EFFECT OF SOME VARIABLES ON THE CARBURIZATION OF A LOCALLY PRODUCED STEEL

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ABSTRACT

The effects of carburizing time, temperature and percentage energizer on the case-depth and hardness of a steel ST37-2 have been studied. For carburizing medium consisting of hardwood charcoal and coke and various amount of sodium carbonate as energizer, increasing carburizing time and temperature increased both the depth and hardness of the case. Increasing both the amount of energizer and carburizing time lowered the activation energy for the carburization process. The average hardness of the carburized layer decreased with tempering. Two processes are found to be operative during carburizing; one which is strongly activation energy dependent and the other which is mildly dependent on activation energy.

INTRODUCTION

There are many articles for which it is desirable to have high surface hardness for wear resistance, while the core may be soft and tough. Articles that belong to this group include gears, cams, ratchet wheels, crushing wheels etc. If high carbon or alloy steels are used to manufacture these articles, the required hardness may be obtained by the usual austenitizing the articles above the A3 line in the Iron - Iron carbide diagram and quenching into suitable liquid to obtain the non-equilibrum phase, martensite. Subsequent tempering at appropriate temperature may be carried out to improve the toughness. On the other hand, if these artiçles have to made from low carbon or structural steels, probably due to non-availability of the desired grade of steels, then special processes are necessary to attain the required high surface hardness. In Nigeria, at present, most of the steels produced are low carbon and structural steels, yet there is growing demand for the production of some machine parts to urgument or replace imported ones. There is therefore the need to understand the science and technology of improving surface hardness of the locally produced steels to meet the ever growing demand.

There are many processes for surface hardening a steel. These processes include case hardening, nitriding, flame hardening and induction hardening. In this paper pack carburization (1,2,) a thermochemical means of producing a certain grade of tool steels from otherwise low carbon steels will be discussed. In the pack carburization process, the component is heated in a carbonaceous environment containing energizers such as barium carbonate, sodium carbonate, calcium carbonate and recently the use of periwinkle Shells.[3] These energizes act as catalysts during the process.

The hardness and case depth achieved in carburizing depend on the rate of diffusion of carbon into the steel. The diffusion rate in turn depends on the chemical composition of the steel, the carburizing temperature, the carburizing time and the chemical composition of the carburizing mixture. For example Aderibigbe el al[4] have shown the optimal mix of carburizing compound to be either 5% $BaCO_3$ and 5% periwinkle in 90% charcoal or 20% periwinkle and 80% charcoal.

At high temperatures also small atoms such as carbon can move readily through the interstices of the lattice. To optimise the properties of the carburized layer, the composition of the carburizing medium and temperature must be controlled. Too high a temperature, although favours diffusion processes, causes a deterioration of the core. It also leads to an uneven distribution of the diffusing species. A high concentration at the surface may lead to the formation of chemical compounds such as carbides and nitrides, which impact high britteness to the surface layer. The yield strength of the core may also be exceeded since this is in a state of residual tensile stress which may be within the fatigue limit. The increased stress of the case is then due to both the increased in strength of the surface layer and to the development of facourable compressive residual stresses close to the surface.[5]

The present study therefore intends to look at the effects of temperature, time and amount of energizer on the rate of carburization and the kinetics of the process.

EXPERIMENTAL TECHNIQUES

The steel RST37-2 having the composition given in table 1 was used for this study.

TABLE 1 - COMPOSITION OF RST37-2 STEEL DIAMETER OF SPECIMEN - 22mm.

C	Si	Mn	P	S	S	Cu	Ni	Sn	Fe
.15	.23	.50	.040	.040	.025	.10	.011	.05	Balance.

The carburizing medium consists of 63% of hardwood charcoal and 37% of coke and addition of varying quantities of soduim carbonate as energizer.

TABLE 2 Shows the composition of the carburizer.

COMPOSITION OF CARBURIZER

Generator (WT%)	Energizer (wt%) (Na_2 Co_3)	
90	10	
80	20	
70	30	

The specimens were packed with the carburizer in the carburizing container making sure that the specimen was covered with about 20mm of carburizer. The lid was luted with clay and placed in the furnace. The specimens were then carburized at different temperatures (820, 860, 900 and 940^{o}C), for different length of time (from one to five hours) and percentages of energizer (10, 20 and 30).

All specimens were quenched from the carburizing temperature, sectioned, ground and polished. The specimens were etched with 25% Nital (25% HNO_3 and 75% ethyl alcohol) for about 10 minutes to reveal the case depth. Case depth was measured with tranvelling microscope and micrometer screw gauge and hand lens. The hardness of the case was measured with microhardness tester using diamond pyramid indenter.

Some of the as quenched specimens were then tempered at 300^{o}c for 1 hr. before hardness was measured.

RESULTS AND DISCUSSION

EFFECT OF CARBURIZING TIME ON CASE DEPTH:- Figs. 1 and 2 show the variation of case depth with carburizing time for different amount of energizer.

Fig. 1 shows the behaviour for the specimen carburized at $820^{o}C$ while Fig. 2 that done at $940^{o}C$. It has been shown [6] that the ideal range of carburization temperatures is between 800 to $950^{o}C$. For both carburizing temperatures, case depth increased parabolically with carburizing time and with percentage energizer. The parabolic nature of the curves suggests that the hardening process is diffusion controlled. These curves showed that increasing the carburizing time above 3 hrs. did not increase the case depth proportionally. It can also be observed that increasing carburizing temperature favoured increase in case depth.

EFFECT OF TEMPERATURE

Fig 3 and 4 show that case depth increased linerly with carburizing temperature for all carburizing time investigated.

