GAS CARBURIZATION OF NIOBIUM MICROALLOYED STEELS

BY

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A thesis submitted to the Department of Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, in partial fulfillment of the requirements for the degree of Master of Science in Engineering (Metallurgical).

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DHAKA, BANGLADESH.
DECLARATION

This is to certify that this research work has been carried out by the author under the supervision of Dr. Md. Mohar Ali, Professor, Department of Metallurgical Engineering, BUET, Dhaka, and it has not been submitted elsewhere for the award of any other degree or diploma.

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Gas carburization of three 0.07 percent carbon steel samples containing a small addition of niobium singly or in combination with nitrogen has been carried out in a natural Titas gas atmosphere at a temperature of 950°C and at a gas pressure of about 15 psia for five different time periods ranging from 1/2 hour to 4 hours followed by slow cooling in the furnace. The microstructures of these steel samples were investigated by optical microscopy and the case depths and the austenite grain size of the case were determined.

Another two sets of specimens of the above steels were carburized for different periods of time under identical conditions of temperature and pressure and quenched in 10 percent brine after pre-cooling them in the furnace from the carburizing temperature of 950°C to 860°C. One set of the quenched specimens was tempered at a low temperature of 160°C. The other set of the quenched specimens was sub-zero treated in liquid nitrogen at -195°C followed by tempering at the same temperature. The microstructure of the heat treated specimens was studied by optical microscopy. The amount of the retained austenite in the hardened cases was investigated by both the optical microscopy and X-ray diffraction technique. Various mechanical properties such as surface hardness, microhardness and wear resistance were also studied systematically by Rockwell hardness testing machine, microhardness testing machine and pin-on-disc type wear testing machine.

The standard Charpy V-notch specimens made of the steel bars were heated at 950°C for 2 hours and quenched in 10 percent brine after pre-cooling to 860°C in the furnace followed by tempering at a low temperature of 160°C and tested for impact energy absorbed in order to assess the toughness of the core of the carburized and heat treated steels.
It has been found that niobium with or without nitrogen decreases the case depth of the carburized steels. Niobium with nitrogen is more effective than niobium without nitrogen in reducing the case depth. Both the undissolved particles of niobium carbide, NbC and niobium carbonitride, Nb(C,N) refine the austenite grain size of the carburized case, but Nb(C,N) is much more effective than NbC in restricting the austenite grain growth in the case of carburized steels.

Under identical conditions, niobium alone and in combination with nitrogen decreases the formation of retained austenite in the case of carburized and hardened steels. Niobium with nitrogen is more effective than niobium in reducing the austenite retention. X-ray diffractometry has shown that sub-zero treatment substantially reduces the retained austenite content in the hardened cases of all the steels.

Niobium improves the surface hardness, maximum hardness, and wear resistance of the cases and core hardness of low carbon steels in the carburized and hardened condition. Niobium in combination with nitrogen causes further improvement in hardness and wear resistance.

Both the NbC and Nb(C,N) particles are detrimental to the toughness of the core of low carbon steels in the carburized and hardened condition, but Nb(C,N) precipitates are less harmful than NbC precipitates.
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INTRODUCTION

There are numerous existing service conditions and potential future demands where the machine parts made of steels such as drive gears, cams, eccentrics, steering parts, bearing and bearing races, etc. require a hard, wear resistant surface supported by a tough and ductile core. Such a combination of properties is not usually possible from the commercial steels as well as conventional heat treatment process of the steels. For example, we can elucidate that a low carbon steel part has sufficient ductility but does not possess hard surface due to which the surface layers wear down rapidly under severe friction, making the power transmission almost impossible. On the other hand, a high carbon steel part can be hardened sufficiently for wear resistant surface but the core would not be tough enough to absorb shock as it is a brittle material. The above problems can be overtaken successfully by saturating the surface layers of the steel parts by a suitable element such as carbon keeping the core composition unchanged. Then the hardness of the surface layers will be increased drastically by employing suitable heat treatment, while a high impact strength, similar to that of low carbon steel will be retained in the core as it changes very little on hardening.

Gas carburization is the latest technique for surface hardening of low carbon steel which is usually conducted by heating
the parts in a gaseous mixture of methane, cracked gas, natural gas, etc. Bangladesh has an enormous deposit of natural Titas gas with a composition of about 97.2% methane, 1.8% ethane, 0.3% propen, 0.2% butane, small amount of higher hydrocarbon and 0.3% nitrogen. According to the previous research works, this locally available natural Titas gas is a very encouraging carburizing medium for surface hardening of low carbon steel parts with a uniform case depth and surface carbon content. On the view point of economical consideration, it is the cheapest technique for Bangladeshi industries.

Machine parts for heavy duty applications such as drive gear, drive shafts, cam shafts, bus and truck gears, transmission gears, ball joints, steering parts, axles, etc. demand an increased hardness and wear resistance at the surface and better toughness in the core. Besides, advanced air-crafts and helicopters require improved transmission gear materials with increased load carrying capacity, longer life and ability for retaining their strength and hardness at elevated temperatures up to about 315°C (600°F). At such high operating temperature, the design criterion for high performance gears and rolling elements depends on the ability of the material to retain hardness and fatigue resistance at the working temperature. These parts used for heavy duty and high temperature applications are usually made of low carbon low alloy steels containing Ni, Cr, Mo, etc.

Improved fuel efficiency for vehicles may be achieved by
reducing the weight of the components. Thus, there is a growing trend towards obtaining greater power output from engine coupled with the smaller transmissions. To resist higher operating stresses by relatively smaller parts, the parts must have higher toughness as well as wear resistance than that of commonly used parts. Increased carbon content impairs the toughness due to which it necessitates to have a low carbon content in the steel for tough matrix. Small additions of alloying elements such as Nb, V, Mo, Ti, etc. can strengthen the steel tremendously and there is additional strengthening effect due to the precipitation of the carbide or carbonitride of the added elements \(^1\)\(^-\)\(^10\). Alloy addition is beneficial to have improved hardness and wear resistance with suitable tough matrix. Thus, the essential prerequisite to fulfill the recent growing trends to have a sophisticated/heavy duty parts particularly for a voracious fuel consuming engine operated at elevated temperatures is to select a high strength low alloy steel for carburizing.

Carburizing behavior of carbon steel is well established. Some work has \(^11\)\(^-\)\(^14\) already been done to investigate the carburizing behavior of low alloy steels containing Ni, Cr, V, Mo, etc. in some advanced countries. Later, recent research \(^15\)\(^-\)\(^17\) has shown that carburizing behavior of low carbon steels are notably influenced by small addition of Ni, Cr and V. But information regarding the carburizing behavior of the low carbon steel containing niobium is not available. This research work has therefore, been undertaken to
investigate the carburizing behavior of niobium microalloyed steel using locally available natural Titas gas as a carburizing medium, subsequently the mechanical properties of the carburized part achieved from the material on hardening.

Most of machine parts essential for the machineries in various industries in our country are imported from abroad. Recently, Bangladesh Government patronizing the production of spares by using the locally available materials and technology. Thus, a proportion of the required spares for our local industries which were imported are being manufactured in our country. Consequently, the dependence on imported spares can be minimized to some extent. Some work of low carbon steel shafts, gears, pinions, rollers, etc. and very recently a few alloy steel parts supplied by outside parties has been carburized by this method and hardened in the Department of Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka. These attempts are undoubtedly encouraging for saving foreign exchange as well as strengthening the national economy.

Niobium microalloyed steel is a tough material and natural gas in our country is cheaper than any other carburizing medium. The attempt for gas carburizing of niobium microalloyed steel may help to engineer the surface condition with tough matrix. Thus, gas carburization of niobium microalloyed steel can play an important role in manufacturing of the sophisticated and heavy duty spare parts as per requirements.
CHAPTER-2

CARBURIZING-A REVIEW

2.1. The Carburizing Process

Some engineering designs require a steel part having a hard and wear resistant surface with a soft and ductile core. Surface hardening can help us to avail the combination of the required properties. Consequently, several commercial processes, known as case hardening have been developed. Among them, carburizing is the cheapest, most satisfactory and widely used method of surface hardening of low carbon steels. In this process the surface of the steel part picks up the carbon from the surrounding medium. For the fulfillment of the particulars of the engineering design and their functional conditions, the first consideration is the selection of a steel which will be tough enough, even in the hardened condition. This steel is then subjected to carburization to an extent of eutectoid-hypereutectoid composition which on subsequent heat treatment gives the desired surface hardness, consequently the wear resistance. Addition of alloying elements in the plain carbon steel is proved beneficial directly by improving the hardenability and wear resistance. These beneficial effects permit the alloy steel for the manufacture of high duty and sophisticated machine parts.
There are three general methods of carburizing, each differing in technique and carburizing medium. The methods are: (1) solid or pack carburizing, (2) gas carburizing and (3) liquid carburizing. The choice of the method to be employed for carburizing depends mostly upon the characteristics of the desired case, available equipment facilities, availability of the raw materials for carburizing medium and the quantity, shape and size of the parts to be handled.

Solid or pack carburizing is performed by employing solid carburizing materials. In this method, the parts to be carburized are packed in a suitable heat resisting metallic container with the carburizing medium. The essential part of the carburizing medium is some form of carbon, usually hard wood charcoal. In this method, charcoal is the basic substance, but no carburizing is performed in the sealed container when all the air or oxygen in the container is removed. Due to this, energizers, which are in carbonate form, such as barium or sodium carbonate are mixed with the charcoal. For pack carburizing, a typical carburizing mixture may have the following compositions:

- Hard wood charcoal = 53-55%
- Sized coke = 30-32%
- Barium carbonate = 10-12%
- Calcium carbonate = 3-4% and
- Sodium carbonate = 2-3%
The box which has been packed with carburizing mixture, is placed in the furnace and heated to a desired temperature for carburization. The part is then kept at this temperature for a predetermined length of time according to the desired degree of penetration of carbon and cooled in the furnace. In this method, the case depth depends upon time, temperature and nature of the ambient mixture. This is essentially a batch method and thus, cannot provide high production rate. Here the equipment cost is lower but the technique has some limitations. The carburizing mixture used in this process has an insulating effect and thus, an excessive time is required to achieve the necessary temperature. In pack carburizing close control of the case depth and surface carbon concentration is not possible. On the other hand, the complication in handling larger and intricate parts and the necessity of frequent replacement of the box make the process back dated. Here the raw materials used are mostly imported. The dependence on the imported raw materials makes the process hardly acceptable in the view point of Bangladeshi industries. Nevertheless, pack carburization is economical and advantageous for small machine parts.

