The Use of River Clam Shells (Aspatharia Sinuata) as an Energizer in Case Carburization of Mild Steels

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River clam shells (aspatharia sinuata) which mainly contains calcium carbonate (CaCO₃) was explored for use as an energizer during pack-carbonization process. The mild steel samples were pack-carbonized at 950°C for various time duration in carbonizing compounds containing a mixture of charcoal and varying amounts of clam shells up to a maximum of 50 % clam shell (CaCO₃) as energizer. Some other samples from the same stock were also pack carbonized using 100 % charcoal. The carburization depths of the heat treated samples were measured using a micro hardness tester. The results showed that river clam shell is an effective energizer with maximum hardness obtained with the composition of 70% charcoal + 30% river clam shells.

KEY WORDS: pack-carburization; energizers; river clam shells; heat-treatment.

1. Introduction

It has been found that some rock minerals when added to charcoal enhances their carbonization process. These additives known as energizers are mainly carbonates of Barium (BaCO₃), Sodium (Na₂CO₃) and Potassium (K₂CO₃). The Iron and Steel industries in Nigeria are still at the developmental stage. There is therefore need to explore all available raw materials to complement the development of these industries. The carbonates (BaCO₃, K₂CO₃, and Na₂CO₃) are minerals not found in commercial quantity in Nigeria and to import them requires a lot of money in terms of foreign exchange. Meanwhile, river clam shell are abundant in the country, mostly at the coastal region of Nigeria where the Delta Steel Company is sighted.

In Nigeria, the mineral that is readily available is limestone (CaCO₃). Sea shell, coconut shell and river clam shell are also waste products from agricultural crops, sea shell and coconut shell have been investigated for a possible use as energizers. Since limestone involves a mining process, it makes it an expensive source of energizer. In this work we examined and study the suitability of the river clam shells as a substitute energizer in the case carburization of steels.

Our analysis of the samples of river clam shells gave us a composition of about 90%CaCO₃. The chemistry of CaCO₃ reveals that it decomposes to metal oxide and carbon dioxide on heating to high temperatures. The available data shows that the decomposition temperature for CaCO₃ is 898°C which falls below the 950°C process temperature of carburization. It is therefore the process of decomposition of carbonates to generate CO₂ that is utilized in the carburization of steels. The carbon dioxide then reacts with charcoal to finally generate atomic carbon as shown in the scheme below.

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \] ........................(1)

The carbon dioxide produced reacts with the charcoal to produce carbon monoxide.

\[ \text{CO}_2 + \text{C} \rightarrow 2\text{CO} \] ........................(2)

This carbon monoxide is unstable at the process temperature and thus decomposes according to the Eq. (3)

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \] ........................(3)

and the atomic carbon (C°) is quickly absorbed at the metal surface and diffuses into the metal. The simplicity of the decomposition process and the relative abundance of river clam shells makes it an attractive energizer in case carburization. Their shell being utilized as industrial raw material will encourage large scale farming of the river clam which is cheaper than the mined limestone (CaCO₃) and other carbonates.

2. Experimental Procedure

The mild steel used for the investigation was obtained from Delta Steel Company Ltd., Aladja- Warri, Nigeria. The steel was classified as RST 37 with the following composition as in Table 1. The river clam shells were obtained as waste products. The carburizing box used measured 80×80×70 mm and was made of heat resisting (Ni-Cr) steel. An electric muffle furnace type 0H85TR made in Hungary was used. Vickers microhardness testing machine
model MHT.1 N0: 8331 made by Matsuzawa Seiki Co. Ltd. of Japan was used. Microstructural observation were made using an Olympus optical microscope, also made in Japan.

Hardwood charcoal was used as a base carburizing compound with the river clam shells acting as energizers. The charcoal and the shells were ground and sieved to particles size of 80 % finer than 425 μm. The charcoal and the shells were mixed at predetermined proportions shown in Table 2.

The mild steel rods of 16 mm diameter were cut into 30 mm length and thoroughly washed in acetone and allowed to dry. The bottom of the carburizing box was covered with a layer of the carburizing compound chosen from Table 2. A single specimen was placed in each box and the remaining space was filled with the carburizing mixture. The box was covered with a lid and sealed with fireclay to prevent infiltrate air from entering the box during carburization.

The six boxes containing the test specimens corresponding to the six carburizing compounds of Table 2 were then placed in the central zone of the furnace which was already at the required temperature of 950°C. Carburizing times of 2, 4, 6, 8 and 10 h were used. At the end of each test, the boxes were taken out of the furnace and air cooled. Each test was repeated at least three times. The carburized steel rods were cut from the central region after which the rods were solution-treated at 850°C in the furnace for 10 minutes and then quenched in water. The samples were then prepared for hardness and microstructural analysis.

3. Results and Discussion

In this research, we first studied the effect of the energizer concentration on the carburization kinetics by varying the concentration of the river clam shells as energizers. The charcoal and the shells were ground and sieved to particles size of 80 % finer than 425 μm. The charcoal and the shells were mixed at predetermined proportions shown in Table 2.

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3. Results and Discussion

In this research, we first studied the effect of the energizer concentration on the carburization kinetics by varying the concentration of the river clam shells for a particular time at the given temperature. We then followed up by increasing the holding time of each set of samples to observe the influence of holding time on carburization rate.