From these curves, it is observed that the lines become closer above carburizing time of 3 hrs. The greatest separation was observed between 1 and 2 hrs. carburizing time. The increase in case depth with temperature can be explained in terms of increase in atomic vacancies which therefore favours the diffusion of carbon atoms. Increase temperature also increases the motion of atoms and decreases the activation energy for diffusion processes.

The longer the time of carburization, the greater the case depth as shown in Fig. 3 and 4. From the analytical solution to the one-dimensional mass transfer for semi infinite stationary medium with fixed surface concentration, the solution to the ficks second Law equation.

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

is given as

$$(Cx,t) = Cs - (Cs-Co)\ \mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad - (1)$$

Cs = Concentration of carbon at the surface

Co = Initial carbon concentration is the specimen

X = Distance from the surface

D = Diffusion coefficent

t = Time.

From the solution, the carbon concentration in the steel is found to increase with time. The mathematical solutions, for the unsteady - state mass transfer in simple geometric shapes with certain restrictive boundary conditions have been presented in a wide variety of charts. The Gurney Lurie charts present solutions for the flat plate, sphere and long cylinder.7

The rate of increase in case depth is fast initially and decreases with further carburizing time. This suggests that the process depends on diffusion processes probably in addition to other processes.

HARDNESS

Figs. 5 and 6 show the variation of hardness with carburizing time for various carburizing temperatures with 10% and 30% energizer respectively. The hardness increased with carburing time and temperature. In addition the hardness for a particular temperature and time of carburization increases with increasing amount of energizer. The energizer provides an initial supply of Co_2 arising from decomposition of the carbonate. The carbon dioxide then reacts with the carbonaceous compound to give carbon monoxide according to the following reactions.

$$Na_2\ Co_3 = Na_2O + Co_2 \qquad (2)$$

$$Co_2 + C = 2Co \qquad (3)$$

$$Na2\ Co_3 + C = Na_2O + 2co \qquad (4)$$

The carbon dioxide produced in equation (2) reacts with the metal oxide to regenerate the carbonate according to the reaction. $Na_2o + Co_2 = Na_2Co_3$ (5) thus explaining the catalytic effect of the energizer. The Co produced becomes dissociated when it comes in contact with hot steel to produce nascent carbon according to the reaction. $2Co = Co_2 + C$ (6)

The nascent carbon then diffuses in the austenite, which is the stable phase at the carburizing temperature. The processes of dissociation of the energizer and the production of nascent carbon are temperature and time dependent. Hence the case depth resulting from combination of nascent carbon with the stable austenite phase increases with both increasing temperature and time. From both Figs. 5 and 6 it is discernible that the carburizing rate was higher at the begining of the cycle and diminished gradually as the cycle is extended. Thus from the two Figs, it is possible to select conditions that would give a particular hardness when the percentage energizer is fixed.

Higher percentage energizer increased the carbon potential and hence more carbon could diffuse into the steel than when lower percentage of energizer was used. An increase in carbon content in the case then caused the formation of more martensite on quenching and hence the enhanced case hardness observed.

Figs. 7 and 8 show the plot of hardness against carburization temperatures for different carburizing time and for 10% and 30% energizer respectively. The increase in hardness with temperature was found to be parabolic suggesting a diffusion controlled process. Again for different amounts of energizer, hardness increased with increasing carburizing times.

ACTIVATION ENERGY

Starting from the Arrhenius Equation 8, the rate constant is related to the temperature by the equation.

$$K = A_e - Ea/_{RT} \quad - (7)$$

where

Ea = Activation energy for diffusion to occur

A = Frequency factor

R = gas constant

T = absolute temperature

Equation (7) can be rewritten as

$$\log_e K = \log_e A - \frac{Ea}{R} \left(\frac{1}{T}\right) \quad (8)$$

A plot of $\log_e K$ versus $(\frac{1}{T})$ would give a slope $-\frac{Ea}{R}$ and intercept $\log_e A$. From the measurement of case depth as a function of carburizing temperatures and time table 3 below was obtained. Here the case depth was taken as the rate constant K.

TABLE 3

Variation of $\log_e K$ with $\frac{1}{T}$ for Various carburizing times, Using 10% $Na_2\ Co_3$ (Energizer) (As quenched)

In verse of Absolute Temp. X $10^{-4}K^{-1}$

Time Hours	9.149	8.826	8.525	8.244
1	-1.90	-1.14	-0.73	-0.51
2	-0.20	-0.60	-0.45	-0.09
3	-0.73	-0.40	-0.15	-0.04
4	-0.56	-0.25	0.02	0.17
5	-0.45	-0.15	0.05	0.25

Similar calculations were done for 20% 30% energizer.

Regression analysis was used to obtain the regression equation from table 3. The equations obtained are shown in table 4.

TABLE 4

REGRESSION EQUATIONS OBTAINED FROM TABLE 3 FOR EACH TIME USING 10% ENERGIZER

Time Hours	Regression Equation
1	$\log_e K = 12.22 - 15295 \left(\frac{1}{T}\right)$
2	$leg_e K = 9.48 - 11584 \left(\frac{1}{T}\right)$
3.	$leg_e K = 7.08 - 8512 \left(\frac{1}{T}\right)$
4	$leg_e K = 6.82 - 8044 \left(\frac{1}{T}\right)$
5	$leg_e K = 6.56 - 7642 \left(\frac{1}{T}\right)$

Similar calculations were done for 20% and 30% energizer. By comparing the regression equations in table 4 with equation 8 the activation energy for each carburization time and percentage energizer can be calculated. For example, the activation energy when 10% energizer was used and carburized for one hour at various temperatures is calculated below.

