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Investigation of Egg Shell Waste as an Enhancer in the Carburization of Mild Steel

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Abstract This work has investigated the possibility of utilizing egg shell waste which is a rich source of calcium carbonate as an enhancer or energizer in the case hardening of mild steel using organic solid wastes like sugar cane, melon shells and aracaceae flower droppings as the carbon source. The mild steel specimens were inserted in carburizing boxes containing the carburizing material and carburized at a temperature of 920 ℃ for 5 hours. They were then quenched in water, after which they were prepared for hardness test using Rockwell hardness tester, and for microscopic examination. The result showed that the carbonaceous organic waste used improved the case hardness of the steel. The result also showed that egg shell containing carburizing material produced higher case hardness on the steel than those carburizing materials without egg shell. Sugar cane waste produced a case hardness of 45.1HRC, with egg shell the case hardness became 45.5HRC. Melon shell waste produced a case hardness of 47.8HRC, and with egg shell the case hardness became 52.6 HRC. This hardness corresponded to an effective case depth of 0.65mm. Aracaceae flower wastes produced a case hardness of 56 HRC on the mild steel this corresponded to an effective case depth of 0.7mm, with egg shell the case hardness became 56.6 HRC with an effective case depth of 0.75mm. The calculated total case depth based on carburizing parameters was 1.34mm. The effect of egg shell waste as an enhancer in the carburization of mild steel has been established the result of the work has clearly shown that egg shell waste can be used in place of calcium carbonate to improve on the hardness value of mild steel during carburization. The success of this work has created another outlet for reducing the waste burden attributed to these solid wastes

Keywords: *carburization, enhancer, egg shells, mild steel, organic solid wastes*

1. Introduction

A clean environment contributes to healthy living this fact has since been realized by developed countries like Japan and many other European countries. These countries have succeeded in integrating clean environment into their cultures [1]. The reverse is the case with most developing economies of the world; in Nigeria for instance a visit to any of the major cities presents obnoxious situation, rubbish, garbage, polythene, plastic wastes, metal scraps, and industrial waste are seen littering the streets. Some of these wastes form breeding places for mosquitoes and other vectors that spread sicknesses. According to Dara [2] `solid waste management is very poor in most developing nations, this is because it comprises of purposeful and systematic control of the generation, storage, collection, transport, separation, processing, recycling, recovery, and disposal of solid waste; most developing countries lack both the capacity and the will power to manage solid waste'[2]. Ayres [3] in analysis the problem of solid waste in cities advocated recycling, stressing that the savings in terms of reduced environmental impact are less obvious but increasingly important [3,13].

Municipal wastes include garbage and rubbish from households, offices, hotels, markets, etc. and also the street refuse such as street sweepings, dirts, leaves, contents of litter receptacles, etc. from the household and market wastes, sometimes can be found large quantities of egg shells and cowbones; these can be separated and used for other industrial purposes. For instance previous works have shown that egg shells and cowbones contain calcium carbonate and their efficacy as energizers in pack carburization of mild steel have equally been proven. In separate works carried out by Ihom [4] and Ihom, et al [5], the authors were able to show that carburization of mild steel is enhanced with the addition of cowbones to the carburization material. The use of municipal and agricultural solid waste in metallurgy and materials engineering is steadily increasing sugar cane bagasse has been used for aluminum alloy particulate composite as well as for case hardening of mild steel [6].

Different materials are used in order to enhance the surface finish of metals; the type of material used depends on the technique and type of surface finish desired. Surface finishing processes include: impregnation of surfaces of metals with different element, heat treatment and others. Impregnation of metal surfaces with different elements include processes like carburization, carbonitriding, and nitriding, which in recent years have undergone a lot of transformation in terms of practice and methods. Commenting on this changes, Oriental Engineering Co. Ltd. in their training manual had this to say 'recent recognition of heat treatment of metals by the general public is remarkable, and it is extremely pleasing to us that heat treatment technology has been making rapid progress together with development of machinery and metal industries including automotives industry [7].

Carburizing technology has also been changing from solid carburizing to liquid carburizing and then to gas carburizing in correspondence to the improvement of heat treatment technology. Of course every one of these type of carburizing has both advantages and disadvantages, and it is necessary to select the most suitable type in correspondence to what is really required by each business and plant [8].