In liquid carburization, the part to be carburized is usually placed in a bath of molten cyanide together with some alkaline earth salts so that carbon can diffuse into the matrix of the part producing a carburized case comparable to solid or gas carburizing. Recently, a research work has been undertaken to study
the carburizing behavior of Carborundum-Soda bath. Operation of cyanide bath is complex and harmful for the personnel involved in the work due to the toxic nature of the gas evolved. Carborundum-soda bath is not as harmful as the cyanide bath. Whatever may be the type of the liquid bath, regular checking and adjustment of the bath composition is necessary for effective carburization and uniform case depth. In this technique, some shape cannot be handled because they either float or will cause excessive drag out of salts and most of the ingredients for the bath are imported and costly. Due to the above unavoidable limitations of the liquid carburizing baths, limited practices are observed. Nevertheless, they are suitable for small and medium-sized parts.

Gas carburization is the latest development in the family of carburizing as well as in the surface hardening techniques. In this process, the carburizing is performed by heating the low carbon steel parts in a gaseous mixture of methane, cracked gas, natural gas, endogas enriched with methane, etc. which is readily decomposed at the carburizing temperature and the atomic carbon thus formed diffuses within the matrix of the heated steel parts. Gas carburization may be either continuous or batch type and lends itself better to production heat treatment. In this method maintenance of proper composition of the carburizing medium is possible because of the continuous flow of gas within the carburizing chamber. This process also facilitates to avail uniform case depth and surface carbon content at a faster rate than any
other methods. This method allows quicker handling by direct quenching, consequently, saves production cost as time is money for commercial purposes. Complicated and large sized machine parts can also be case hardened by this technique. Therefore, gas carburization subsided any other carburizing technique and is practiced extensively in commercial plants. Some plus points such as huge reserve, easy availability of the gas in the local industries and lower cost make this process further encouraging as a carburizing medium in Bangladesh.

2.2. Theory of Carburization

The carburization of steel comprises three elementary processes which are the formation of the diffusing element in an atomic state, contact of the diffusing element with the surface being treated and its penetration within the matrix of the steel. For the achievement of the requirements for carburizing, the most important variants are temperature, time and atmosphere composition. The combined effects of time, temperature, atmosphere composition and the carbon concentration on the diffusion of carbon in austenite can be expressed by Fick's law of diffusion. Fick's first law describes diffusion under equilibrium condition and it states that the flux of the diffusing elements perpendicular to a plane of unit cross-sectional area is proportional to the local carbon gradient perpendicular to the plane. Mathematically, it can be expressed as:
The constant of proportionality $D_1$ is the diffusion coefficient, which has the unit \((\text{distance})^2/\text{time}\), $J_1$ is the resulting flux gradient.

Fick's second law is a material balance within an elemental volume of the system and expresses the non-equilibrium condition of diffusion, where the concentration changes with time as in the given mathematical relationship:

$$
\frac{dc}{dt} = (d/dx)D_1(dc/dx) \quad \text{(Ref. 19)} \quad \text{--------(2)}
$$

The diffusion coefficient for carbon in austenite is a function of carbon and temperature which can be obtained from Tribbett's mathematical relationship as given below:

$$
D = 0.47\exp[-1.6C - (37000 - 6600C)/RT] \quad \text{(Ref. 20)} \quad \text{--------(3)}
$$

where, $D$ is in \(\text{cm}^2/\text{s}\), $C$ is the weight percent of carbon, $T$ is the temperature in degrees Kelvin and $R$ (1.98) is the gas constant.

Carburizing is a non-equilibrium process, i.e., the gaseous constituents of the atmosphere are not fully in equilibrium with one another and the atmosphere is not in equilibrium with the steel being carburized. Nevertheless, several important reactions for
carburizing approach rapidly enough to permit the prediction of equilibrium state. The equilibrium state of the chemical reactions may be represented by numerical constant, $K_p$, derived from the general expression:

$$\log K_p = \frac{A}{T} - B$$

where, $K_p$ is a numerical factor termed as 'equilibrium constant'. The subscript $p$ denotes the dependency of chemical reaction on pressure, $T$ is the absolute temperature, $A$ and $B$ are constants derived for particular reaction.

Without developing the basic principle, the mechanism of carburization may be analyzed from the nature of carbon flow by stating the controlling factors which are:

(1) Factors that control carbon flow in iron
(2) Factors that influence the transfer of carbon to the iron surface.

2.2.1. Flow of Carbon in Iron

In carburizing the carbon atoms dissolved in the austenite of the surface layer of the steel part comprising an interstitial type solid solution. From the iron and iron carbide thermal equilibrium diagram given in Figure 1, it is evident that solubility of carbon in austenite depends on temperature. At a
temperature lower than about 910°C, pure iron exists as ferrite, a body centered cubic structure which transforms to austenite, a face centered structure above this temperature. The packing density of ferritic and austenitic iron are 68% and 74% respectively and in both, carbon atom dissolves interstitially. Due to the presence of an atom at the center of ferritic iron, the maximum radius of the foreign atom permissible to be dissolved within it is limited to 0.385 Å. In austenite total void is less than that of ferrite but it can permit the foreign atom to enter into the void having the radius up to 0.52 Å because of the absence of the central atom. So, carbon atom having a radius of 0.77 Å can enter into the interstices of austenite creating lower distortion than that for ferrite. So, carbon solubility in austenite is more than ferrite. At lower temperature face centered cubic iron transforms to body centered cubic iron and its interstitial voids become narrower. Consequently, the solubility of carbon in body centered cubic iron becomes much more limited.

The maximum penetration of carbon into the matrix of steel will depend upon temperature, time and carburizing agents. Since, the solubility of carbon in steel is the highest above upper critical temperature, carburizing takes place readily above this temperature. This higher operating temperature also favors the rapidity of carburization because for every 20-degree centigrade rise in temperature, the diffusion co-efficient becomes double. At higher temperature, the saturating element can transform into
nascent state, which is prerequisite for case hardening operation. For the above experimental evidence, it is customary to select a temperature about $40^\circ$C above the $A_1$ point of the particular steel to be carburized.

The rate of flow of carbon in austenite depends on values for the diffusion co-efficient and characteristics of the concentration gradient. The diffusion co-efficient is in turn a function of temperature and carbon concentration. The diffusion of carbon proceeds from the higher concentration developed from the supply sources to the lower concentration of the core.\footnote{22}

The general form of the carbon gradient is influenced only by the range of concentration from the surface to the core. For a given temperature, the rate of diffusion increases with the increase in carbon concentration.

The maximum rate at which the carbon can be added into a steel matrix is mostly limited by the rate of diffusion of carbon in austenite. This diffusion rate increases greatly with the increase in temperature.\footnote{20} From experiment, it is evident that the rate of carbon addition in steel at $925^\circ$C is about 40% greater than that at temperature $870^\circ$C. Due to this positive effect of temperature, the most commonly selected carburizing temperature is $925^\circ$C, which permits a reasonable carburizing rate without excessively rapid deterioration of the furnace equipment.\footnote{20} Sometimes the carburizing temperature is raised to 955 or $980^\circ$C for the purpose requiring deep case with shorter period. Conversely,
shallow case is performed at lower temperature because case depth can be controlled accurately with slow carburizing rate obtained at lower temperature. Various alloying elements such as Cr, Ni, Mo, etc. have a great influence on the activity of carbon dissolved in austenite. This influence is due to the effect of alloying elements in steel on the driving force for surface reactions \(^{20}\). To obtain the true driving force somewhat higher temperature is selected for carburization of alloy steels.

In case hardening practices, case depth is specified up to a depth below the surface with a definite extent of carbon saturation from which the desired mechanical properties can be achieved on subsequent heat treatment. A case depth to a hardness of 50 HRC or a case depth having a carbon content of about 0.4 weight percent is the example of specification of an effective case depth \(^{20}\). The commonly used term 'the total case depth' is somewhat vague for general use as a specification because of the gradual transition between case and core properties in most carburized parts. Nevertheless, the case depth of a carburized steel is a function of time and temperature. Harris \(^{22}\) has developed a mathematical expression as given below showing the effect of temperature and time on the extent of penetration of carbon for normal carburizing:

\[
\text{Case depth} = \frac{(31.6t)}{(10^{6.700/T})} \quad \text{(Ref.22,23)} \tag{5}
\]
where, case depth is in inches, t is time in hours and T is the absolute temperature in degrees Rankine. For a specific carburizing temperature, the expression becomes very simple as shown below:

\[
\text{Case depth} = K f t
\]

\[
= 0.025f t \text{ for } 1700^\circ F
\]

\[
= 0.021f t \text{ for } 1650^\circ F
\]

\[
= 0.018f t \text{ for } 1600^\circ F
\]

Harris has also developed a method for calculating the carburizing time and diffusion time to produce a carburized case of predetermined depth and carbon concentration at the surface as follows:

\[
\text{Carburizing time} = \text{Total time}\left\{(C - C_i)/(C_0 - C_i)\right\}^2 \text{ (Ref.21)(6)}
\]

\[
\text{Diffusion time} = \text{Total time} - \text{Carburizing time}
\]

where, total time is in hours, C is the final desired carbon concentration at the surface, \(C_0\) is the surface carbon concentration at the end of the carburizing cycle and \(C_i\) is the concentration of carbon at the core.

