

Potential of Cow Horn for Carbonitriding Treatment of Steel

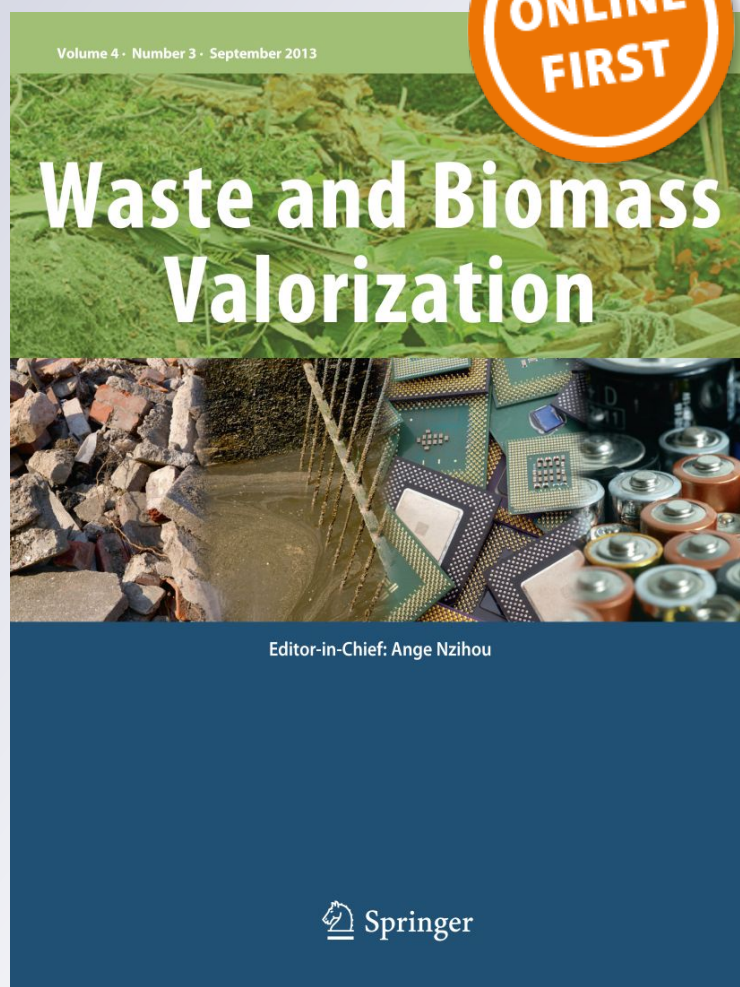
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Potential of Cow Horn for Carbonitriding Treatment of Steel

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Abstract

The potential of carbonitriding treatment of steel with cow horn was investigated in line with abattoir waste to wealth approach of waste management. The objectives of the study included processing of cow horn into different morphologies namely: powder and flakes for carbonitriding heat treatment, and, chemical analyses of cow horn with Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) techniques to determine the chemical composition and phases of cow horn respectively. The heat treatment was carried out at 850 and 450 °C for carburizing and nitriding dominated processes respectively. Vickers hardness measurement was carried out to determine the hardness profile on carbonitrided samples. Optical metallography was carried out for microstructural examination and to investigate phase contrast between the case and core of carbonitrided sample. The result of hardness test observed is consistent with the case hardening profile with higher hardness value at near surface decreasing towards core. Sample heat treated with horn flakes showed higher hardness than those with horn powder. Microstructural phase contrast showed delineation of the hardened case and soft inner core. The high hardness of case was attributed to diffusion of carbon and nitrogen atoms from the cow horn to iron interstices. This supposition was corroborated by detection of carbon and nitrogen with EDS and XRD tests. It was therefore concluded that cow horn could be processed as candidate materials for carbonitriding of steel.

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[6, 7]. Recent studies by Mikulíková et al. [8], on analysis of saiga horn using high performance liquid chromatography with mass spectrometry and polyacrylamide gel electrophoresis, revealed the presence of basic protein namely: keratins and collagen. One of such example of β -keratins is fibroin, which is characterized with antiparallel molecular chains having an alternating C $\rightarrow$ N orientation [9, 10].

