means that the treatment time has no effect on the phases that were formed.

Although cassava leaves powder was used as a source of hardening species (Carbon and Nitrogen), no iron nitride phase was identified in the cases formed. Also, nitrogen was not included among the elements revealed by the EDS spectra of the cassava leaves powder used for this study (Fig. 1). The reason for this could be attributed to the processing route employed in the drying of cassava leaves. In the present work, matured cassava leaves were dried in accordance with Arthur et al. [10]. However, Julie et al. [16] reported that sun-drying of cassava leaves removes substantial amount of its cyanide content. Research is currently on-going to confirm the reason for this in order to establish the best drying method for the cassava leaves being used for case hardening of low carbon steels.

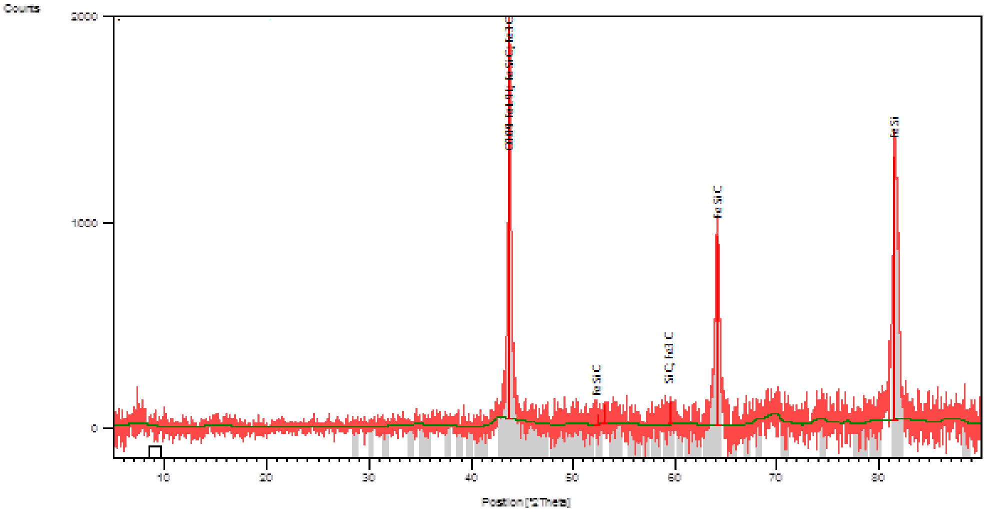

Fig. 13. XRD Pattern of 1018 Steel Case-Hardened at 950°C with $BaCO_3$ Energizer for 2 hrs (The intense peak contained Fe_3C, FeSiC & $C_{0.09}Fe_{1.94}$ phases)