2.2.2. Flow of Carbon from the Supply Source

Whatever may be the carburizing medium, the carburizing
agent responsible for the actual supply of the carbon to be
diffused in the steel matrix is a some form of carbon compound. For
carburizing, this carbon compound have to be dissociated at the
carburizing temperatures. During heating, the carburizing steel
which contains about 0.1 - 0.25 percent carbon, transforms to
austenite completely at the carburizing temperature. At this
temperature austenite can absorb carbon up to 1.7 percent to be
saturated making an interstitial solid solution. At this higher
temperature, when a source of carbon such as carbon monoxide, is
brought in contact with the steel, there will be a transfer of
carbon from the gaseous medium to the steel part. For exact form of
carbon before it is to be absorbed by austenite, there are
different opinions from different investigators. Some investigators
feel that there is an interaction of carbon monoxide with iron to
form iron carbides. Another group feels that carbon being brought
to the surface of the metal as CO₂, will breakdown to form atomic
carbon in presence of the austenite and the atomic carbon diffuses
as such in the iron. In the present work let us assume the
carburizing as the action involving the formation, absorption and
diffusion of carbon in iron.

The extent to which various carbon compound may supply
atomic carbon is related to some conditions that determine the
equilibrium with the surface of the steel. The equilibrium
composition of the products and the reactants is a function of
temperature and carbon concentration at the surface.
carburizing, though solid compound is used but they are essentially a gas producer. Here the carbon monoxide formed is dissociated to atomic carbon and carbon dioxide where the atomic carbon is subsequently absorbed by the austenite. The carbon in the gas carburizing chamber is in the form of gaseous hydrocarbon compound or carbon monoxide. At the carburizing temperature they are dissociated to atomic carbon and the nascent carbon is then absorbed by the steel part which has been explained later in detail. In liquid carburizing, the required atomic carbon is formed by some complex chemical reactions between the ingredients of the fused salt which is subsequently absorbed by the steel part immersed in the bath.

2.2.2.1. Mechanism of Surface Saturation in Gas Carburization

When low carbon steel part is heated to the carburizing temperature, the steel is transformed to austenite at this temperature. This austenite is capable of holding an amount of carbon in solid solution approaching the saturation limit of 1.7 percent. In gas carburizing, the part to be carburized is exposed in a carbon rich atmosphere such as methane, cracked gas, natural gas, endogas enriched with methane, etc. When the natural Titas gas is used as the carburizing medium, the main gas constituents are \( \text{CH}_4, \text{C}_2\text{H}_6, \text{CO}, \text{N}_2 \), etc. where, \( \text{N}_2 \) is inert acting as diluent only. During carburizing the exact sequence of the reaction is not known in detail, but it is known that carbon can be added or removed
rapidly from steel by the overall reversible reactions. In this respect, the overall reactions in the carburizing chamber will be two fold which are:

1. The interface reaction
2. The reaction away from the interface.

In the case of interface reactions for three carbon compounds, methane, ethane and carbon monoxide may be written as follows:

\[
\begin{align*}
\text{2CO} & \rightarrow \text{C(in Fe)} + \text{CO}_2 \quad \text{--------(7)} \\
\text{CH}_4 & \rightarrow \text{C(in Fe)} + 2\text{H}_2 \quad \text{--------(8)} \\
\text{C}_2\text{H}_6 & \rightarrow 2\text{C(in Fe)} + 3\text{H}_2 \quad \text{--------(9)} \\
\end{align*}
\]

For same carbon compound, the reactions away from the interface may be as follows:

\[
\begin{align*}
\text{2CO} & \rightarrow \text{CO}_2 + \text{C (solid carbon)} \quad \text{---------(10)} \\
\text{CH}_4 & \rightarrow 2\text{H}_2 + \text{C (solid carbon)} \quad \text{---------(11)} \\
\text{C}_2\text{H}_6 & \rightarrow 3\text{H}_2 + 2\text{C (solid carbon)} \quad \text{---------(12)} \\
\end{align*}
\]

Sometimes, water vapor may present in the supplied gas which acts as a decarburizing agent and removes carbon from the surface by the following reaction:

\[
\begin{align*}
\end{align*}
\]
\[ 2\text{H}_2\text{O} + \text{Fe}_3\text{C} \text{ (in austenite)} \rightarrow 3\text{Fe} + \text{CO}_2 + 2\text{H}_2 \quad \text{(13)} \]

Now, the possible gaseous species which may be present in the chamber atmosphere are CO, CO\(_2\), H\(_2\), H\(_2\)O, N\(_2\), CH\(_4\) and C\(_2\)H\(_6\). If it is possible to know the equilibrium composition of the gases in the chamber then the carbon potential of the atmosphere can be found by writing the following equilibrium relationship from the equation (7):

\[ K_1 = \frac{a_c \cdot P_{\text{CO}_2}}{(P_\text{CO})^2} \quad \text{(Ref.20)-----(14)} \]

where, \( P_\text{CO} \) and \( P_{\text{CO}_2} \) are partial pressure of CO and CO\(_2\) respectively, \( a_c \) is the activity of carbon, \( K_1 \) is the equilibrium constant for the reaction. The carbon activity is related to the carbon content of the austenite as in the following expression:

\[ \ln a_c = \ln y_c + \frac{(9167 y_c + 5093)}{T} - 1.867 \quad \text{(Ref.20)-----(15)} \]

where, \( y_c = \frac{(4.65 w)}{(100 - w)} \), \( T \) is the temperature in degrees Kelvin, \( w \) is the weight percent of carbon in austenite and \( y_c \) is the atom ratio of carbon to iron.

2.3. **Atmospheric Conditions for Gas Carburization**

For natural Titas gas as carburizing medium the possible constituents of the gas carburizing atmosphere are CO, CO\(_2\), H\(_2\), H\(_2\)O, N\(_2\), CH\(_4\) and C\(_2\)H\(_6\). For uniformity of carburizing the above gases have
to be well circulated within the chamber and the parts being carburized must be well spaced to allow the atmosphere to penetrate within the load. A positive furnace pressure is another atmospheric parameter for effective carburization. Proper maintenance of this parameter has two fold benefits as it prevents infiltration of air within the chamber, consequently, the chance of oxidation of the part being carburized is minimized as well as enhance the carburization rate. For gas carburizing a positive furnace pressure of about 12 to 37 pa is satisfactory and it can be controlled by adjusting the gas flow rate.

Usually the volume of the chamber of gas carburizing furnace is small and the chamber is sealed, which ensure small volume of gas requirement for each working shift. For a pit furnace having a working chamber 25 inches in diameter and 36 to 48 inches deep, the commonly used gas flow rate is 8 to 15 ft per hour. The rate at which the furnace atmosphere responds to changes in inlet gas composition depends on the mean residence time of the atmosphere gases in the furnace. The mean residence time \( t_{res} \) is approximately:

\[
 t_{res} = \left( \frac{V \cdot T_A}{F \cdot T_f} \right) \quad (Ref. 20)----------(16)
\]

where, \( V \) is the furnace volume, \( F \) is the carrier gas flow rate, \( T_A \) is the absolute ambient temperature and \( T_f \) is the absolute furnace temperature. The residence time may be 2 to 15 minutes.
2.4. **Sooting in Gas Carburizing and Its Remedy**

The excessive amount of free carbon deposited on the work piece and in the furnace is termed as soot. Sooting can occur from the atmosphere of very high carbon potential providing a loss of carbon. Once this problem is commenced, the furnace atmosphere becomes uncontrollable. One symptom of sooting condition is a pronounced drop in the CO content of the carburizing chamber due to hydrogen dilution. From sooting various problems such as uneven carburization, deterioration of the furnace, high cleaning costs and unpleasant working condition may arise. Sooting problem can be minimized by mixing the carrier gas with hydrocarbon gas and well judged flow rate from which a reasonable rapid carburizing can be achieved without excessive sooting. The only practical way to remove the soot formed in the continuous carburizing chamber is to empty the furnace, introduce air and burn out the soot. In the case of batch type operation, the soot can be removed by proper brushing.

Sometimes oxide layer may remain on the work piece which is subsequently reduced at the furnace temperature producing tenacious soot on the surface of the objects by the following reactions:\(^23\):

\[
\begin{align*}
\text{FeO} + \text{Fe}_3\text{C} & = 4\text{Fe} + \text{CO} \quad \text{------(17)} \\
2\text{CO} & = \text{CO}_2 + \text{C} \quad \text{-------(18)}
\end{align*}
\]
The above problem can be avoided by eliminating the oxide layer of the work piece before its loading in the carburizing chamber.

2.5. Safety Measures for Gas Carburizing

The outlet gas from the gas carburizing chamber is very toxic and highly inflammable whether it is mixed or unmixed with air. For this, a safety program is essential to avoid the risks of the operation especially for the personnel under work. As a safety measure, all the gas discharged from the furnace have to be burned to ensure that poisonous carbon monoxide has been converted into carbon dioxide. Therefore, a pilot flame have to be maintained until carburizing gas flow is continued. For safety measure, it is convenient to have a source of inert gas, such as nitrogen for an automatic purging.

2.6. Heat Treatment for Carburized Steels

Carburization is usually employed for the parts that necessitate a hard, wear resistant surface with a tough, ductile core which can not be availed from the as carburized objects. If a carburized part is slowly cooled from the carburizing temperature, the surface hardness will be quite low, since it is essentially an annealed high carbon steel. The case of the carburized part has a composition of an eutectoid or hypereutectoid steel. When the carburized case is in the hypereutectoid steel composition, slow
cooling results a cementite network and induces brittleness which is always to be avoided. Some times objects to be carburized may be originally coarse grained, then as a result of being held for a long time at the elevated temperature, the grain is further coarsened badly. Due to the above inherent limitations of the as carburized steel parts, they must be heat treated.

A carburized steel is effectively a combination of steels containing various carbon concentration from the surface to the core, which makes the heat treatment process somewhat complex. For a carburized part, what is done with the surface must be done with the interior. In spite of this complication, treatment can be given that will produce the desired results without introducing any new metallurgical principle. It is observed that the case consisting of fine grained crystalline martensite with small included cementite grain and fine grained core gives most satisfactory properties. Thus, the heat treatment process to be employed to avail the optimum properties must be selected considering the treatment temperature, the composition of the case and the core, the purpose for which the part is intended for, the properties that must be gained to meet the specifications, etc. Taking the above factors in consideration, three different heat treatment techniques can be practiced for carburized steels as described below.