The regression equation is $\log_e K = 12.22 - 15{,}295 \left(\frac{1}{T}\right)$

comparing with equation 8

$leg_e A = 12.22$

$\frac{-Ea}{R} = -15{,}295$

$Ea = 15295\ R$ -(8)

$= 127.163$ KJ/mol

Similar calculations were carried out for other times and plots of activation energy against carburizing time for various percentages of energizer are shown in Fig. 9.

While Fig. 10 shows plots of activation energy against percentage energizer for various carburizing times.

From Fig. 9, two clear stages are discernible namely a stage where the activation energy decreased sharply with increasing carburizing time up to 3 hrs. and a second stage that showed a more gradual decrease. The reduction in activation energy with energizer was found to be more significant for 10% energizer than higher percentages. This results suggests that above a certain amount of energizer much benefit may not be derived from mere increasing the energizer content. The first stage may be under surface activation energy control while the second will be under diffusion control.

In Fig. 10 activation energy also decreased with increasing amount of energizer. More significant reduction was observed for carburizing time of 1 and 2 hours the period that may probably be dominated by the preduction of nascent carbon which will invariably diffuse into the steel. For higher carburizing times 3hrs. and above, the activiation energy decreased linearly with percentage energizer.

From Fig. 9 it seems that the initial state of the carburigation process is more under activation control than the letter stages. For example the rapid decrease in activation energy observed between carburizing between 1hr. and 3hrs. is more significant than that observed between 3 and 5 hrs. although the same time internal operates under both conditions. The section strongly under activation energy control is probably the time for the decomposition and reformation of the energizer and the time for the formation of the mascent carbon which subsequently diffused into the steel. All these processes are bond to depend on the reaction kinetics on the surface of the steel and hence the surface activation energy. As soon as enough nascent carbon in produced the diffusion of this within the lattice will depend more lattice inhomogeneity and will depend less on activation energy. During stress corrosion cracking of Titanium - oxygen alloy in methanolic solution it has been shown (8) that the stage 1 in the log stress corrosion velocity against stress intensity factor was independent of solution viscosity which implies that the stage was under activation control rather than diffusion control. In the present work it is therefore to be expected that the section under activation control will respond more strongly to addition of energizer than the section under diffusion control. This trend is clearly shown in Fig. 10.

EFFECT OF TEMPERING ON CASE HARDNESS

Some specimens carburized between 820°c and 940°c were quenched and subsequently tempered at 300°c for 1 hr. before the hardness readings were taken.

Table 3_a and 3_b shows the results obtained.

Table 3(a)

Showing variation of average hardness with temperature for various times of carburization using 10% $Na_2 Co_3$ energizer (As quenched)

Temperature °C

Time Hours	820	860	900	940
2	520	570	602	630
3	550	591	64	656
4	565	610	640	675

Table 3 (b):-

Showing variation of average hardness with temperature for various times of carburization using 10% Na_2Co_3 energizer (As tempered)

Temperature ^oC

Time Hours	820	860	900	940
2	425	455	472	528
3	440	472	615	640
4	491	528	640	697

The tables show that tempering reduces hardness. The reduction in hardness with tempering is due to the redistribution of the carbon in the highly strained martensitic laltice. The redistribution lowers the strain in the laltice and hence the hardness. In addition the reduction in hardness increases the toughness of the case depth thereby improving its wear resistance.

METALLOGRAPHY

Specimens carburized at various temperatures and times with different percentages were prepared for macrostructure and eteched in 25% Nital. The results obtained are shown in plates 1 (a) and 1 (b) for specimens carburized at same temperature and same amount of energizer but at different times. Plates 2(a) and 2 (b) are for specimens carburized at different temperatures but for the same specimens carburized at different temperatures but for the same time and in environments containing same amount of energizer. From these plates it is obvious that the case depth increased with time of carburization for fixed temperature and energizer. Similarly case depth increases with carburizing temperature for fixed amount of energizer and carburizing time.

CONCLUSIONS

The results obtained showed that it is possible to increase the surface hardness of a mild steel by carburizing in an atmosphere containing carbonaceous material and some energizer. The surface hardness obtained was found to be a function of both carburizing time, temperature and amount of energizer. While the hardness varied parabolically with temperature, it varied linearly with carburizing time.

The activation energy for the process of carburization, can be divided into two parts, i.e. activation energy for surface reactions such as dissociation and formation of nascent carbon and that for diffusion process. Experimental results suggested that the activation energy for surface reaction decreased with carburizing time and percentage energizer. The lowerest amount of energizer gave a more rapid decrease in activation energy with carburizing time suggesting that increasing the amount of energizer unnecessarily may not produce proportional reduction in activation energy. This suggests that an optimum amount of energizer may be required for any carburizing effect.

Initial reactions during carburization is more strongly dependent on activation energy than subsequent reactions. From the experimental results it is possible to select the necessary combinations of temperature, time and amount of energizer to achieve a desired hardness. It is therefore possible to use locally produced steels for producing some tools provided necessary carburization and tempering processes are carried out.