There are different carburizing materials with different carburizing potentials; some however have low carburizing potentials. The carburizing potential of such materials with low carburizing potential can be raised by the use of energizers these energizers enhance the carburizing potential of the carburizing material [4,9]. Different carbonates are used as energizers or enhancers in carburizing, notable among these carburization enhancers are sodium carbonate, barium carbonate, and calcium carbonate. These are used in varying percentages with the carburizing material [9].

This work looks at the possibility of using waste egg shells as an enhancer in the carburization of mild steel using different carburizing materials. Egg shell contains a substantial amount of calcium carbonate just like periwinkles, snails' shells, and others in that mollusc family. The objective of this work is to comprehensively establish that egg shell has the ability to act as an enhancer in the carburization of mild steel, which need hard case particularly when used in the production of gears and spindle shafts.

2. Materials and Method

2.1. Materials

The egg shell that was used in the work was collected from waste dump at Asak village of Plateau state. The mild steel was obtained from the producers in Kaduna state of Nigeria. Waste sugar cane, and melon shell were sourced at a waste dump in Jos. Aracaceae flowers droppings were collected at National Metallurgical Development Centre Jos directly under the plants. Consumables for metallography were those of the NMDC metallographic laboratory. Table 1 shows the chemical composition of the steel used.

Table 1.Chemical composition of the steel used

Element	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	Co	Ti	Nb
%	0.25	0.19	0.70	0.06	0.03	0.08	0.04	0.01	0.01	0.26	0.01	0.002	<0.01
Element	V	W	Pb	B	Sn	Zn	As	Bi	Ca	Ce	Zr	La	Fe
%	0.002	0.02	0.006	0.001	0.02	0.005	0.006	<0.02	0.006	0.004	0.002	0.004	98.1

2.1.2. Equipment

The equipment used for the research included the following: Rockwell hardness testing machine, electric tubular furnace, lathe machine, grinding mill, metallographic equipment and hacksaw.

2.2. Method

2.2.1. Materials Preparation

The melon shells, sugar cane waste, and egg shells were pulverized using a grinding mill. The aracaceae flower droppings were however, not pulverized. The mild steel was cut to 20mm x 20mm, it was then washed in acetone and rinsed in water to remove dirts. It was then dried using warm air from hand blower. For each of the carburizing materials two carburizing boxes were used one containing only the carburizing material embedded with the mild steel. The second box was filled with the carburizing materials and 50g of egg shell. The lids to the carburizing boxes were then replaced and sealed using clay paste to avoid air ingress so that oxidation will not take place.

2.2.2. Carburizing Process

The carburization operation was carried out using an electric tubular furnace. The carburization was carried out at a temperature of 920℃ and a holding time of 5 hours. The furnace had automatic control; once the data was entered the operation subsisted only for the entered data. The quenching was done in water immediately after removal from the furnace to avoid temperature drop.

2.2.3. Hardness Profile

Hardness profiles of the test specimens were measured using Rockwell hardness testing machine. The scale C was selected for the test measurements. The hardness tests were performed on the samples in accordance with the standard of hardness testing of metallic materials as per DIN 50103; ISO/ R80; and ASTM E18 based on Rockwell hardness 'C' scale. The hardness tester used was Frank hardness tester welltest 38506 designed in accordance with DIN51224 and ISO/ R716. A minor load of 10 kg (980 N) was applied first to seat the brale, after which a major load of 150 kg (1471N) was applied for the indentation. Three indentations were made on each test specimen and the average was calculated for the resultant hardness. At the beginning of the test the hardness tester was checked with a standard block of 59.6HRC to ensure that the machine was not out of calibration. These precautions are very important for accurate result. Some of the specimens were selected and hardness profiles were obtained at an interval of 0.5mm this was used to get the effective case depth of the specimens.

2.2.4. Microstructure Examination

One of the carburized specimen and the un-carburized mild steel were cut, ground and polished. A belted grinding machine with grits 240-600 was used. The specimens were then transferred to a pre-polishing disc where alumina powder paste of 1 micron was used for pre-polishing. The specimens were finally polished on the finishing disc, 0.5 micron of alumina paste was used. It was ensured that the surfaces were devoid of scratches and it was thoroughly washed and dried using a hand blower to avoid chemical corrosion. 2% nital solution was used to etch the specimen and rinsing was done using clean water. It was then dried using a blower before transferring to the microscope for viewing and taking of the photomicrograph of the microstructure.