2.6.1. Direct Quench Technique

When the carburizing temperature is just above the $Acm$
temperature and the carbon content of the case does not exceed eutectoid composition then this technique can be practiced. In this technique, the carburized part is quenched directly from the carburizing chamber into a suitable quenchant followed by immediate tempering to reduce the brittleness of the case and to minimize the danger of cracking. This technique is very simple, inexpensive and gives minimum distortion. But the obtained grain size of the case and the core is relatively coarse and a considerably high proportion of austenite is retained in the case. The above drawbacks make the adoptability of this technique limited to inherently fine grained steels and service conditions where coarse grained structure is not objectionable.

2.6.2. **Double Quench Technique**

When the carbon content in the case exceeds eutectoid composition and the steel is inherently coarse grained, double quench technique will give the best combination of hardness and wear resistance and fine grained case with a tough, refined core. For this, the steel part is slowly cooled from the carburizing temperature, then reheated to above the \( A_1 \) temperature of the core and quenched in a suitable quenchant. This will produce excellent grain refinement, consequently better toughness for the core. The steel is then reheated to above the \( A_{1,1} \) temperature, quenched and tempered which refines the grains of the case sufficient for desired hard and wear resistant surface. This technique also has
some limitations such as lengthy operation, possibility of decarburization of the case, excessive tendency for distortion and cracking. But it is the best heat treatment method for the steel that coarsens badly at the carburizing temperature, although it is neither the cheapest nor the easiest technique of heat treatment for a carburized part.

2.6.3. Intermediate Technique

In this technique the first reheating above the $A_1$ temperature in the double quench technique is avoided and the other steps are followed. This process gives better properties than that can be achieved from direct quench technique and inferior to that of double quench. Thus, the part can not be used in service under high stress.

2.7. Quenchants for Carburized Steels

For hardening the steel part is quenched into a certain medium known as quenchant to ensure the required rate of cooling. There are numerous quenchants such as brine, caustic solution, water based polymer quenchants, oil, molten salts, etc. If the part is to be used as heat treated condition without any finishing operation to control dimensional accuracy, marquenching can be employed. For this the part is quenched into molten salts or hot oil keeping the quenchant temperature above the $M_s$ temperature of the case, but below the $M_s$ temperature of the core. This treatment
gives a mixed structure of martensite, bainite and ferrite for the core and the case transforms to martensite while it cools in air after leaving the quenchant. Rings and shafts are often press quenched, that is, clamped in a fixture while heated and sprayed with oil to reduce distortion.

2.8. Heat Treatment of Gas Carburized Steels

The carburized part can be heat treated by employing any technique explained above. But the technique selected must be compatible with the carburizing temperature, alloy content of the steel part, sequence of the subsequent manufacturing operations, etc. Quenching directly from the carburizing temperature can be conducted when the carburizing temperature is low and the steel part is inherently fine grained. Gas carburizing is best suited for complex shaped parts. In this case, direct quenching is usual practice to avoid undue cracking and distortion. The parts carburized at relatively higher temperature (940-950°C) can be cooled in the furnace to a lower temperature (840-860°C) and then quenched. In this technique, the temperature level before quenching must be such that no carbide can be precipitated at the grain boundaries. If the boundary carbides are developed, the following difficulties are likely to result:

(1) Reduced mechanical properties
(2) Breaking of the case at the sharp corners
(3) Service failures
Alloy content and the nature of the alloying elements have a potential impact on the choice whether the work should be directly quenched or slowly cooled or reheated. For example, high alloy steels (high nickel grades) will retain excessive amount of retained austenite when quenched directly from about 930°C. Therefore, parts of such a steel are slowly cooled in furnace and then reheated to quenching temperature and quenched.

The type of carburizing furnace used has an influence on the choice of the heat treatment technique. The Pusher-type continuous furnaces are ideally suited for direct quenching while pit-type furnaces are not. Because, close control of temperature is not possible in pit-type furnace and the process is potentionally hazardous for health of the personnel under operation.

After quenching, the part is tempered at a low temperature of 150 to 180°C to relieve stress. The retained austenite transforms into martensite in the temperature range of 220 to 260°C. If the parts require best possible stability then the treatment should be designed to eliminate retained austenite. In such cases sub-zero treatment can be employed. The sub-zero treatment or cold stabilization can be conducted using many well established methods such as the use of mixtures of dry ice and alcohol for temperature down to -73°C, mechanical refrigerators for temperature down to -100°C and liquid nitrogen for temperature as low as -195°C. According to some investigators any interruption in the cooling cycle to sub-zero temperatures stabilizes the
austenite and reduce the effect of sub-zero treatment. Due to this, sub-zero treatments are always conducted immediately after quenching.

2.9. **Carburization of Low Alloy Steels**

Low carbon steel is usually used for carburizing because of its excellent toughness. Sometimes alloy steels are also carburized for additional properties of both the case and the core in the case of high duty applications. In alloy steels, the alloying elements remain in the form of various carbide and nitride precipitates. To take the precipitates into solution higher temperature is required. For this reason, comparatively a higher carburizing temperature is usually selected for alloy steels. Low alloy steels containing nickel, chromium, manganese, vanadium, molybdenum, etc. singly or in combination usually have sufficient hardenability. From these steels maximum case hardness can be attained by oil quenching and desired core properties up to a tensile strength of 200,000 psi is obtainable with suitable toughness by proper selection of the steel compositions.  

Some works have already been done to investigate the carburizing behavior of low alloy steels both in home and abroad. It has been reported that chromium increases the case depth whereas nickel decreases it. Both nickel and chromium enhance the formation of the retained austenite but chromium is more effective in promoting retained austenite formation in the hardened case.
They also deteriorate the core toughness in the carburized and hardened condition.

It has also been reported that chromium bearing steels absorb more carbon than pure iron whereas, nickel bearing steels absorb lower carbon. Thus, carbide is formed in chromium bearing steels at lower carbon potential than that of carbon steels. Carburization of chromium steels followed by heat treatment raises the wear resistance by a factor 1.5 compared to plain carbon steel due to the presence of carbides in the subsurface layer.

Alloying element vanadium with or without nitrogen reduces the case depth but vanadium without nitrogen is more effective in reducing case depth. Vanadium in the solid solution can raise the hardenability but as undissolved carbide and nitride it may decrease the hardenability. This variable influence can also be observed for molybdenum and titanium.

Increase in chromium and manganese content increase the hardenability. But these elements are prone to internal oxidation during gas carburizing. Nickel and molybdenum addition raises the hardenability and improves fracture properties.
EXPERIMENTAL SET-UP

The gas-fired gas-carburizing furnace constructed by Rahman 27 was used in this research project after some modifications. Initially, the furnace was 30 inches in height and 34 inches in external diameter with a mild steel carburizing chamber of about 18 inches in height and 11 inches in diameter. The furnace was fired with two burners housed in the side walls. There was some problems in attaining the required temperature of carburization in this furnace. It took about three hours time to attain 820°C. The temperature required for carburizing experiments in this research work was 950°C. Trials were therefore, made to attain the required temperature of 950°C and the following points were thought to be the probable causes of not attaining the required carburizing temperature within a reasonable time period:

(1) Back firing
(2) Improper position and passage size of the exhaust
(3) Insufficient space between the fire brick wall and the wall of carburizing chamber.

In order to observe the individual effect of the above
listed factors on achieving the required temperature, at first the position of the two exhausts were raised by 3 inches and the passage size was widened, from which reduction of back firing, consequently, a higher temperature was expected. After this modification, firing in the furnace was commenced again and from this, a little improvement in temperature achievement as well as reduced back firing problem was observed. But achievement of the required temperature was not possible and hence, further modification became essential.

After the first stage of modification, the target was to increase the space between the fire brick wall and the carburizing chamber as a second stage of modification so that the flame can easily escape through the wider exhaust space after easy and proper whirling action in the furnace. For this, the mild steel carburizing chamber was replaced by a stainless steel chamber capable of giving a prolonged life. The internal diameter of the carburizing chamber was reduced from 11 inches to 8.5 inches keeping the chamber height unchanged. After this complete replacement, trial firing was carried out and thermocouple placed inside the carburizing chamber showed 850°C at the end of 3 hours of firing, that is, no satisfactory results was observed from this modification. Moreover, the wide spread flame through the newly constructed exhaust space made the furnace operation risky. In order to overcome this additional problem, two chimneys with a square hollow passage of 5 inch X 5 inch size were constructed at the widened exhaust space as
a third stage of modification. This modification was carried out so that the exhaust flame can not spread out and consequently a safe carburizing operation as well as a higher temperature can be achieved due to a relatively higher residence time and increased pressure of the flame within the furnace. When the construction of the chimneys was completed, a positive result was experienced and about 900°C was possible to achieve after 2.5 hours firing against 820°C with 3 hours firing from the unmodified furnace. But the temperature thus achieved was much below of the temperature required for the present research work. After the third stage of modification, it became clear that achievement of the required temperature would not be possible without blowing secondary air in combination with gas and thus, a fourth stage of modification became imminent to make the furnace workable.

The fourth stage modification was somewhat elaborate and time consuming because, a large number of accessory parts had to be prepared for this. Here, burners used previously were removed and mild steel sheets with a hole of 2 inches diameter were welded at the opening for each of the burners. Within each of the hollow space of the mild steel sheet a socket of 2 inches size was fitted by means of welding. Then one end of a tee was joined with the socket and the other two ends were connected with a hose pipe line and a 1 inch reducing socket respectively. A 3/4 inch stainless steel pipe was allowed to pass through the reducing socket up to the furnace chamber. The hose pipe and the stainless steel pipe
were connected to the blower line for air flow and the gas line respectively. After this, it was observed that there was no opening available to commence firing in the furnace chamber and this situation was overcome by building a 2 inch X 2 inch opening just above one burner. To avoid the back firing through the newly constructed opening, a box of 4 inch X 5 inch was made on the surface wall of the furnace around the opening and after initiating the firing, the open space was allowed to shut-off by a refractory brick conformable within the box.