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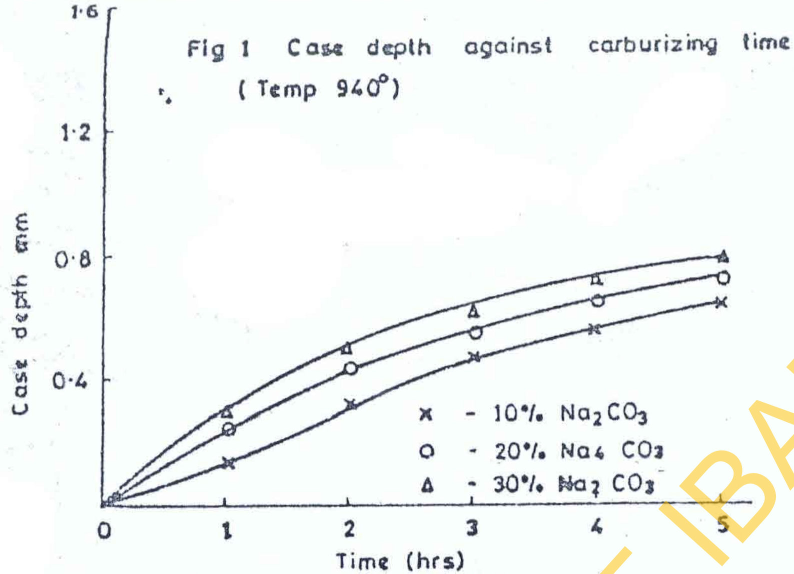

Fig 1 Case depth against carburizing time (Temp 940°)

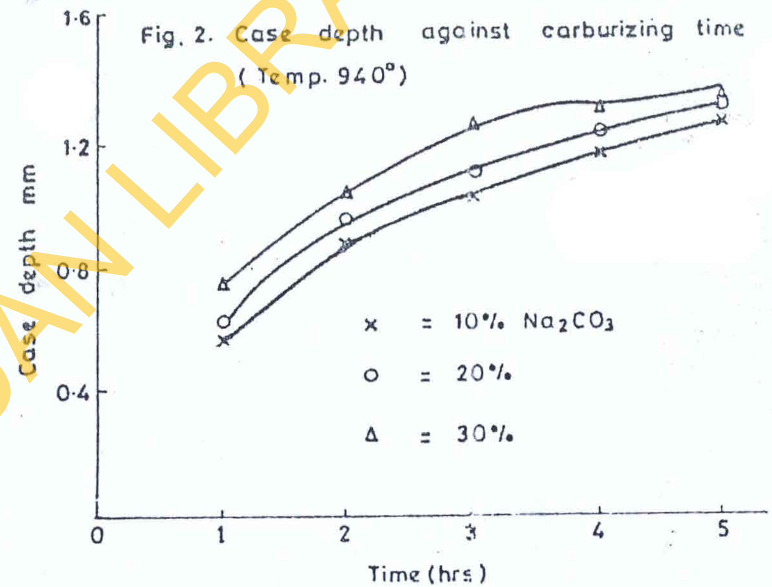

Fig. 2. Case depth against carburizing time (Temp. 940°)

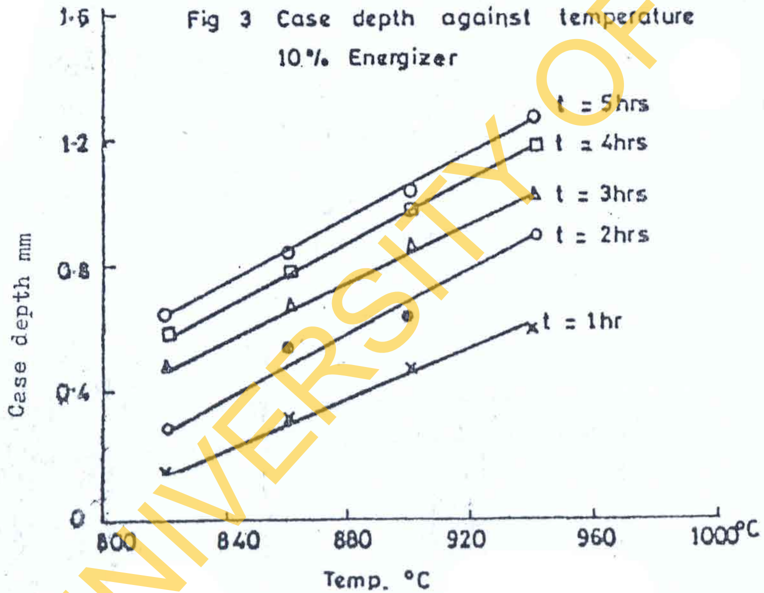

Fig 3 Case depth against temperature 10% Energizer

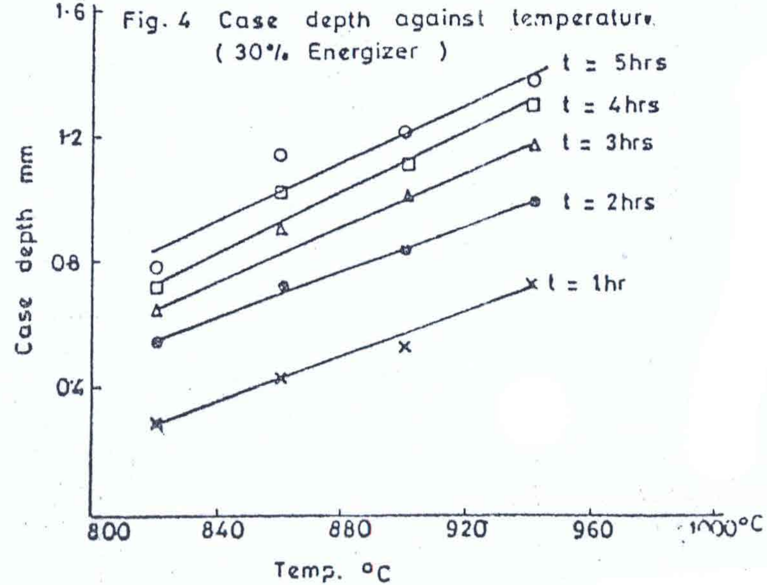

Fig. 4 Case depth against temperature (30% Energizer)