3. Results and Discussion

3.1. Results

The results of the research are as presented in Table 2, Table 3, Figure 1 and Plates 1-2. The un-carburized mild steel has a hardness value of 30 HRC.

Table 2. Hardness values of mild steel carburized with waste carbonaceous materials and waste carbonaceous materials mixed with egg shell

S/NO.	Wastes/Indentations	1	2	3	Average Hardness value (HRC)
1	Sugar cane waste	45.3	43.8	46.3	45.1
2	Sugar cane +Egg shell	47.8	43.8	44.8	45.5
3	Melon shells waste	49.8	46.8	46.8	47.8
4	Melon shells +Egg shell	53.3	51.8	52.8	52.6
5	Aracaceae flower wastes	56.3	55.3	56.3	56.0
6.	Aracaceae + Egg shell	58.3	55.3	56.3	56.6

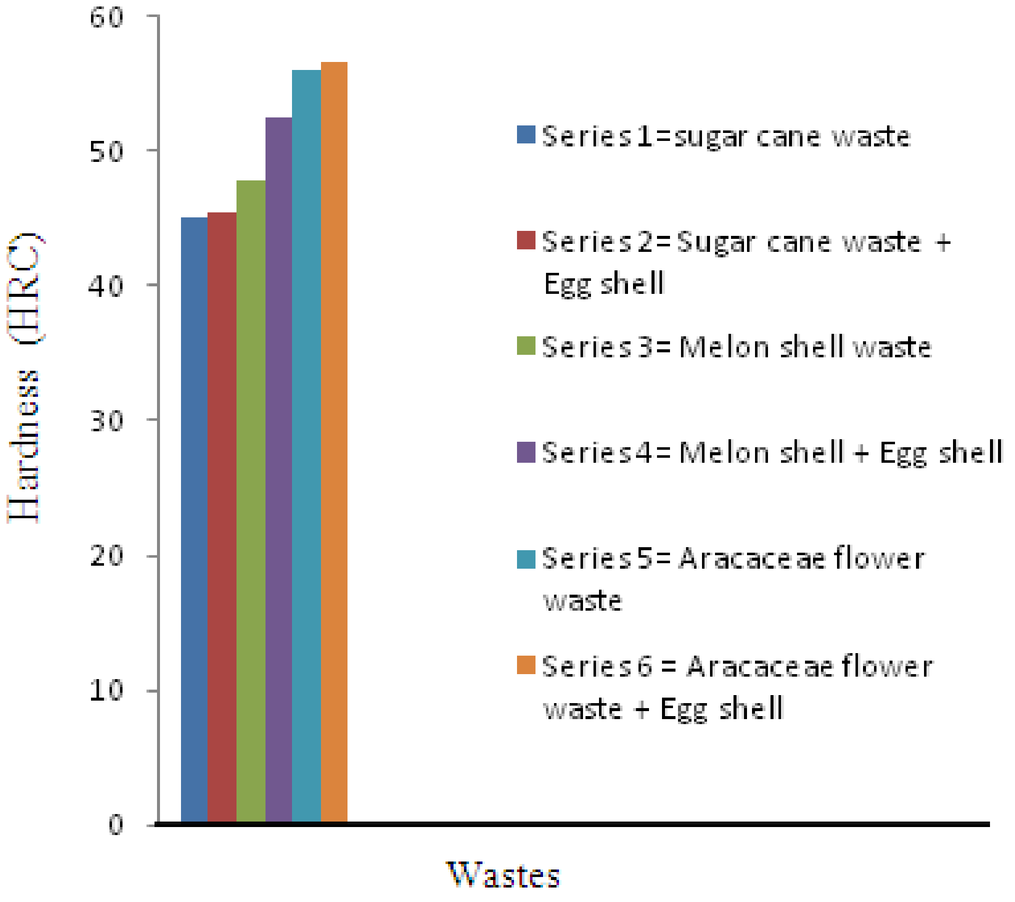

Figure 1. Column Chart Showing the Hardness Values of the Carburized Mild Steel using different Carbonaceous Wastes and Wastes Mixed with Egg Shell Wastes