After the fourth stage of modification, a trial firing was started again supplying air in combination with gas and a significant positive result was observed, that is, the carburizing temperature of 950°C for the current research work was achieved within an hour. Before modification, no air was blown within the furnace and the temperature of the furnace was controlled automatically by controlling the gas flow with the help of a solenoid valve actuated by a pyrometer. But in this research work, gas and secondary air were supplied through two different supply line and thus, the controlling system was somewhat different from the operation of the unmodified furnace. When the firing was commenced, both air and gas were supplied within the furnace with full capacity of the supply line and only gas was allowed to flow through the solenoid valve. When the temperature within the carburizing chamber was about 900°C, both air and gas flow rate was lowered to a predetermined level. After this action, the tendency
of the furnace temperature was still rising for few minutes and within this period, the knob of the temperature controller was gradually rotated and finally fixed up at 950°C. The temperature controller which was connected to the solenoid valve was also connected to the cold junction of the thermocouple. In order to avoid the contamination of the chromel-alumel thermocouple from the reducing environment within the chamber, it was isolated from the carburizing atmosphere by inserting it within a stainless steel tube. When the required temperature was reached, the solenoid valve stopped the flow of gas into the burner without hampering the air flow, as air flow was through another line isolated from the solenoid valve. In order to avoid the bothering sound caused by the sudden flow of gas during the resumption of combustion, a little gas flow, insufficient to cover the heat loss at the controlled temperature, was maintained through a by-pass line. Due to heat loss, when the temperature of the carburizing chamber dropped below the required level, the solenoid valve resumed the gas flow and in this way a close control of temperature (±2°C) was possible from this arrangement.

In order to seal the carburized chamber a steel lid lined with fire brick was placed on the top of the chamber and during loading and unloading of the work pieces it was handled manually before modification, which was a very risky operation, especially for quenching. To make this operation more convenient and safe for the personnel engaged in this work, a lever arm arrangement was
also set-up on the top of the furnace as a fifth stage of modification, by which mechanical handling of the lid was possible.

For the current research work, all of the carburizing operations were be carried out within an identical atmosphere. In order to ensure identical carburizing atmospheric conditions, the maintenance of constant gas flow and gas pressure within the chamber are extreme prerequisite and these were possible by passing the carburizing gas through a rator meter and a pressure gauge. To know the amount of gas flow per unit time, the rator meter was also calibrated. A schematic diagram of the experimental set-up is shown in Figure 2.
CHAPTER-4

EXPERIMENTAL PROCEDURE

4.1. Materials and Specimens Preparation

Three different steels containing 0.07 percent carbon were used in this experiment. The compositions of the steels are given in Table 1. The steels were made in an air induction furnace using high purity materials in the Department of Metallurgy, University of Sheffield, England. All the melts were teemed at about 1600°C and sound ingots were produced. The ingots were then rolled down to a size of about 16 mm in diameter and were used as the stock materials for carburizing. Steel 1 is the base steel with which the carburizing behavior of the other two steels containing Nb alone (steel 2) or in combination with nitrogen (steel 3) were compared. From the stock materials of steels 1 to 3 specimens having dimensions of about 10 mm x 10 mm x 8 mm were cut out. A small hole of about 1.5 mm diameter was drilled at one corner of each specimen. Surface condition of the specimens can hamper the carburizing behavior of the steels. The surface of the specimens was polished by emery polishing papers up to grit No. 2/0. These polished specimens were washed in running water and dried in aceton. The polished and dried specimens were then stored in a desiccator. These stored specimens were used for carburizing.
4.2. **The Carburizing Operation**

The polished specimens of steels 1 to 3 stored in the desiccator were hung into the carburizing chamber by means of nichrome wire in such a way that the tip of the thermocouple and the specimens were as close as possible to each other. In order to seal the atmosphere in the carburizing chamber from outer atmosphere, the top of the chamber was closed with a lid. To avoid possible oxidation of the specimens due to the air present in the chamber, gas flow was made for a while before the firing of the furnace was started. Then the firing was commenced through two burners housed at the outer surface of the furnace near its bottom and the controller was set for the desired temperature. After commencing the firing the required temperature was achieved within an hour.

The flow rate of the carburizing gas into the chamber has a great effect on the carburizing rate. To study the effect of gas flow rate on the carburizing behavior three different flow rates as 6 ft$^3$/hr, 10 ft$^3$/hr and 12 ft$^3$/hr were used. For each case a constant flow rate was maintained using a flow rator meter. The first two flow rates were used for furnace cooled specimens carburized only for 1 hour. The third flow rate was used throughout the whole experiment. To ensure the continuous gas flow within the chamber a signal flame was maintained at the top of a glass jet. From the visible flame height of moderate length on the top of the glass jet, the operator can be sure that the chamber is full of gas and a proper carburizing environment has been maintained.
For all the gas flow rates, the carburization of the specimens was carried out at a constant temperature of 950°C and at a pressure of 15 psia. Another batch of samples of steels 1 to 3 was carburized for five different time periods as 1/2 hour, 1 hour, 2 hours, 3 hours and 4 hours at the above mentioned temperature and pressure with a gas flow rate of 12 ft³/hr. After the predetermined time, the firing was stopped and the specimens were allowed to cool in the chamber to room temperature. The gas flow through the carburizing chamber was maintained during the cooling period until the temperature in the chamber came down to about 500°C. This was done as a measure of precaution to prevent any possible oxidation due to infiltration of air. After cooling the specimens were taken out of the chamber for required investigations.

4.3. Optical Microscopy and Case Depth Measurement of Carburized and Furnace Cooled Steels

The carburized and furnace cooled specimens were cut into two pieces at right angles to reveal the section orthogonal to the treated surface. During cutting, a copious flow of water was maintained. One piece of each specimen was then mounted by bakelite powder, polished by standard techniques and etched in 2 percent nital. The microstructures of these specimens were observed by optical microscope and photographs of the microstructures of each specimen were taken using photomicroscope.
The measurement of the extent of carburization i.e. the effective case depth was attempted. The case depth is usually specified as the depth of carbon penetration below the surface at which a definite value of some property occurs. In this work, a case depth corresponding to a carbon content of 0.4 weight percent was considered for an effective case depth following Stickels. Then the effective case depth was measured linearly from the microstructures of these specimens by using a micrometer eye piece fitted to a Shimadzu optical microscope.

4.4. Determination of Austenite Grain Size of the Carburized Case of the Steels

The three important zones of the carburized case are hyper eutectoid zone, eutectoid zone and proeutectoid zone. In the case of slow cooled hyper eutectoid steels, proeutectoid cementite precipitates at the austenite grain boundaries and finally a continuous network is formed around the remaining austenite grains which subsequently transforms to pearlite during cooling. The prior austenite grain size of this zone was revealed by the cementite network. In proeutectoid zone, the proeutectoid ferrite is expelled from the austenite grains at the grain boundaries forming discontinuous ferrite networks. These ferrite networks outline the prior austenite grains. It is very difficult to reveal the grain boundaries of eutectoid steels. The grain size of the case was thus obtained by taking the average grain size of hypereutectoid and proeutectoid zones.
For austenite grain size measurement, the mean linear intercept method was employed. A total of about 300-400 intercepts were counted for each specimen.

4.5. Carburization and Heat Treatment

4.5.1. Introduction

To study the structure and properties of the steels in the carburized and heat treated conditions the carburizing parameters such as temperature, gas flow rate, gas pressure, etc. were kept identical as in the case of the carburized and furnace cooled specimens except the time of carburization. In this case three different time periods as 1 hour, 2 hours and 4 hours were selected for carburizing.

To observe the effect of sub-zero treatment on the retained austenite content of the case higher carburizing time as 4 hours and moderately lower carburizing time 2 hours were selected.

4.5.2. Carburization and Hardening

Two sets of previously prepared specimens from each of steels 1 to 3 were carburized at 950°C for 1 hour, 2 hours and 4 hours in the same process described in section 4.2. At the end of the predetermined time period, the specimens were cooled to about 860°C in the carburizing chamber. The gas flow into the chamber was then stopped and the lid of the chamber was then removed by means
of a lever arm arranged on the top of the furnace. A little gas flow was maintained during cooling to the hardening temperature to avoid decarburization of the carburized specimens. The specimens were then quenched into 10 percent brine immediately after removing them from the chamber.

4.5.3. **Sub-zero Treatment**

One of the two sets of the quenched specimens from each steel carburized for 2 hours and 4 hours was subjected to sub-zero in order to reduce the retained austenite content in the case of the carburized and hardened steels. This was done by immersing the carburized and hardened specimens into liquid nitrogen taken in a previously conditioned flux and kept them in it for an hour following Lakhtin 6.

Since the liquid nitrogen is extremely cold substance, the flux was conditioned to withstand low temperature before the transfer of liquid nitrogen from the dewer container to the flux. As a part of temperature conditioning, the flux was filled with ice to achieve the ice temperature in the chamber of the flux. After this, the ice was removed and the flux was partially filled with liquid nitrogen. The chamber was then filled with liquid nitrogen up to the required level by several steps.
4.5.4. Tempering

The other set of the quenched specimens without sub-zero treatment from each steel was tempered immediately after quenching at a low temperature of 160°C for half an hour to transform the hardened martensite into tempered martensite, relieving the residual stresses developed during quenching.

Sub-zero treated hardened specimens were also tempered to transform the hardened martensite into tempered martensite, relieving the residual stresses developed during quenching and sub-zero treatment in the liquid nitrogen.