In engineering, numerous machine components require wear and fatigue resistance on the outer surface known as case and a relatively softer, tougher interior of parts referred to as core [11, 12]. This is achieved through the process of case hardening, often carried out on low carbon steels to develop components with a balanced of tougher inner core and hard outer shell [13]. Case hardening helps to transform a thin layer of material at the near surface of the part, through carbon or nitrogen enrichment, to a relatively harder shell than the base metal alloy [14]. Typical area of application of case hardening treatment is heavy duty gears in which teeth surfaces are subjected to continuous and severe frictional contact. Case hardening may be achieved through the method of carburizing [15, 16], nitriding [17] and carbonitriding [12, 14] by the addition of carbon, nitrogen and both elements respectively, in solid state [17].

Other hardening which does not involve diffusion of carbon and/or nitrogen atom into work piece include laser hardening [18], flame hardening [19] and induction hardening [20]. One major advantage of carbonitriding is that, the nitrogen absorbed during processing lowers the critical cooling rate of steel. This suggests, hardenability of the case is significantly greater when nitrogen is added during carbonitriding than when the same steel is carburized. This permits the production of steels on which ordinarily, uniform case hardness may be difficult to achieved if it is only carburized and quenched. Carbonitriding permits the use of low-carbon steels, which cost less and may have better machinability or formability [21].

Case hardening is a thermo-chemical process in which some heat is needed to enhance the diffusion of hardening elements into the steel surface. The depth of diffusion is time dependent according to Eq. 1:

$$\text{Case Depth} \propto K\sqrt{\text{Time}} \quad (1)$$

where the diffusivity constant, K , depends on temperature, the chemical composition of the steel, and the concentration gradient of hardening element. The diffusivity constant increases exponentially as a function of absolute temperature. Concentration gradients also depend on surface kinetics

and reactions of a particular process [15]. The diffusion process during the case hardening is governed by Fick's laws of diffusion (Eq. 2) which relates the diffusive flux to the concentration under the assumption that a solute will move from a region of high concentration to a region of low concentration across a concentration gradient.

$$J = -D \left[\frac{dc}{dx} \right] \quad (2)$$

where J is the diffusion flux in amount of solute (atoms, or grams, or moles) per unit area per unit time, C is the concentration of solute in amount (atoms, or moles, or grams) per unit time, x is the distance, $[dc/dx]$ is the concentration gradient across the plane and, D is the diffusion co-efficient in (square length) per unit time. When C is in atoms/cm³, x is in cm, and D is in cm²/s, the flux, J , is equal to the number of atoms moving across the plane at x in the x -direction per cm² of the plane per second [22].

The aim of this work is to study the potential of abattoir waste (horn) for carbonitriding treatment of steel. The objectives of the study included processing of cow horn into two morphological forms namely: powder and flakes for carbonitriding heat treatment; chemical analyses of cow horn with Energy Dispersive Spectroscopy (EDS) and X-ray Diffraction (XRD) techniques for determination of chemical composition and phases of cow horn respectively; characterisation of carbonitrided steel using microhardness tester and optical microscopy; and finally, correlation of the hardness results with that of chemical analyses of the horn.

Materials and Methods

Materials

The animal horns used for the carbonitriding heat treatment was cow horn. The horn was obtained from Ipata market (abattoir), Ilorin (Fig. 1). The low carbon steel used for the experiment was mild steel, AISI 1018. The chemical composition of the mild steel is given in Table 1. The chemical composition was determined by spectrometric analysis carried out at Nigerian Foundry Limited (NFL) Sango-Ota, Ogun state. The steel sample was sectioned into dimensions 26 mm $\times$ 31 mm $\times$ 13 mm (length $\times$ width $\times$ height) under running water to reduce heat generation during cutting.