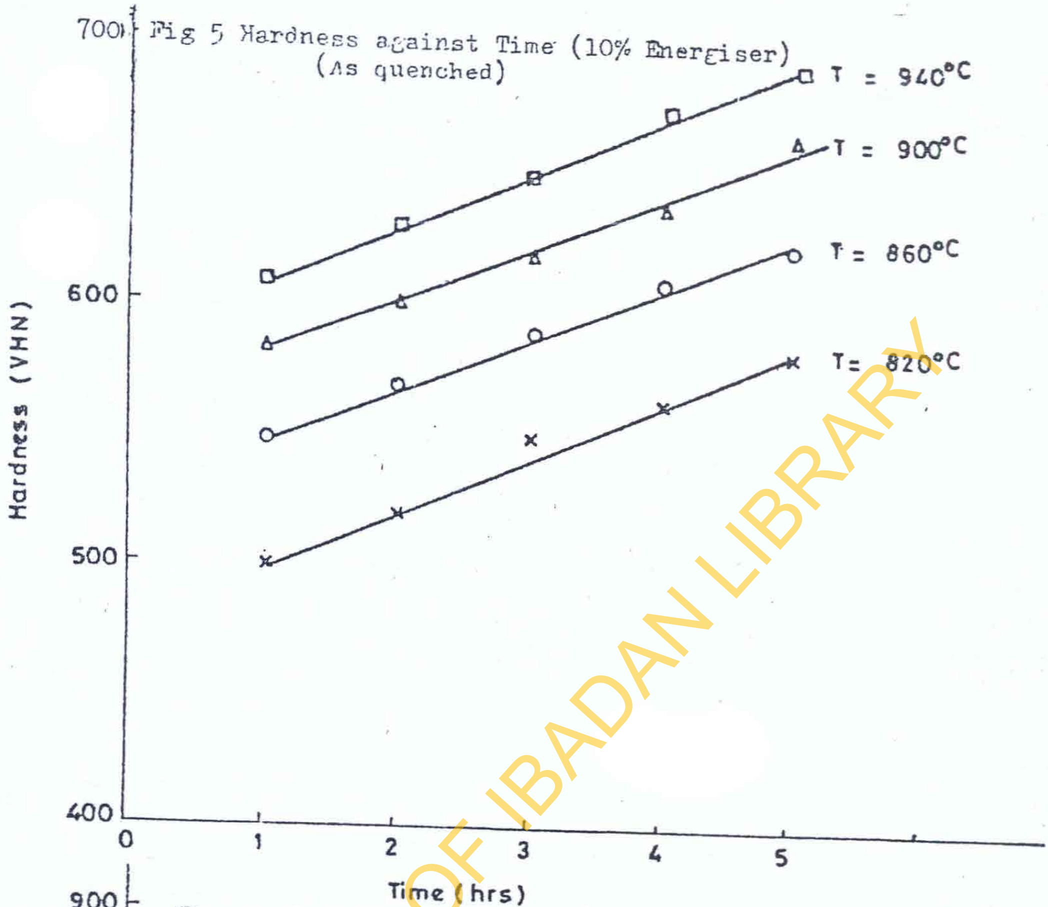

Fig 5 Hardness against Time (10% Energiser)
(As quenched)