4.6. Surface Hardness and Microhardness Measurement of the Carburized and Heat Treated Steels

The hardness measurement at the surface of the carburized and heat treated specimens was performed by Rockwell hardness testing machine. After measuring the hardness at the surface, the heat treated specimens were then sectioned using a silicon carbide disc cutter with copious flow of water to avoid softening due to heat generated. The surface of the sectioned specimens were made parallel by a surface grinding machine and one of the pieces from each specimen was mounted in bakellite powder and polished by standard metallographic technique. These polished specimens were then lightly etched in 2 percent nital and microhardness measurement was then performed by using Shimadzu microhardness tester. Here 100 gm load was applied and 5 seconds time was allowed to
cause the indentations on the polished and lightly etched specimens. By measuring the diagonal length of the indentations, VHN at the corresponding point was obtained from the calibration chart. The hardness profiles were then drawn by using the VHN at different points from the subsurface to the core. From hardened specimens, carbon percentage can not be measured. So, case depth measurement was not possible following the procedure adopted in the case of annealed specimens. For hardened specimens, effective case depth was considered up to a depth corresponding to 540 VHN following Stickels for carbon steels. After taking microhardness from the subsurface to the core, the specimens were again polished properly and etched in 2 percent nital. Optical microscopy and photomicroscopy were then carried out.

4.7. Determination of Retained Austenite by X-ray Diffractrometry

In a carbon steel when the carbon content exceeds 0.65 percent, the $M_f$ temperature (the temperature at which all the austenite transforms to martensite) shifts to below the room temperature and all the austenite can not be transformed to martensite during quenching. This problem is vital for the treatment of carburized steels or steels containing austenite stabilizing elements such as manganese, nickel, etc. On the other hand, retained austenite in the hardened case of a carburized part deteriorates the wear resistance which is prerequisite for
transmission parts. Retained austenite also hampers the dimensional stability of the parts. So, retained austenite content in the hardened case of carburized parts must be known before their application for proper functioning under service. Here retained austenite content was measured by X-ray diffraction technique and for this purpose a JEOL DX-GE-2P X-ray diffractometer was used. A substantial amount of retained austenite was observed by optical microscopy in the hardened structures of the specimens carburized for 4 hours. For this reason, the X-ray diffraction was carried out for the specimens of steels 1 to 3 carburized for 4 hours duration.

In this present work, the purpose of X-ray diffraction study was to investigate the relative amount of retained austenite in quenched, sub-zero treated and tempered (QST) specimens and quenched and tempered (QT) specimens and to study the effect of sub-zero treatment on the transformation of the retained austenite of the QT specimens. For this, the X-ray diffraction was conducted by CuK\(_\alpha\) radiation on all of the specimens of each of the steels 1 to 3 and individual structural information of the specimens was recorded on the chart papers. The chart papers were then analyzed and the possible phases with their planes responsible for the recorded peaks in the chart papers were identified first with the help of the manual available in the X-ray diffractometry laboratory. The specimens were not in the powder form and they were composed of multi phases with nonuniform microstrain. Thus, a
slight deviation of the peak position was observed for all the specimens. After detecting the phases, their planes for individual peak, the peak height or area under the peaks, the relative amount of austenite in the structure was determined by using direct comparison technique explained by B.D. Cullity. For this, the following mathematical relationships were used:

\[ R = \frac{1}{v^2} |F|^2 P\{\frac{1+\cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta}\} \cdot e^{-2K} \]

where, \(v\) = the volume of unit cell of the respective phase

\(|F|\) = structure factor

\(p\) = multiplicity factor

\(e^{-2K}\) = temperature factor

\(2\theta\) = angle at the specific peak position

The values of \(|F|\), \(p\), \(e^{-2K}\) and \(\theta\) were known with the help of the information provided by Cullity. By calculating the values of \(R_A\) (R for austenite) and \(R_M\) (R for martensite), the relative amount of austenite and martensite were known by using the following relationships:

\[ \frac{I_A}{I_M} = \frac{(R_A \cdot C_A)}{(R_M \cdot C_M)} \quad \text{and} \]
\[ C_A + C_M = 1 \]

where, \(I_A\) = peak height or area under the peak of austenite phase

\(I_M\) = peak height or area under the peak of martensite phase
\[ C_A = \text{concentration of the austenite phase in the structure} \]
\[ C_M = \text{concentration of the martensite phase in the structure} \]

In this present work, area under the peaks of different phases was considered as the magnitude of I.

4.8. Preparation, Carburization, Heat Treatment and Testing of Wear Specimens

The cylindrical specimens used for wear testing were prepared with a dimension of 8 mm in diameter and 6.5 mm in length using the stock materials of steels 1 to 3. These prepared specimens were then carburized maintaining the identical conditions. For wear testing specimens, two different carburizing time periods as 2 hours and 4 hours were used. The specimens of each steel were carburized for the predetermined time. After carburization, the specimens were heat treated. The wear tests were carried out under a dry sliding conditions using a pin on disc type apparatus as shown in Figure 3. The Carburized and heat treated specimens were used as pins. Hardened steel discs with a hardness value of 50 RC having 80 mm diameter and 10 mm thickness were used as the counter body. Before the tests both the pin and the counter body were degreased, cleaned thoroughly in running water and dried immediately by aceton. Each of the pin of steels 1 to 3 was weighed before the test to determine the weight loss due to wear. During the test 1500 gm dead load was used to press the pin against the
disc while the disc was moving in the horizontal plane as shown in Figure 3. The rpm of the moving disc was kept at 300 which gave a linear speed of 0.88 m/s. The tests were conducted for a duration of 2 hours for each specimen. After the predetermined time, the specimens were cleaned in water, dried in aceton and weighed. From the difference between the two weights obtained before and after the tests, the weight loss due to wear was measured. The wear rate for each specimen was calculated by dividing the weight loss by the total sliding distance. In order to study the effect of retained austenite on the wear rate, the tests were carried out on both (i) carburized, hardened and tempered and (ii) carburized, hardened, sub-zero treated and tempered specimens using the identical conditions.

4.9. Preparation, Heat Treatment and Mechanical Testing of Charpy V-Notch Specimens

For impact testing, three standard Charpy V-notch impact test specimens were prepared as per British Standard. The specimens of all the steels were prepared by machining 16 mm diameter bars. For a carburized and hardened steel, the service conditions require a tough core. During carburizing, the composition of the core remains unchanged. Slight variation of the core properties is due to heating, soaking at the carburizing temperature and subsequent heat treatment. To assess the toughness of the core of the carburized and heat treated steels, the Charpy V-notch
specimens were heated to about 950°C in a blue M furnace and soaked at this temperature for 2 hours. The specimens were then cooled slowly in the furnace to about 860°C and then quenched in 10 percent brine and tempered at 160°C for half an hour immediately after quenching. These quenched and tempered Charpy V-notch specimens were tested by means of a Universal impact testing machine with a range of 0-240 ft-lbs. All the tests were carried out at room temperature in the ambient air.
CHAPTER 5

EXPERIMENTAL RESULTS

5.1. Optical Microscopy of Carburized and Furnace Cooled Steels

The structures in the case and core of the specimens of steels 1 to 3 carburized for five different time periods as 1/2 hour, 1 hour, 2 hours, 3 hours and 4 hours at 950°C and cooled slowly in the furnace were studied by optical microscope.

5.1.1. Case

In carburized specimens variable carbon concentration was revealed in the case along its depth, decreasing from the surface towards the core of all the steel specimens. According to the variation of carbon concentration from surface to core three different zones, namely: (1) hyper eutectoid zone, consisting of pearlite and cementite, forming a network along the former austenite grains; (2) eutectoid zone, consisting of only lamellar pearlite and (3) hypo eutectoid zone, consisting of ferrite and pearlite, were distinguished. After the eutectoid zone, discontinuous ferrite network was observed around pearlite. This zone is known as proeutectoid zone. The amount of ferrite in the last zone continuously increases toward the core where the original structure of the steel exists. The microstructures of all the
steels were observed and the optical micrographs of steels 1 to 3 carburized for 1 hour, 2 hours and 4 hours are presented in Figures 4, 5 and 6 respectively.

Depending upon the carburizing time, variable thickness of the cementite networks and their continuity were observed for all the steels. The cementite networks of steel 1 were found thicker than those of steels 2 and 3. Among the three steels, steel 3 produced the thinnest cementite networks. Steel 2 showed thinner cementite networks than 1 but thicker than 3 for all the carburizing periods.

In steel 1 carburized for 4 hours, some feathery cementite networks around the pearlite grains as shown in Figure 6(a) were found in the hypereutectoid zone near the surface. Whatever was the carburizing time, no feathery cementite network was found in the structures of steels 2 and 3.

Cementite plates in the form of needles as in Figure 6(a) were also found in some pearlite near the surface in the hypereutectoid zone of steel 1 only for 4 hours carburizing period. But this structural feature was not found in steels 2 and 3 at any of the carburizing periods used.

In all the steels, a gradual thickening tendency of the cementite networks with increasing carburizing time was observed. For higher carburizing time as 2 hours, 3 hours and 4 hours, continuous cementite networks were observed. But for lower carburizing periods, discontinuous cementite networks were observed.
in the case of steels 2 and 3. For 1/2 hour carburizing period, the hypereutectoid zone of steels 2 and 3 were not developed. In all cases, the depth of hypereutectoid zone in steel 3 was found lower than those of steels 1 and 2. With decrease in carburizing time, the proeutectoid zone became less well-defined. This tendency was most influential for steel 3.

5.1.2. Core

A ferrite-pearlite structure was observed in the core of the carburized and furnace cooled specimens of steels 1 to 3 for all the carburizing time periods.

5.2. Case Depth

The extent up to which a steel part can be carburized within a predetermined time is very important for its mechanical properties. During carburizing three different gas flow rates such as 6 ft\(^3\)/hr, 10 ft\(^3\)/hr and 12 ft\(^3\)/hr were used. The variation of case depth with gas flow rate for 1 hour carburization is shown in Table 2. From Table 2 it is clear that the effective case depth for all the steels increases with the increase in gas flow rate.

The effective case depth of steels 1 to 3 carburized for 1/2 hour, 1 hour, 2 hours, 3 hours and 4 hours at a gas flow rate of 12 ft\(^3\)/hr and cooled slowly in the furnace are shown in Table 3 and plotted in Figure 7 as a function of carburizing time. From the data for case depth given in Table 3 and Figure 7, it is clear that
for all the steels case depth increases with the increase in carburizing time at the specified temperature. The graphical representation (Figure 7) shows that at the specified temperature the growth rate of the carburized layer maintains a parabolic law with carburizing time for all the steels.