Table 1 Chemical composition (weight percent) of AISI 1018 steel plate used

C	Si	S	P	V	Mo	Mn	Ni	Cr	Cu	Fe
0.152	0.181	0.020	0.014	0.001	0.001	0.676	0.015	0.025	0.028	98.8

Methods

Scanning Electron Microscopy and Energy Dispersive Spectroscopy

The scanning Electron Microscopy (SEM) with Jeol JSF-7600F was done on cow horn as precursor to determination of its chemical composition by Energy Dispersive Spectrometry (EDS) [23, 24]. Secondary electron image was acquired at an Accelerating Voltage of 15 keV and Working Distance (WD) of 11 mm. Energy dispersive spectroscopy was carried out using INCA software. Spectra of suspecting elements generated from area mapping of the SEM secondary electron image were processed for quantitative analysis.

Post carbonitriding treatment chemical analyses of steel samples were carried out to investigate the carbon and perhaps, nitrogen pick-up after the heat treatment. Area mapping were carried out at the case shell and the core of the sample to compare and contrast their chemical composition.

X-ray Diffractometry

The XRD of cow horn was carried out on Philips X'Pert PANalytical Diffractometer using the Copper anode radiation tube. The power rating of the X-ray generator used was 45 mA and 40 kV. The K-Alpha and K-Beta wavelengths of Cu anode used were 1.5406 and 1.3922 Å respectively. The goniometer radius of 240 mm was used for the scanning along the goni axis. The length of samples used was 10 mm. The measurement was carried out at 25 °C. X-ray intensities were measured at Bragg angle 2θ between 5° and 90° and at step size of 0.01 µm and at 30 s per step.

Carbonitriding Heat Treatment of Steel

The sectioned steel samples were wet grinded with abrasive papers of grit sizes: P240, P400, P800 and, P1200. This was carried out to remove layers of oxides and deep

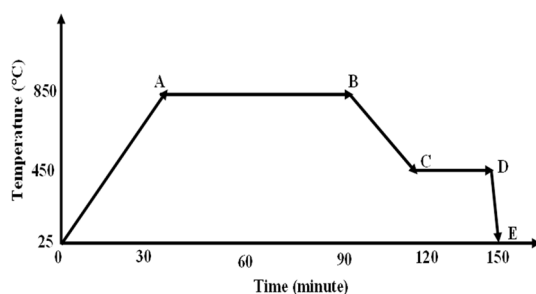


Fig. 2 Schematic illustration of carbonitriding process

scratches on samples prior to carbonitriding heat treatment. Carbonitriding with cattle horns was carried out in two morphological forms namely: flaky and powdered forms. The powdered horn was achieved using manual grater and then subsequently blade milled into finer powder form. This was done to ensure a uniform powder grain size. Powder grain size of 0.60 mm used was achieved using sieve analysis. On the other hands, flaky form was achieved by cutting the horn with hacksaw into pieces. An average flake size of 60 mm×25 mm was used for the experiment. The amount of powdered and flaky horn used for the heat treatment was 150 g.

Two cylindrical crucibles, each with dimensions of 110 mm×96 mm (length×diameter), were labelled I and II for powdered and flaky horn carbonitriding samples respectively. Two steel samples were placed in each crucible initially without horn, covered with lids and then placed inside the muffle furnace. The steel samples in the crucibles were preheated to 850 °C to ensure homogeneous heating (0-A, Fig. 2). The crucibles were brought out of the furnace and 150 g horn were introduced into the crucible, covered and were quickly returned back to the furnace to allow for carburizing heat treatment. The temperature was allowed to reach 850 °C again and then soaked for 60 min (a, b, Fig. 2). After soaking for 60 min, the sample was then furnace cooled to 450 °C (b, c, Fig. 2) and another 150 g of horn was introduced into the crucibles again and returned back into the furnace for nitriding dominated heat treatment (c, d, Fig. 2). The samples were soaked at 450 °C for another 30 min, before the samples were finally taken out of the crucible and quenched in water (d-f, Fig. 2). The order of the heat treatment processes was consistent with the fact that nitrogen tends to inhibit carbon diffusion if carried out other way round [15].

Micro-hardness Measurement

The carbonitrided samples were prepared for micro-hardness measurement. Surface to be tested required a metallographic finishing, considering the smaller the load used for micro-indentation. The carbonitrided samples were then wet grinded as described above. The grinded samples were then polished with diamond pastes of grain sizes 0.5 and 0.25 µm. This was carried out to obtain a scratched-free surface required for micro-hardness measurement.