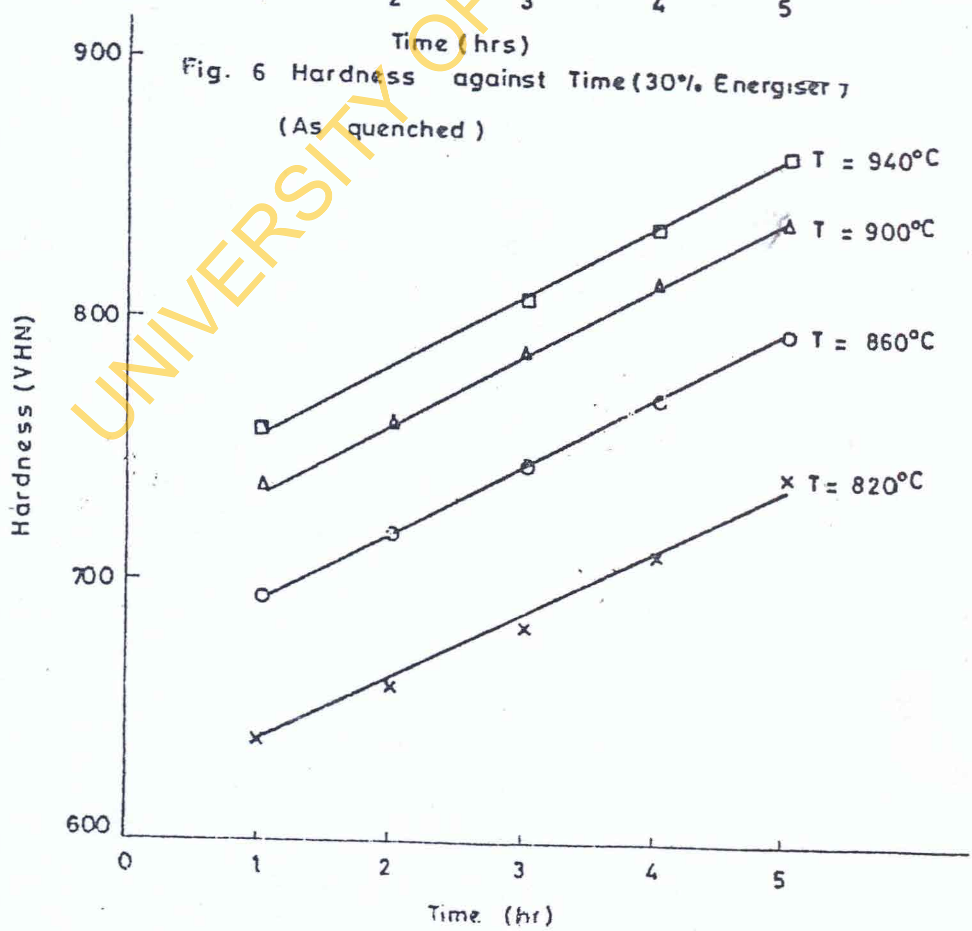

Fig. 6 Hardness against Time (30% Energiser)
(As quenched)

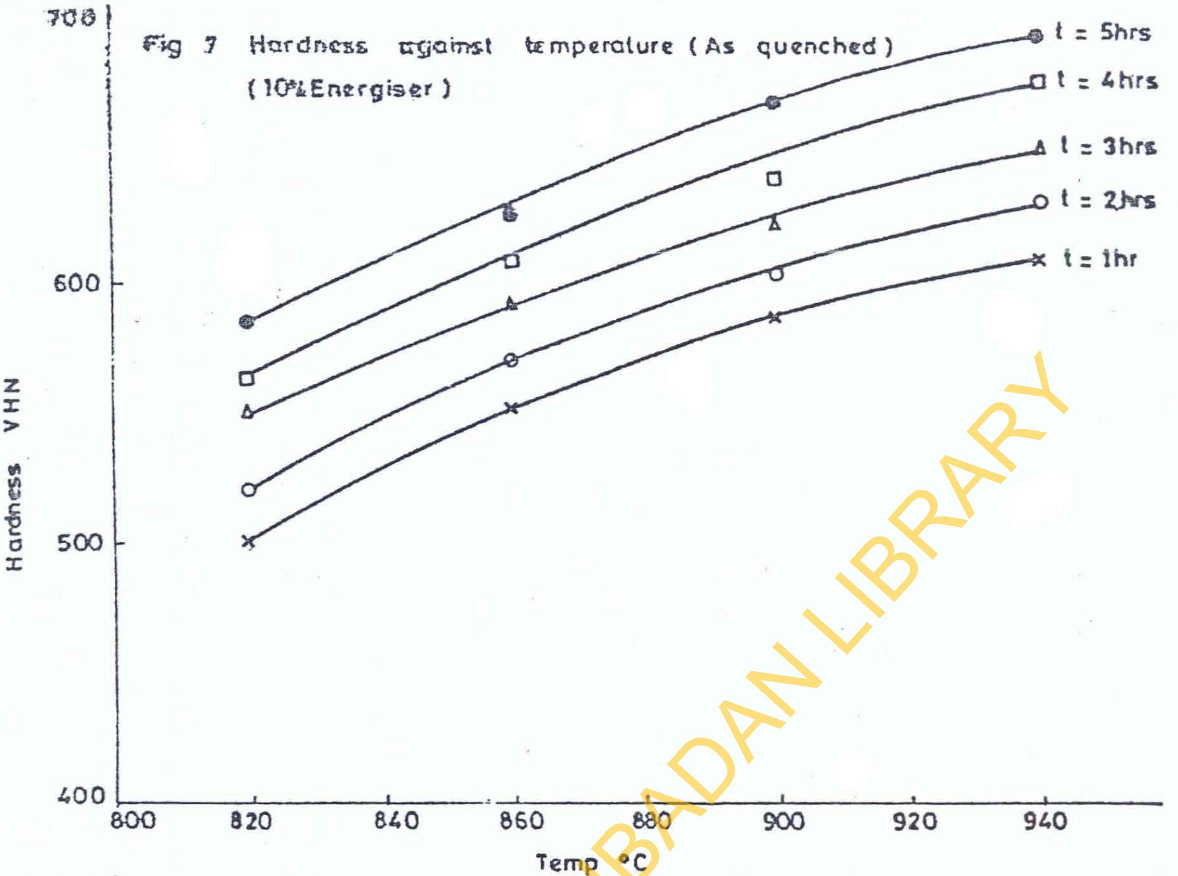

Fig 7 Hardness against temperature (As quenched) (10% Energiser)