From the data given in Table 3 and graphical representation in Figure 7, it is evident that under the identical carburizing condition, the microalloyed steels 2 and 3 produced lower case depth than the plain carbon steel 1 (base steel). Between the two microalloyed steels, steel 2 with niobium produced higher and steel 3 with niobium and nitrogen produced lower case depth.

5.3. Prior Austenite Grain Size

Prior austenite grain size controls the structures of both the case and core of a carburized steel. In this respect, the prior austenite grain size is also very important for the mechanical properties of the steel parts. Therefore, the grain size of the case of carburized and slowly cooled specimens of steels 1 to 3 was measured for different carburizing time. The data of prior austenite grain size thus obtained are listed in Table 4 and graphical representation of the grain size as a function of carburizing time is shown in Figure 8.

Table 4 and Figure 8 show that the prior austenite grain size of steels 1 to 3 increases with increase in carburizing time. It is also evident from Table 4 and Figure 8 that plain carbon
steel 1 produced the coarsest grain size while steel 3 produced the finest grain size of all the steels and steel 2 produced coarser grain size than that of steel 3. Table 4 and Figure 8 also show that the rate of increase of prior austenite grain size of steel 1 is the highest while steel 3 has the lowest growth rate. On the other hand, intermediate type grain growth rate is observed for steel 2. It is also clear from Table 4 and Figure 8 that the prior austenite grain size of steels 2 and 3 are very close to each other for lower carburizing period. But the difference between them increases with the increase in carburizing time at the specified temperature.

Typical optical micrographs illustrating the grain size of the case of steels 1 to 3 carburized for 2 hours and cooled slowly in the furnace are shown in Figure 9.

5.4. **Optical Microscopy of Carburized, Hardened and Tempered Steels**

After polishing and etching of the carburized, hardened and tempered specimens of steels 1 to 3, the microstructure was examined by optical microscopy and photographs of the structure of each specimen were taken using a Swift Master optical microscope. In the carburized steel part, the carbon concentration varies from the surface towards the core. Thus, there exist a variable structures in the case and core of a carburized, hardened and tempered specimen.
5.4.1. Case

The structures in the case of steels 1 to 3 carburized, hardened and tempered consist of tempered martensite and retained austenite. Steel 1 produced the maximum amount of retained austenite along with tempered martensite while steel 3 produced the minimum and steel 2 produced a little higher amount of retained austenite than steel 3 in the case near the surface of the hardened and tempered specimens. For all the steels the percentage of retained austenite decreases towards the center in the case and about 100 percent martensite exists at some depth. Optical micrographs of steels 1 to 3 carburized for 2 hours and 4 hours, hardened and tempered are presented in Figures 10 and 11.

Retained austenite content increases with the increase in carburizing time in all the steels. Optical microscopy revealed 10-12 percent, 8-10 percent and 8-9 percent retained austenite respectively in steels 1 to 3 carburized for 1 hour, hardened and tempered. For 2 hours carburization, about 15-18 percent, 12-14 percent and 10-12 percent retained austenite were observed in hardened and tempered steels 1, 2 and 3 respectively. When the carburizing time is 4 hours, the amount of retained austenite were observed to be 25-28 percent, 20-22 percent and 18-20 percent for steels 1, 2 and 3 respectively.

Among the three steels, steel 1 produced the coarsest martensite while the finest martensite was found in the case of steel 3. In all the steels, coarse martensite was found in the case
near the surface and the coarseness of the martensite decreases towards the center in the case (Figures 10 and 11). When the carburizing time is 4 hours, a few fine cementite networks were also found in some regions in the case of hardened and tempered specimens of steels 2 and 3.

5.4.2. Core

Low carbon martensite was found in the core of the carburized specimens of steels 1 to 3 in the hardened and tempered condition. Steel 1 produced the coarsest and steel 3 produced the finest low carbon martensite while steel 2 produced low carbon martensite coarser than steel 3.

Some ferrite net was also observed along with the low carbon martensite in the core of all the steels. The amount of ferrite net in steel 1 is smaller than that of steels 2 and 3 while steel 3 produced greater amount of ferrite net than steel 2. The ferrite net observed in the core of steel 1 is coarser than those of steels 2 and 3 while steel 3 produced finer ferrite net than steel 2. For all the steels both the low carbon martensite and ferrite net were observed to be coarsened with increase in carburizing time. The optical micrographs of the core of steels 1 to 3 carburized for 2 hours, hardened and tempered are presented in Figure 12 illustrating the above mentioned features.
5.5. **Optical Microscopy of Carburized, Hardened, Sub-zero Treated and Tempered Steels**

The carburized, hardened and tempered (QT) specimens have a great tendency to retain austenite in the case. Sub-zero treatment can eliminate this retained austenite. Since, the structures of the case and core of a carburized and hardened steel are different, the effect of sub-zero treatment on the case and core structures is also different. Steels 1 to 3 carburized for 2 hours and 4 hours and hardened were subjected to sub-zero treatment.

5.5.1. **Case**

Steels 1 to 3 carburized for two hours in the hardened, sub-zero treated and tempered (QST) condition showed tempered martensite along with very small amount of retained austenite near the surface. About 8-10 percent retained austenite in steel 1, 7-8 percent in steels 2 and 3 carburized for 4 hours were found in QST condition. The optical micrographs of steels 1 to 3 carburized for 4 hours in the QST condition are presented in Figure 13.

5.5.2. **Core**

Low carbon martensite along with some ferrite net as in the core of QT specimens was found in the core of QST specimens. No remarkable structural features different from those of QT specimens was found in QST specimens.
5.6. **Microhardness and Hardness Profiles**

In a carburized part a variation of carbon concentration occurs from the surface to the core. The concentration of carbon is high at the surface and decreases towards the core of the specimens. Due to this variation in carbon concentration, a hardness gradient exists in the carburized case in the hardened condition. Because carbon content plays an important role on the desired harness of a hardened steel. Usually the hardness profile of a carburized and hardened steel depends on (1) carburizing temperature, (2) carburizing time, (3) pressure in the carburizing atmosphere, (4) concentration of the alloying element in the metal and (5) the strength of the solute-carbon interaction. Depending upon the above mentioned factors, the hardness profile of a carburized and hardened steel may follow two extreme patterns. The profile may be steep with a somewhat sharp line of demarcation between the carburized case and core or the profile may be very shallow i.e. the transition from the case to the core is very gradual. A profile with an intermediate nature is also very often observed. The hardness profiles from the subsurface to the core of the hardened and tempered specimens of steels 1 to 3 carburized for various time periods at 950°C have been plotted in Figures 14 to 16 and those for the hardened, sub-zero treated and tempered specimens of steels 1 to 3 carburized for 2 hours and 4 hours have been plotted in Figures 17 and 18 respectively. Figures 14 to 18 show that the hardness of the carburized case does not remain constant.
throughout the case. The hardness of the case is found somewhat lower near the surface for all the steels under all the heat treatment conditions employed. With the increase in distance from the surface towards the core, the hardness gradually increases up to maximum hardness and then decreases to core hardness. Figures 14 to 18 show that the hardness profile of steel 1 is somewhat steeper than those of microalloyed steels 2 and 3 and the steepness increases with carburizing time. The hardness profiles of steel 3 are less steeper than those of steel 2 but the variation in steepness is very little. It is observed from the hardness profiles that, in general, the case depth increases with increase in carburizing time. The case depth obtained from these hardness profiles also confirms the case depth values measured from the carburized and furnace cooled steels. It is also seen from the hardness profiles that with increasing treatment time at the carburizing temperature, the hardness curves have a steeper slope from the case to the core.

From Figures 14 to 18, it is also evident that for all the steels the hardness profiles of QT specimens from the subsurface to the maximum hardness zone are much steeper than those of QST specimens and the difference in the steepness increases with the increase in carburizing time. The microhardness value at any point of QST specimens is found always higher than that of QT specimens at the corresponding point for the same carburizing period (Figures 14 to 18).
Another important information from the graphical representation of VHN values against the distance from the edge towards the center of all the steels is that the hardness of the core decreases with the increase in carburizing time. The above phenomenon is observed for both the QT and QST specimens of steels 1 to 3.

Figures 14 to 18 and Tables 5 and 6 show that under the identical condition of carburizing and hardening, plain carbon steel 1 produced minimum case hardness and microalloyed steel 3 produced maximum case hardness whereas steel 2 produced lower case hardness than steel 3.

The maximum hardness of the carburized case varies with the carburizing time. From the hardness profiles (Figures 14 to 18 and Tables 5 and 6), it is found that all the steels show the highest hardness at the longest carburizing time of 4 hours.

It is seen from Figures 14 to 18 that steel 2 showed the maximum and steel 1 showed the minimum core hardness while steel 3 showed core hardness in between steels 1 and 2.

5.7. Surface Hardness and Maximum Hardness

The carburized steels retain austenite in the hardened case near the surface. It is very difficult to avoid this retained austenite even if it is small in amount. Due to this problem, surface hardness values obtained by microhardness tester may not be the representative surface hardness of the carburized and hardened...
steel. To avoid this difficulty, the surface hardness measurement was carried out by using Rockwell hardness tester.

The surface hardness of the QT and QST specimens of carburized steels 1 to 3 as measured by Rockwell hardness testing machine are presented in Tables 5 and 6 along with the maximum hardness and core hardness obtained from microhardness tests and hardness profiles of Figures 14 to 18. The surface hardness and the maximum hardness of the QT specimens of steels 1 to 3 as a function of carburizing time are plotted in Figures 19 and 20 respectively. From the experimental results of Table 5 and Figures 19 and 20, it is clear that the surface hardness and the core hardness decrease and the maximum hardness increases with the increase of carburizing time for QT specimens of steels 1 to 3. For QST specimens of steels 1 to 3 similar trends for surface hardness, core hardness and maximum hardness were observed.