The Vickers hardness test was carried out at Engineering Materials Development Institute (EMDI), Akure. The test involved application of diamond pyramid indenter with a controlled pressure load of 980.7 mN for a standard dwell time of 10 s. The diagonal of the resulting indentation was measured under precision microscope at higher magnification of ×50 and measured to an accuracy of + 0.5 µm. The length of the diagonal of indentation

Table 2 Vickers hardness result of carbonitrided 1018 steel

Distance from surface (mm)	Mean Vickers hardness values Hv (Kgf/mm ²)		Standard deviation	
	Powdered	Flakes	Powder	Flakes
1	147	201	34	53
2	122	154	4	7
4	118	133	3	13
7	112	112	5	1

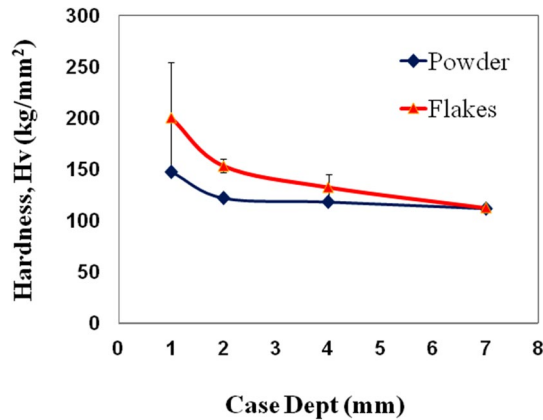
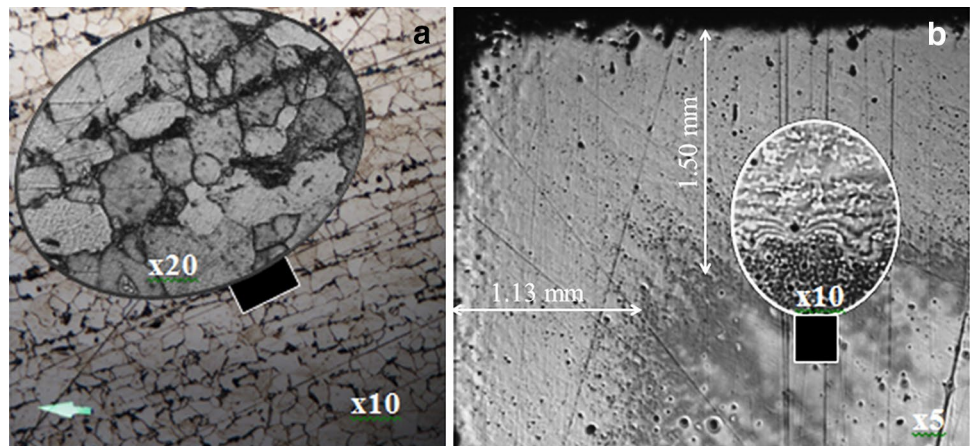


Fig. 3 Micro-hardness of 1018 steel carbonitrided with cattle horn

and the test load were used for the calculation of Vickers hardness value. The Vickers Diamond Pyramid harness number, H_V was calculated according to Eq. 3, where F is applied Load in kgf, d is mean of the two diagonals, d_1 and d_2 in mm.

$$H_V = 2F \sin^{136/2} / d^2 \quad (3)$$

Fig. 4 Optical micrographs of 1018 steel carbonitrided with horn powder showing: microstructures (a) and hardened case and core contrast (b)



Optical Metallography

The carbonitrided samples were also prepared for post-heat treatment optical metallography. The optical metallography was carried out at Engineering Materials Development Institute (EMDI) Akure. Similarly, the samples were grinded and then polished with diamond pastes of grain sizes 0.5 and 0.25 μm . This was carried out to obtain a scratched-free surface required for metallographic examination of the materials. The polished sample was then etched with 2% Nital solution to reveal the microstructures and particularly the interface between the hard shell and the core.