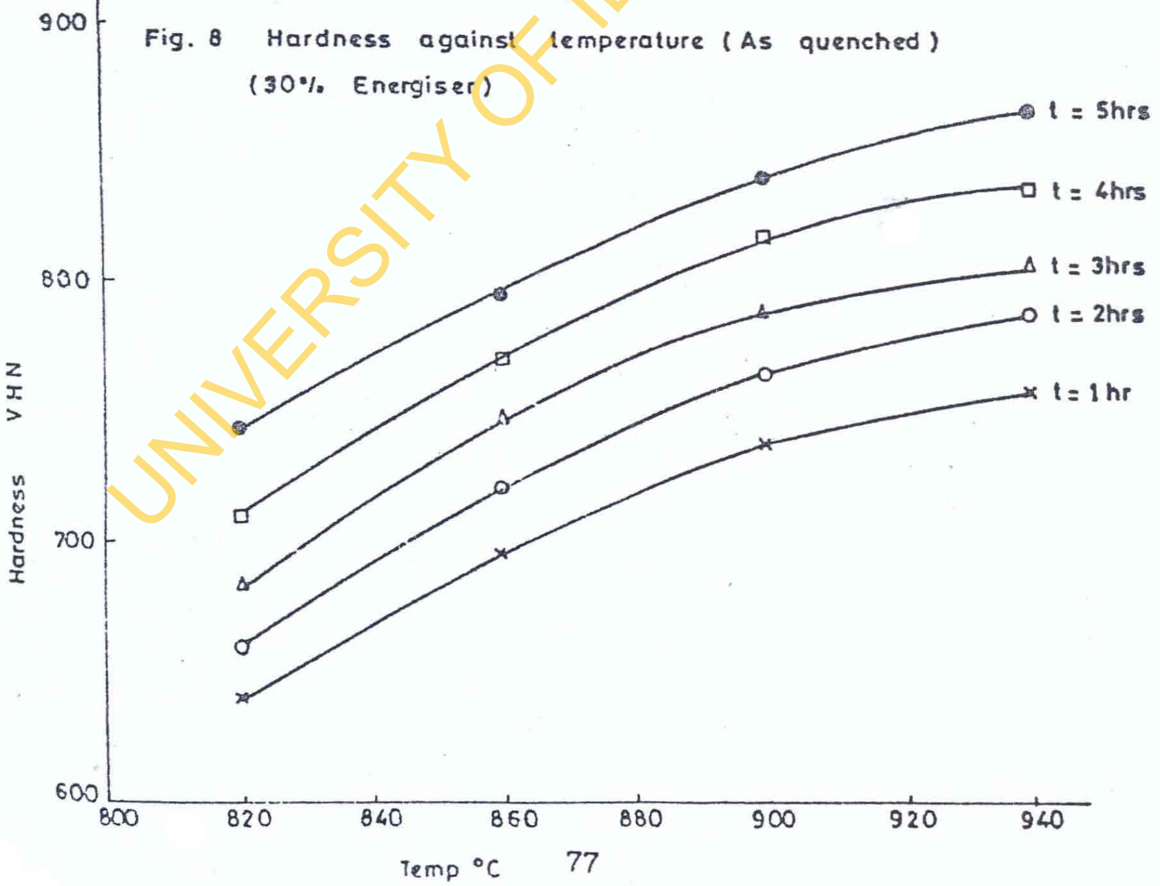

Fig. 8 Hardness against temperature (As quenched) (30% Energiser)