Table 3. Effective case depth of some of the carburizing waste materials extracted at 50 hrc from the surface of the carburized steel specimens

Carburizing Material	Effective Case Depth (mm)
Melon shell + Egg shell	0.65
Aracaceae flower waste	0.70
Aracaceae waste + Egg shell	0.75

Using the carburizing temperature, time and proportionality factor that varies with temperature the theoretical case depth was estimated using the formula [5,9]:

$$d = \Phi\sqrt{t} \quad (1)$$

Where, d = total case depth, t = carburizing time in hours = 5hours

Φ = depth factor in mm / $\sqrt{h}$ = 0.6 at 920 ℃

Inserting the above data in Eq 1, the theoretical total case depth = $0.6\sqrt{5}$ = 1.34mm.

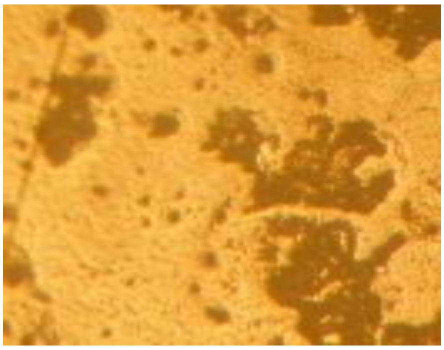

Plate 1. Microstructure of the Mild Steel after treatment with Arecaceae Flower Droppings with dark phases of martensite and varying degrees of carbide, obviously indicating increased carbon content at the surface,(2% nital etched 100 x)

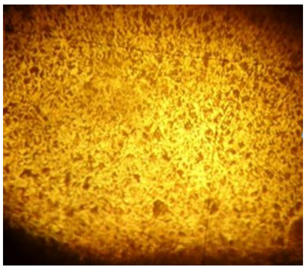

Plate 2. Microstructure of the untreated Steel with a pearlite Structure in a Ferritic Matrix,(2% nital etched 100x)

3.2. Discussion

3.2.1. Hardness and Case Depths

Different waste materials have been used as carburizing material for mild steel, this include the energizer used which is also a solid household waste. The results of the study have shown that these wastes can indeed be use as carburizing materials for mild steel. The mild steel used is shown to have a carbon content of 0.25% as indicated in Table 1. The mild steel in the un-carburized condition have a hardness value of 30 HRC. Table II however, gave the hardness values of the mild steel after it was carburized with the various wastes at 920℃ for 5 hours. The result of the hardness test showed that the hardness value produced by the mixture of the waste and egg shell was higher than when the waste was used alone. Sugar cane waste produced a hardness of 45.1HRC but when it was mixed with egg shell the hardness became 45.5. Melon shell waste produced a hardness of 47.8 HRC on the mild steel but when it was mixed with egg shell the hardness became 52.6 HRC. Arecaceae flower waste produced a hardness value of 56 HRC on the mild steel specimen but when it was mixed with egg shell the hardness produced on the mild steel specimen became 56.5 HRC. The result has shown that egg shell waste is an enhancer in the carburization of mild steel. Egg shell contains $CaCO_3$ and the use of carbonates like calcium carbonate, barium carbonate, sodium carbonate as energizers in pack carburization have been explained by many [4,9,10,11]. The mechanism of the carburization process is summarized in the equations below:

$$CO_2 + C \rightarrow 2CO \quad (2)$$

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$

$$CO_2 + C \rightarrow 2CO \quad \text{(Carbondioxide from Eq 3)}$$

$$2CO \rightarrow C + CO_2 \quad (4)$$

$$CaO + CO_2 \rightarrow CaCO_3 \quad (5)$$

$$3Fe + 2CO \leftrightarrow Fe_3C + CO_2 \quad (6)$$

$$Fe_3C + 2H_2 \leftrightarrow 3Fe + CH_4 \quad (7)$$

$$3Fe + CO + H_2 \leftrightarrow Fe_3C + H_2O \quad (8)$$

The rate of diffusion of carbon into the steel will depend on the carburizing temperature, the composition of the carburizing mixture, and the type of steel. A case depth of about 0.2mm may be obtained after 1 hour at 900℃, but in practice, the carburizing rate becomes progressively slower. Both temperature and time are important factors in carburizing. The carbon content in the case becomes higher as temperatures are increased. The case depth progresses with time but not in direct proportion to it. The wastes decomposes at the high carburizing temperature releasing a mixture of gases, nitrogen, hydrogen, carbonmonoxide, carbondioxide, and also leaving behind a carbonaceous substance. The calcium carbonate in the egg shell also decomposed as in eq 3. The carbondioxide produced by the wastes and the decomposed egg shell combined with the carbon from the wastes to form carbonmonoxide. The carbonmonoxide dissociate on the surface of the steel, producing nascent carbon which diffuses into the steel as in eq 4 and eq 6. Meanwhile the calcium oxide produced during the decomposition of calcium carbonate recombines with carbondioxide to produce calcium carbonate again. This reaction helps in raising the carbon potential of the carburizing mixture as the calcium carbonate decomposes again more carbonmonoxide is produced and nascent carbon is again deposited on the surface of the steel and the carburizing process continues. The hydrogen in the carburizing atmosphere reduces the carbon in the steel, but in the presence of sufficient carbonmonoxide nascent carbon is deposited on the steel surface and the hydrogen is oxidized to steam, see equations 7 and 8. The carbon deposited on the surface of the steel is dissolved by the austenite phase of the steel and diffuses into the steel which on subsequent quenching in water develops a hard case [4,10]. The reactions taking place with the steel are equilibrium reactions, since they may go either way depending upon the chemical make up of the carburizing mixture [4,10].

The depth of case hardening is normally influenced or determined by the carbon potential (activity) of the carburizing medium. The higher the carbon potential, the higher the equilibrium carbon concentration at the surface of the steel, and thus the deeper the carburizing depth [9,10]. Thus the role of an energizer is thought to be related to its ability to raise the carbon potential of the carburizing medium. This explains why in all the carburizing mixtures with egg shell the result showed improvement in the hardness value over the carburizing mixtures without egg shell. How an energizer does this has not been clearly outlined and indeed why only a particular energizer should be a more effective energizer is still a matter of some conjecture though chemical stability is thought to be an important factor [12].

Figure 1 is a column chart and it has clearly illustrated the carburization enhancement capabilities of egg shell in each case the carburizing mixture with egg shell has a higher hardness value than the waste without egg shell. The chart shows that aracaceae flower waste with egg shell has the highest hardness value of 56.6HRC followed by aracaceae flower waste alone. Melon shell waste with egg shell then followed, and then melon shell waste, which is then followed by sugar cane waste with egg shell and lastly sugar cane waste alone. The carburization mechanism was explained above and the reason for the different hardness values can be linked to the variation in the carbon potential of the carburizing materials [4,11].

Table 3 shows the effective case depth produced on the steel specimens by three of the carburizing materials which have high hardness values sufficient to use ASM Committee's specification for measuring effective case depth according to the Committee, 'effective case depth is the perpendicular distance from the surface of a hardened case to the farthest point at which a hardness of 50 HRC is measured' [9]. Aracaceae flower with egg shell produced the highest effective case depth of 0.75 mm on the steel specimen and is followed by aracaceae waste alone with an effective case depth of 0.7 mm. Melon shell wastes with egg shell produced an effective case depth of 0.65mm. This result further strengthens the position of other results that egg shell is an enhancer in the carburization of mild steel.

The diffusion of carbon proceeds from the higher concentration at the workpiece surface to the lower concentration at the core [5,9,12]. When consistent concentrations (surface and core) are maintained, the depth of case may be predicted for any constant temperature of operation, for this work the total case depth was predicted to be 1.34mm based on the input data provided above.

3.2.2. Microstructure

Efforts were made to observe if there were microstructural changes associated with the carburization process at the case area of the mild steel although this was not the objective of the work. Plate 1 and 2 clearly indicated that there was indeed a change in the case area of the mild steel which is reflected in the increased hardness of the carburized specimen. The un-carburized steel microstructure shows a pearlite structure in a matrix of ferrite. This structure is a contrast to the carburized structure which has dark phases of martensite and varying degrees of carbides [9,10,11,12].

4. Conclusion

The effect of egg shell waste as an enhancer in the carburization of mild steel has been established the result of the work has clearly shown that egg shell waste can be used in place of calcium carbonate to improve on the hardness value of mild steel during carburization. The egg shell serve as an energizer during the carburization process by raising the carbon potential of the carburization mixture.

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