Results and Discussion

Hardness

One of the main goals of this research was to investigate the potential of cow horns as candidate material for carbonitriding and to determine the effects of horn morphologies on the hardness profile. The results of the micro-hardness test carried out on the carbonitrided 1018 steel are shown in Table 2.

From Table 2, it can be deduced that steel samples carbonitrided with flaky horn possess higher hardness values compared with sample heat treated with powdered horn. This observation may be attributed to lower rate of release of gases from flaky horn during each of the processes on account of its relatively smaller surface area compare with powdered horn. Again, the hardness value was relatively higher at the near surface (case) and reduces towards the centre (see Fig. 3). It was observed that the hardness values at the centres of all samples were the lowest. Hence, the hardness at the centre of each sample was considered to be the control sample hardness value. Again, the results of optical metallography were quite informing showing the

phase contrast between the hardened case and soft inner core depicted by hardness results.

Microstructural Analysis

The optical micrographs of steel samples carbonitrided with horn powdered are shown in Fig. 4. The microstructures observed in the micrograph (Fig. 4a) include room temperature ferrite (dark), pearlite (white) and retained delta ferrite which appeared sandwiched between grains at the boundaries (darker continuous strips). The grains appeared fairly equiaxed except the continuous stripes of retained delta ferrite whose shape could be attributed to the primary hot rolling. Figure 4b showed the optical micrographs of carbonitrided specimens at low ($\times 5$) and high ($\times 10$) magnifications (inset). Figure 4b showed the contrast between hardened case at the near-surface and the soft inner core. The inset in Fig. 4b showed the interface between the hardened case and the core. The average depth of the hardened case measured was 1.31 mm.

Another probable non equilibrium microstructure that may be localised at the near surface is martensite, which may develop from diffusion-less transformation of austenite, if stabilised below the A1 temperature line, prior to quenching. The presence of carbon and nitrogen being austenite stabilising elements can enhance austenite stability below the A1 temperature line and hence its propensity for transformation to martensite during water quenching from 450 °C to room temperature cannot be ignored [25, 26]. Frandsen et al. [27] in their work, attributed the enhanced surface hardness to the development of C/N-expanded martensite and austenite at intermediate to low nitriding potential and carburizing. The ascription of hardness result with carbon and nitrogen diffusion to interstitials of iron atom prompted the use of SEM and EDS for qualitative analysis of the cow horn and carbonitrided samples.

Scanning Electron Microscopy and Energy Dispersive Spectrometry

The results of SEM and EDS carried out on cow horn are shown in Fig. 5. Figure 5a was the SEM micrographs and showed the size of area mapping from which the spectra in Fig. 5b were obtained. The carbon and nitrogen spectra were quite significant amidst other elements spectra. To guarantee the integrity of the EDS data, the normalised average of the mean data of five different data measured were calculated. The confirmation of the presence of carbon and nitrogen in cow horn corroborated the attribution of hardness profile to diffusion of the two interstitial elements to the case during the carbonitriding heat treatment.

The dominant elements in cow horn were carbon, oxygen and nitrogen, while significant amount of sulphur was registered, with other elements in traced amount. This result is consistent with the EDS analysis of Bighorn sheep by Tombolato et al. [7] where carbon, oxygen and sulphur were equally observed. The chemical signatures likened cow horn to thermoset polymer which is probably cross-linked by sulphur and oxygen atoms.

The energy dispersive spectra of the carbonitrided steel sample obtained from the hardened case (spectrum 1) and the core (spectrum 2) were contained in Fig. 6. The height of Carbon spectrum in the case (Fig. 6b) was significantly more than the carbon spectrum in core (Fig. 6c). These results corroborated the suggested carbon pick-up at the sample case.

After the presence of carbon and nitrogen had been established with EDS, it was equally important to understand the molecular composition of the various elements observed with EDS. This therefore necessitated the use of XRD techniques for phase identification in the cow horn.