The hardness profile of the uncarburized steel was first taken at 0.2 mm interval and the mean was found to be 211.95 with a standard deviation of 1.40. The profile was taken from the edge to 4 mm depth. Table 3 is a summary of the result of hardness measurements in carburized samples using charcoal and river clam shell. A plot of the data on Table 3 is presented in Fig. 1. From Table 3 and Fig. 1 it could be observed that initially, as the amount of river clam shell increases, the rate of carburization also increases. It is also observed that the optimal hardness value occurred at 30 % river clam shell and 70 % charcoal. Above 30 % river clam shell, the hardness value are observed to decrease. This implies that the furnace atmosphere is highly rich in CO2, giving rise to decarburization. On the other hand, below 30 % addition, the furnace atmosphere could be deficient in CO and hence the slow carburization kinetics.

The ease of generation of CO2 in Eq. (1) is supposed to have a direct consequence of increase in the concentration of atomic carbon (C°) as shown in Eq. (3). From the relationship in the Eqs. (1)–(3), one would expect a direct linear relationship between the concentration of the river clam shell and the degree of carburization. However, it was observed that the optimum carburization occurred at 30 % river clam shell addition. Equations (2) and (3) imply that the Bourdourd reaction equilibrium must be satisfied at that reaction temperature. From Eq. (2),

\[ \text{CO}_2 + \text{C} \rightarrow 2\text{CO} \]

where \( K_p \) is the equilibrium constant.

The effect of holding time on the carburization rate of mild steel using Vickers Hardness profile at 950°C is shown in Table 4. The values shown in Table 4 were obtained for the optimal hardness value at 30 % river clam shell and 70 % charcoal. As can be observed from the table, at a fixed case depth, the hardness value increased with holding time. Figure 2 is a plot of hardness profiles against distance at various holding time of the carburization compound. The graphical determination of the case depth was based on 50 % martensite, 50 % pearlite phase commonly taken at Hv 550 as shown in Figs. 1 and 2. Values of case depth at 2, 4, 6, 8 and 10 h are displayed in Tables 5 and 6. The case depth is maximum at 30 % river clam shell and increase
Carburization is diffusion controlled and applying Fick’s first law of diffusion for the rate of increase in case length, \( l \). An expression

\[
l = \sqrt{2D t}
\]

was obtained where \( \theta^1 \) is a constant with unit of \( \text{cm}^2 \cdot \text{s}^{-1} \) and is approximated to the diffusivity of the medium. The diffusivity \( (D) \) of carbon in austenite at 950°C is given as \( 1.8 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1} \) and \( 1.3 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1} \) by Geiger and Poirier and Weast, respectively. From Eq. (5), the average value of \( \theta^1 \) was determined to be \( 2.34 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1} \). This value is in agreement with published value for \( D \) in carbon diffusion in austenite. Using the case depth of 2 h and 30% river clam shell addition, the corresponding diffusivity value was \( 1.69 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1} \), which compares to the value that we earlier reported as \( 1.46 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1} \) using sea shells as energizers; Okongwu and Paranthaman also had a value of \( 1.7 \times 10^{-7} \text{cm}^2 \cdot \text{s}^{-1} \) using lime stone as energizer.

The efficacy \( (\text{case depth with energizer/case depth in 100% charcoal}) \) obtained for 2 h carburization of 30% river clam shell is 2.69. This value is 84% as efficient as 20% BaCO₃ which has efficacy of 3.2 and is claimed to be the

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**Table 4. Effect of holding time on the hardness profile of the carburized mild steel with 70% charcoal + 30% river clam shell at 950°C.**

| Distance (mm) | 2h | 4h | 6h | 8h | 10h |
|--------------|----|----|----|----|-----|
| 0.2          | 815| 874| 1130| 1153| 1167|
| 0.4          | 790| 852| 1102| 1102| 1123|
| 0.6          | 762| 821| 1083| 1097| 1105|
| 0.8          | 723| 780| 990 | 1070| 1095|
| 1.0          | 655| 740| 922 | 982 | 1020|
| 1.2          | 606| 680| 871 | 897 | 972 |
| 1.4          | 572| 640| 840 | 828 | 900 |
| 1.6          | 545| 605| 800 | 790 | 832 |
| 1.8          | 526| 503| 752 | 722 | 811 |
| 2.0          | 515| 564| 688 | 683 | 800 |
| 2.2          | 504| 545| 643 | 650 | 702 |
| 2.4          | 497| 535| 602 | 623 | 668 |
| 2.6          | 489| 530| 561 | 590 | 625 |
| 2.8          | 465| 495| 525 | 566 | 584 |
| 3.0          | 441| 464| 493 | 542 | 540 |
| 3.2          | 412| 430| 460 | 502 | 502 |
| 3.4          | 376| 399| 432 | 450 | 448 |
| 3.6          | 331| 350| 412 | 390 | 390 |
| 3.8          | 330| 348| 411 | 388 | 388 |
| 4.0          | 330| 348| 410 | 389 | 387 |

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4. Conclusions

The suitability of river clam shell as substitute energizer in pack carburization has been studied and the following conclusion are arrived at:

1. There is significant increase in the carburization rate of mild steel by the addition of river clam shell to charcoal.

2. A 70% charcoal and 30% river clam shell produced optimal carburizing effect at all temperature and holding time.

3. Effective average case depth of 1.60, 2.20, 2.69, 2.96 and 2.96 mm were observed at 2, 4, 6, 8 and 10 h of carburizing with the optimal mixture at 950°C compared to a depth of 1.42 mm for charcoal only at 10 h.

4. The river clam shell compares quite favorably with BaCO₃ as an energizer, given a relative efficiency of 84%, even though 30% of river clam shell is required compared to 20% BaCO₃.

5. River clam shell is strongly recommended as a better substitute for BaCO₃, considering its ready availability, cost and chemical efficacy.

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