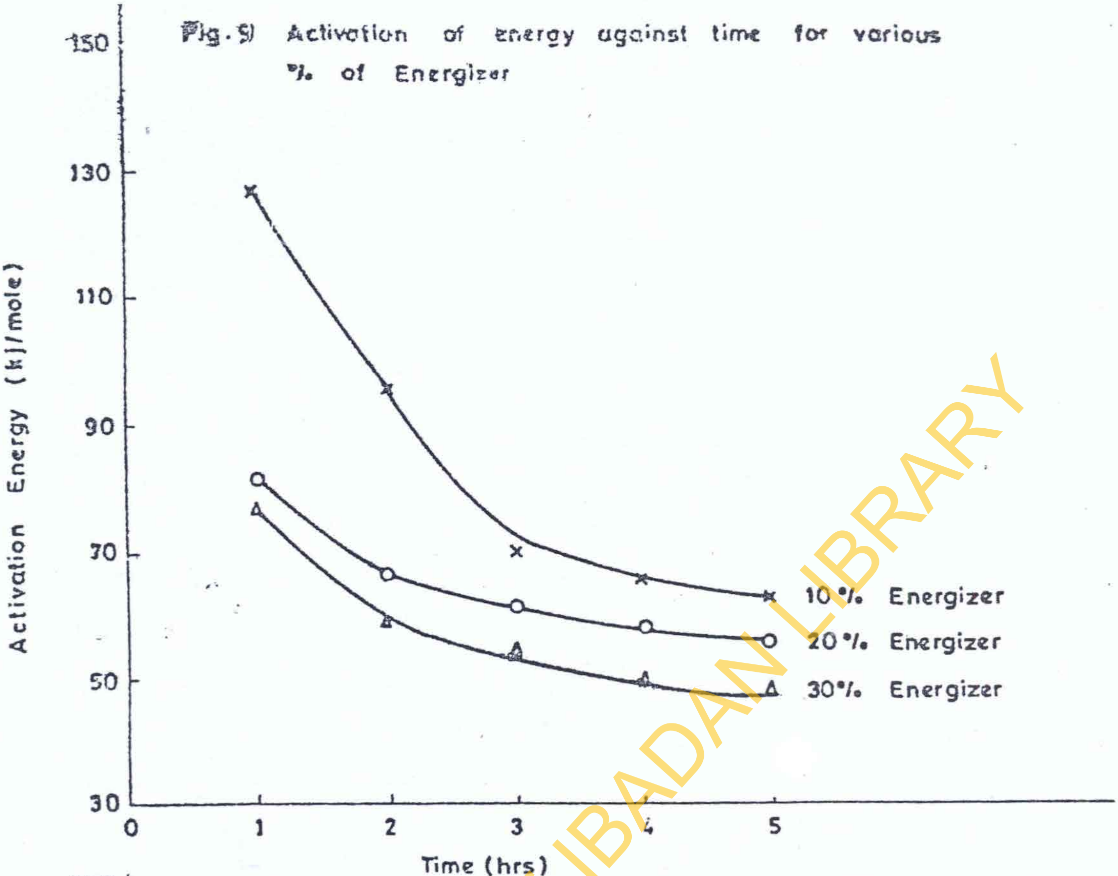

Fig. 9) Activation of energy against time for various % of Energizer

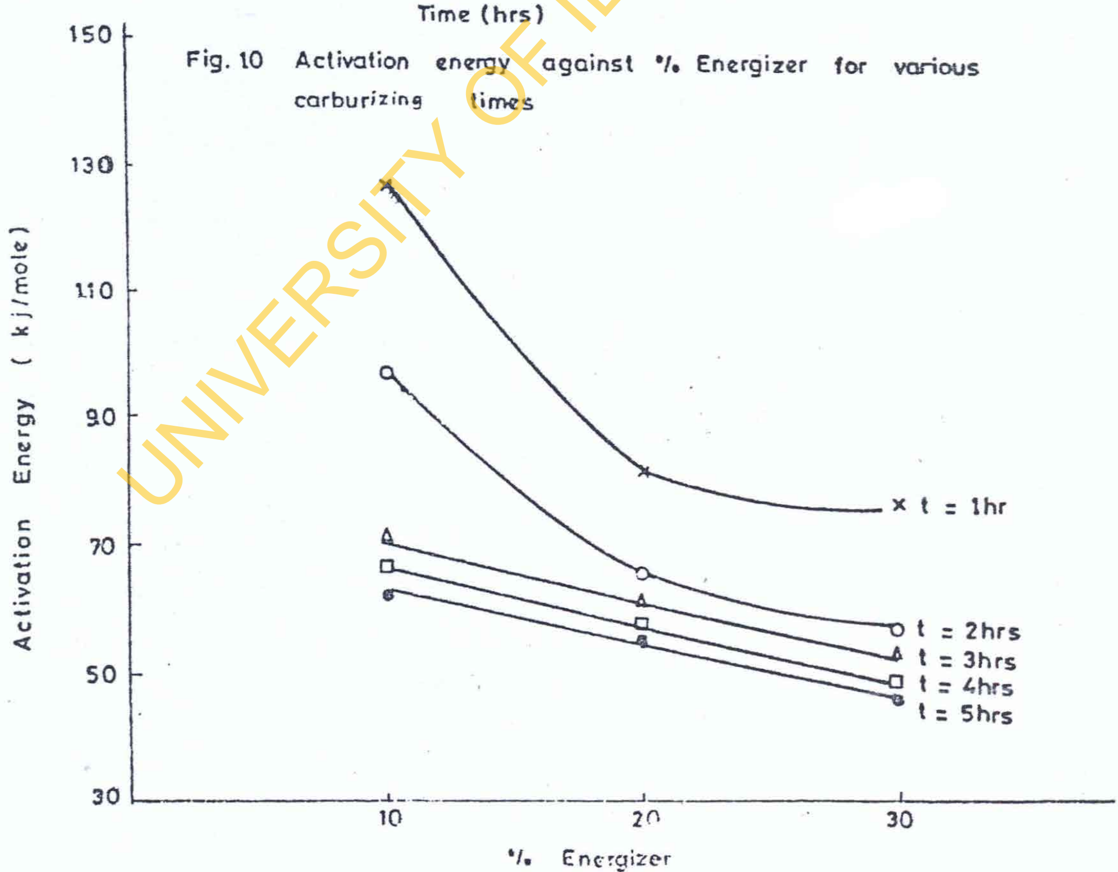

Fig. 10 Activation energy against % Energizer for various carburizing times

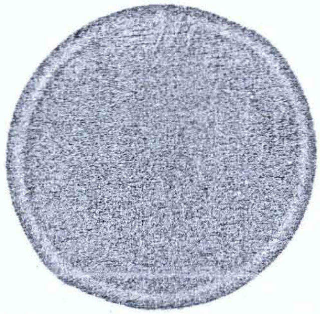

Plate 1(a)

Macrostructure of a carburized specimen of Aladja Steel. Carburized at 940°C for 3 hours with a carburizer containing 20% Na_2CO_3. X2. Etched in 25% Nital.

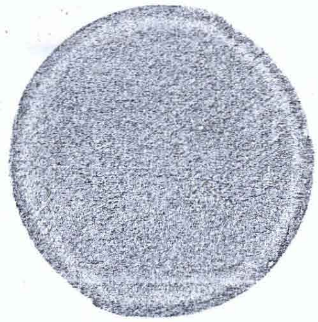

Plate 1(b)

Macrostructure of a carburized specimen of Aladja Steel. Carburized at 940°C for 4 hours with a carburizer containing 20% Na_2CO_3. X2. Etched in 25% Nital.

Plates 1(a) and 1(b) show the effect of carburizing time on the case depth. The ring shape layer in the case. The inner ring is the transition zone where the carbon content of the case decreases gradually into the carbon content of the case.

Plate 2(a)

Macrostructure of a carburized specimen of Aladja Steel. Carburized at 900°C for 3 hours with a carburizer containing 20% Na_2CO_3. X2. Etched in 25% Nital.

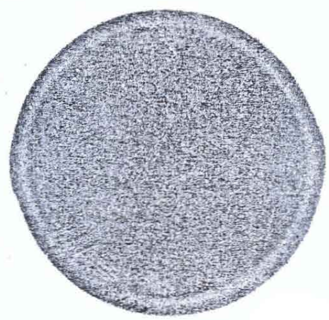

Plate 2(b)

Macrostructure of a carburized specimen of Aladja steel. Carburized at 940°C for 3 hours with a carburizer containing 20% Na_2CO_3. X2. Etched in 25% Nital.

Plates 2(a) and 2(b) show the effect of temperature on case depth. The ring shape layer is the case. The inner ring is the transition zone where the carbon content of the case decreases gradually into the carbon content of the core.