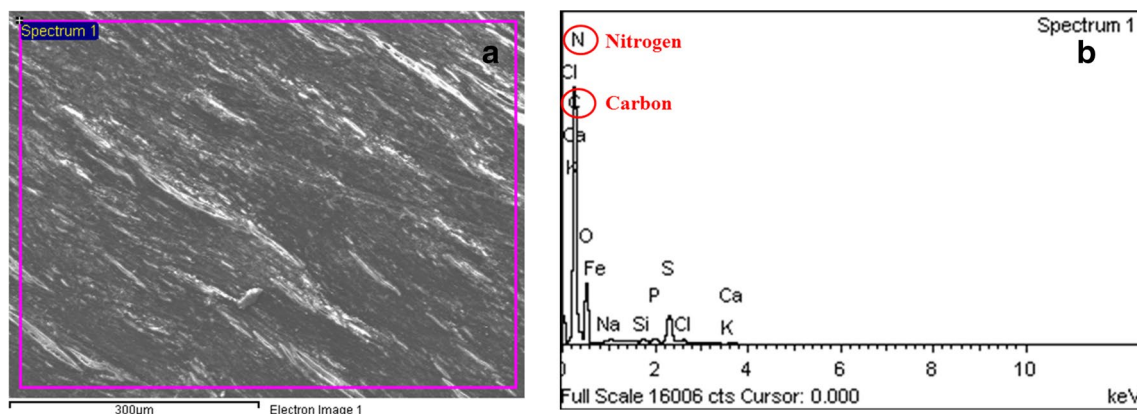


Fig. 5 Scanning electron micrograph (a), and energy dispersive spectral (b) of cow horn

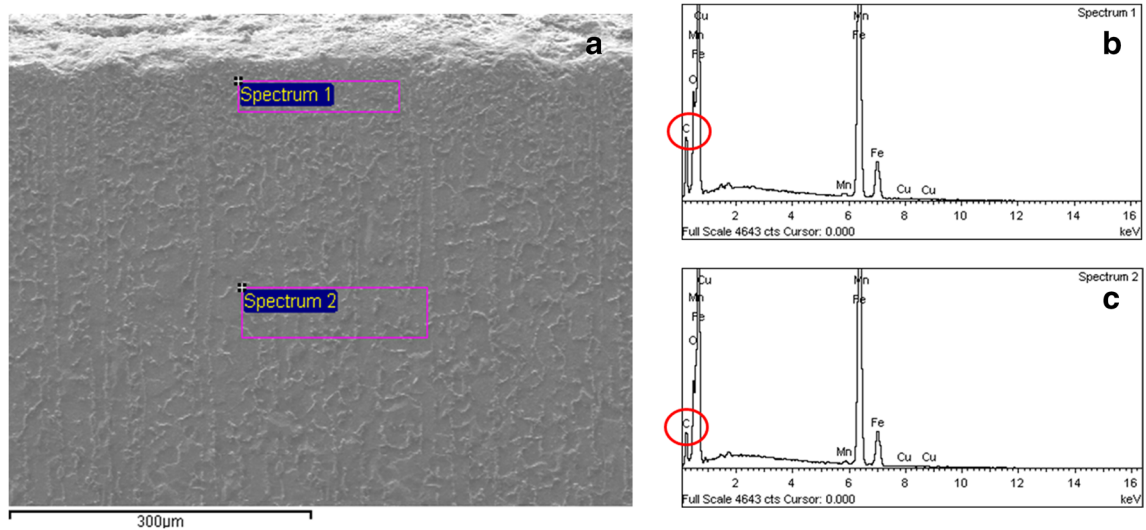
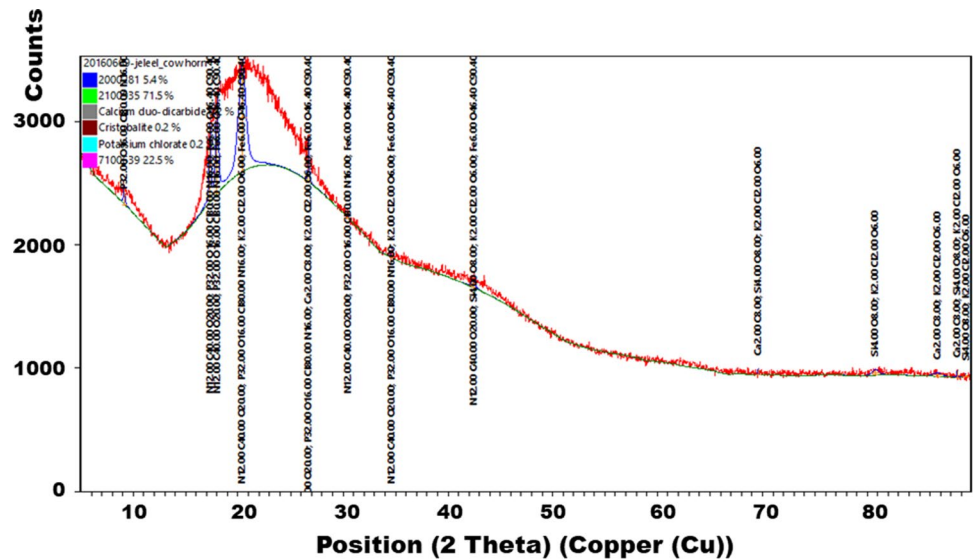