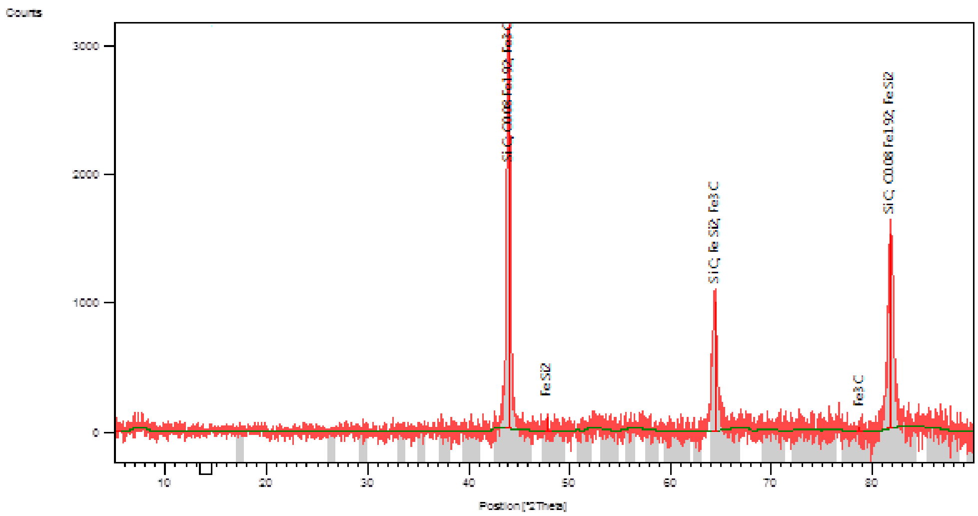

Fig. 14. XRD Pattern of 1018 Steel Case-Hardened at 950°C with $BaCO_3$ Energizer for 5 hrs (The intense peak contained Fe_3C, SiC & $C_{0.06}Fe_{1.92}$ phases)

4. CONCLUSION

The following conclusion can be drawn from the study:

1. It affirmed the suitability of cassava leaves for case-hardening of low carbon steels as established by earlier authors
2. It identified the phases that constitute cassava-leaf case-hardened mild steel
3. It showcased how the case depth could be digitally determined from the microstructure using Clemex Vision^{TM} 3.0 image analyzer software
4. It also showed that high temperature pack-cyaniding using cassava leaves results in carburizing
5. It hinted also on the best method for processing cassava leaves to be used for case-hardening; as sun-drying tends to pave way for a covert escape of cyanide/nitrogen in the cassava leaves.
6. The study presented innovation trends after using standard analytic techniques for characterization of mild steel case-hardened with processed cassava leaves. The results obtained are promising and have potentials for replacing conventional cyaniding that involves the use of toxic synthetic cyanide salt.

ACKNOWLEDGEMENTS

The authors acknowledge the financial sponsorship of the study by Pan African Materials Institute (PAMI) domiciled in African University of Science and Technology (AUST), Abuja and NEEDS Assessment Academic Staff Training and Development (AST & D) Programme of Obafemi Awolowo University (OAU), Ile-Ife. The authors also acknowledge the equipment support of the Centre for Electron Microscopy, University of Birmingham, UK.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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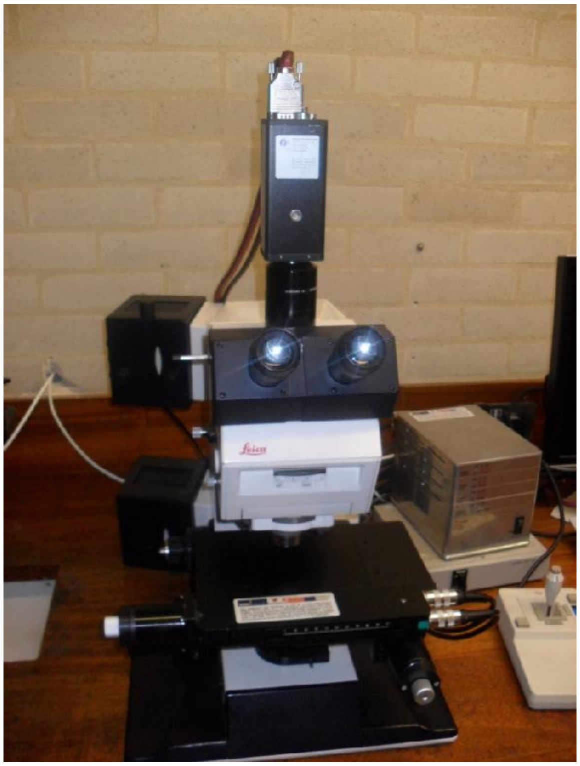
APPENDIX

Appendix A: Four Volumes of Cassava Powder (green heaps) and One Volume of Barium Carbonate Energizer (white heaps)

Appendix B: Image showing the Crucible Containing the Case-hardening Mixture after offloading from the Furnace

Appendix C: Image showing the Red Hot Muffle Furnace during Samples Off-loading.



Appendix D: Advanced Leica Optical Microscope used for the Research

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