Fig. 6 Scanning electron micrograph of carbonitrided AISI 1018 steel **(a)** showing EDS area mapping positions of spectrum 1 **(b)** and spectrum 2 **(c)**

Fig. 7 X-ray diffractogram of cow horn showing the crystalline peaks and amorphous base



X-ray Diffractometry of Cow Horn

The result of XRD of cow horn is shown in Fig. 7. The diffractogram indicated the presence of different phases in the cow horn based on few identifiable crystalline peaks (Fig. 8). The details of the phases and the nomenclatures of the identified compounds and their respective chemical compositions are presented in Table 3.

The diffractogram in Fig. 7 contained the crystalline phase peaks with broad amorphous background. The background phase is dominated by $\text{P}_{32}\text{O}_{16}\text{C}_{180}\text{N}_{16}$ while other dominant phases observed in cow horn were $\text{N}_{15}\text{C}_{40}\text{O}_{70}$ and

Fe₆O₄₆C₉₀ phases. The chemical composition of the dominant phases observed confirmed the presence of carbon and nitrogen atoms required for carbonitriding purposes (see Fig. 8). This result is consistent with the report elsewhere [28] which attributed hardness effect to solid state diffusion of carbon and nitrogen, and therefore in agreement with supposition of hardness profile in Fig. 3 being caused by carbon and nitrogen diffusion to the case during the heat treatment at high temperature.

Figure 9 showed explicitly the individual phase peak positions between 5° and 90° along the Bragg's angle 2θ . Figure 9 enabled identification of exact location of the

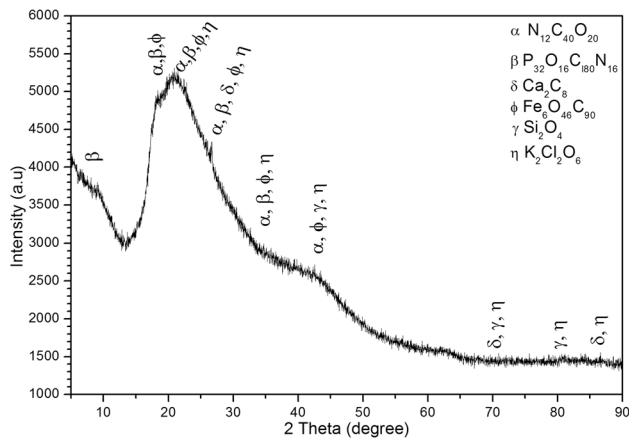


Fig. 8 X-ray diffractogram showing the phases in cow horn

diffraction angle which appeared as overlaps in Fig. 7. Understanding of the peak position is quite significant as it reveals the correlation between material deformation and shift in the position of the peaks.

Generally, it was observed that, the average hardness value measured on the samples carbonitrided with horn flakes was relatively higher than samples carbonitrided with horn powder. The difference was obviously higher at the near surface and decreased toward the core which ended with 112 kg/mm² at 7 mm depth. The higher hardness value at near surface is consistent with the established hardness profile of carburizing, nitriding and indeed carbonitriding [25]. This could be attributed to the diffusion of carbon and nitrogen to the interstices of the host atoms [29]. The hardness gradient observed was consistent with the variation of diffusion of the carbon and nitrogen with distance as indicated by Ficks first law of diffusion [22].

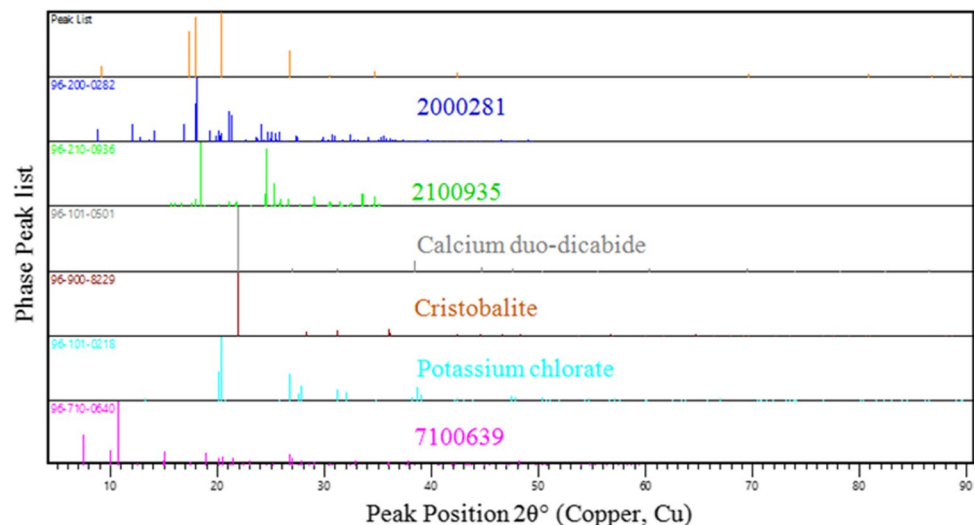
The lower hardness values observed in horn powder sample was attributed to large surface area of horn powder compared to horn flakes. The horn powder must have burnt sufficiently faster enough to rapidly release the volatile matters and oxidised carbon at higher temperature. It is suggested that the flakes would have burnt relatively slower than the horn powder and hence conserve the release of volatile matters and oxidation of carbon needed for diffusion into the steel.

Table 3 Phase identification in cow horn with XRD

Ref. code (JCPDS*)	Phase	Chemical composition	Suggested nomenclature
96-200-0282	α	$N_{12}C_{40}O_{20}$	2000281
96-210-0936	β	$P_{32}O_{16}C_{180}N_{16}$	2100935
96-101-0501	δ	Ca_2C_8	Calcium duo-dicarbide
96-900-8229	ϕ	Si_2O_4	Cristobalite
96-710-0640	γ	$Fe_6O_{46}C_{90}$	7100639
96-101-0218	η	$K_2Cl_2O_6$	Potassium chlorate

*Joint committee on powder diffraction standards

Fig. 9 Phase peak positions on the Bragg's angle 2θ



This work demonstrated that animal horn could be used as alternative material for carbonitriding rather than been discarded indiscriminately into the environment. This will help to reduce their adverse environmental impact, consequent upon air pollution from indiscriminate burning and health hazard associated with dumping ground.

Conclusion

The following conclusions are made at the end of the study investigating the potential of animal horn for carbonitriding of AISI 1018 steel:

1. Carbonitriding with cow horn produced hardness gradient with hardened outer case and soft inner core;
2. Energy dispersive spectroscopy of the cow horn showed the presence of carbon and nitrogen required for carbonitriding in significant amount;
3. Cow horn contains six molecular compounds in different phases and the presence of carbon and nitrogen were quite significant in some of the phases;
4. This research work showed that cow horn could be processed as candidate materials for carbonitriding of steel;
5. The best carbonitriding was achieved with flaky horn having produced the hardness gradient which is relatively higher than powdered horn and less labour intensive processing involved;
6. The use of animal horn as a secondary material for steel production will help to control indiscriminate waste disposal to the environment and ensure healthy living; and lastly,
7. The conversion of wastes to wealth arising from the processing and use of animal horn for surface treatment of steel will help in the creation of job opportunity.

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