Attempts were also made to observe whether there is any relationship between the surface hardness and the maximum hardness of the carburized and heat treated steel. The surface hardness was found always lower than the maximum hardness for the both QT and QST specimens for any specified carburizing time. Tables 5 and 6 show that the difference between the surface hardness and maximum hardness increases with the increase in carburizing time. This difference is more noticeable for QT specimens than that of QST specimens of all the steels.
From the data presented in Tables 5 and 6, it is also evident that for any carburizing period the surface hardness, maximum hardness and core hardness of QST specimens of all the steels are always higher than those of QT specimens.

5.8. X-ray Diffractometry Data

Since no powder specimen was used in this experiment, slight deviation between the actual position of the peak and the recorded peak position is resulted. The ideal peak position of strong 110 martensite peak is 44.73° but the recorded peak position is 45.6°. Similarly, peak position of strong 200 peak of austenite phase for CuKα radiation is 50.70° but in the chart paper used, the recorded peak position is 50.0° as shown in Figures 21 and 22. On the other hand, a line broadening effect is resulted in the recorded peak (Figures 21 and 22) due to solid block specimen instead of powder specimen and nonuniform microstrain in the hardened structures. The line broadening effect on martensite peak and austenite peak is not identical and thus, relative phase amount measurement using peak height may be misleading. To avoid such a situation, area under the peak was considered as the value of I. The condition under which the X-ray diffraction was carried out is shown in Table 7 and the X-ray diffractometry results of steels 1 to 3 carburized for 4 hours both in QT and QST conditions are presented in Table 8.

According to X-ray diffraction results recorded in Table 8 QST specimens of each of the carburized steels have much lower
retained austenite content than QT specimens of the corresponding steel. It is evident from Table 8 that about 27 percent retained austenite was found in the structure of steel 1. After sub-zero treatment the retained austenite content of this steel was found to be about 10.6 percent, i.e., about 60.74 percent retained austenite is transformed to martensite by one cycle of sub-zero treatment in steel 1. The retained austenite content in steels 2 and 3 is nearly same for both the QST and QT conditions. In the case of steel 2, retained austenite content is about 22.0 percent in the QT condition and about 10.0 percent in the QST condition. Whereas, about 21.2 percent and 10.1 percent retained austenite are resulted in the QT and QST conditions of steel 3 respectively. According to the data given in Table 8 sub-zero treatment to recover the retained austenite is more effective for steel 1 than microalloyed steels 2 and 3. Between the two microalloyed steels sub-zero treatment is more effective for steel 2.

5.9. Wear Test Data

The weight loss (mg) and wear rate (mg/m) obtained from the wear test of steels 1 to 3 carburized for 2 hours and 4 hours in both the QT and QST conditions are presented in Table 9. The wear tests were carried out under dry sliding condition at room temperature in the ambient air and the wear rate was expressed by weight loss per unit sliding distance due to wear.
It is evident from the data recorded in the Table 9 that maximum wear rate is resulted from steel 1 for both the QT and QST specimens whereas, minimum weight loss is resulted from steel 3 and the weight loss in steel 2 is slightly higher than that in steel 3. For all the carburized steels, wear rate of the QT specimens was always higher than that of the QST specimens for any carburizing period. With the increase in carburizing time, the wear rate also increases for all the steels both in the QT and QST conditions.

5.10. Impact Test Data

The impact test of the Charpy V-notch specimens of steels 1 to 3 were carried out at normal atmospheric condition and the impact energy absorbed by different steels are presented in Table 10. According to the experimental result, steel 1 showed the maximum toughness and microalloyed steel 2 showed the minimum. Microalloyed steel 3 showed toughness slightly higher than that of steel 2.
According to the composition of the steels 1 to 3 shown in Table 1, the second phase particles in steels 2 and 3 are expected to be essentially niobium carbide, NbC and niobium carbonitride, Nb(C,N) respectively. These were identified and confirmed by transmission electron microscopy.

6.1. Metallography

Optical microscopy revealed variable carbon concentration from the surface to the core of the carburized specimens. This is because, carburizing is a diffusion controlled process, where the atomic carbon formed in the carburizing medium concentrates on the surface of the part to be carburized. From surface, the atomic carbon gradually penetrates within the matrix by means of diffusion maintaining a gradient in carbon concentration.

The cementite networks of steels 1 were found thicker than those of steels 2 and 3 while steel 2 produced thicker cementite networks than steel 3 (Figures 4 to 6 and 9). This phenomenon indicates that the carbon concentration in the case of steel 2 is lower than that of steel 1 but higher than that in steel 3.
Optical microscopy also revealed a few feathery cementite networks around the pearlite grains and cementite plates in the form of needles within some pearlite grains near the surface of steel 1 carburized for 4 hours and cooled in the furnace. This is due to the supersaturation of austenite with respect to carbon. From the presence of feathery cementite networks and needlelike cementite plates only in steel 1, it is clear that under identical condition, the carbon absorbing capacity of steel 1, i.e. plain carbon steel is much higher than that of microalloyed steel containing niobium or niobium in combination with nitrogen. This higher carbon absorbing capacity of steel 1 makes the austenite supersaturated more readily than steels 2 and 3. Austenite which is supersaturated with carbon develops internal stress. This stress might cause the formation of sub-grain boundaries generally in a straight line due to the alignment of dislocations of identical types. This may act as a source for the nucleation of cementite plates. After carburizing and furnace cooling, the austenite transforms to pearlite while the cementite plates remain unchanged. These plates when sectioned for metallographic observations appear as feathers from the cementite network at the main austenite grain boundary towards the interior of the grain. Other vertical plates from the top or bottom of the grains when sectioned horizontally appear as needles within the grains.

For all the steels, a gradual thickening tendency of the cementite networks with carburizing time was observed (Figures 4 to
6 and 9). This is because, at a certain temperature the austenite can absorb certain amount of carbon making interstitial type solid solution. Any carbon excess than the fixed amount is expelled as cementite precipitates at the austenite grain boundaries. During cooling carbon is expelled further as cementite precipitates. These cementite precipitates ultimately form cementite network. With the increase in carburizing time, more carbon is diffused within the specimens. But carbon solubility at this temperature is fixed and thus, the excess carbon is continuously expelled from austenite increasing the thickness of the cementite networks with carburizing time.

Retained austenite as shown in Figures 10 and 11 was found in the case of almost all the steels carburized, hardened and tempered. It has been reported that when carbon percentage in a steel exceeds 0.65 percent, the \( M_f \) temperature shifts to below room temperature \( 25 \) and all the austenite can not transform to martensite. The presence of retained austenite in the case of all the steels thus clearly indicates that the carbon content in the surface of all the carburized steels was much more than 0.65 percent and the \( M_f \) temperature was much below the temperature of the quenching medium (10 percent brine) used.

It was also found that steel 1 produced the highest percentage of retained austenite. This is due to the fact that the carbon concentration in the case of steel 1 is maximum which depresses the \( M_f \) temperature much more than those of steels 2 and
3. Carbon concentration in steel 2 is lower than that in steel 1 but higher than that in steel 3. Its retained austenite content is expected to be in between steels 1 and 3 and that was, in fact, observed to be the case.

It has also been found that the amount of retained austenite decreased towards the center and at some depth martensite became about 100 percent. The concentration of carbon in a carburized specimen is maximum at the surface and decreases towards the center. The amount of austenite to be retained depends on the carbon concentration. As the concentration of carbon in the case decreases from surface to the center, the retained austenite content also decreases.

The retained austenite content also increased with the increase in carburizing time in all the steels (Figures 10 and 11). The reason for this is that the carbon concentration in the case increases with increase in carburizing time and the higher carbon concentration lowers the $M_f$ temperature drastically. Thus, an increased amount of austenite is retained in the cases of all the steels.

From Figures 10 and 11, it has also been revealed that steel 1 produced the coarsest martensite while steel 3 produced the finest at all the carburizing periods. The coarsest martensites in steel 1 are due to its coarsest austenite grains and the finest martensites in steel 3 are due to the finest austenite grains present in it (Figures 4 to 6 and 9 and Table 4). Steel 2 showed
coarser martensite than steel 3. This difference in size of martensite is clearly due to the observed difference in the austenite grain size of these two steels.

For all the steels, size of the martensite in the case near the surface is always coarse and the coarseness decreases with distance from the surface towards the core (Figures 10 and 11). The reason for this is that the prior austenite grain size in the case near the surface was coarse from which coarse martensite was formed. The finer austenite grains produced finer martensite towards the center of the case.

With the increase in the carburizing time, the coarseness of the martensite size also increases for all the steels. The explanation for this is that with the increase in carburizing time, the prior austenite grain size was also increased (Table 4 and Figures 4 to 6 and 9) from which subsequently coarse martensite was resulted.

For longer carburizing period (4 hours), a few cementite networks were found in some regions in the case of microalloyed steels 2 and 3 in both the QT and QST conditions. This is believed due to the fact that alloying element in steels 2 and 3 raises the critical temperature. Thus, the presence of a few cementite networks along with high carbon tempered martensite in the cases of carburized and heat treated microalloyed steels 2 and 3 is not unexpected in the view of quenching temperature ($860^\circ$C) used.
Figures 10, 11 and 13 revealed that carburized steels 1 to 3 produced less retained austenite in the QST condition than in the QT condition. This is because a certain proportion of retained austenite was transformed to martensite during sub-zero treatment.

Low carbon martensite along with some ferrite net was observed in the core of all the steels in carburized, hardened and tempered condition (Figure 12). The presence of ferrite in steels 1 to 3 indicates that the critical cooling rate in each of these steels was faster than the actual cooling rate.

In the core of the sub-zero treated carburized specimens low carbon martensite with some ferrite net identical to the carburized specimens in the QT condition was observed. This is clearly due to the absence of retained austenite which can be transformed to more stable phases at the sub-zero temperature in the core of the carburized and hardened specimens.

6.2. Case Depth

The flow rate of the carburizing gas in the chamber has a great effect on the carburized case developed within a specified time period. To study the effect of gas flow rate, three different rates were used and the study with various gas flow rates was performed only for 1 hour carburizing period. The variation of the effective case depth with gas flow rate for 1 hour carburizing period is presented in Table 2. From this Table, it is clear that with increase in gas flow rate, the effective case depth increased
for all the steels. This is thought to be due to the fact that with the increase in gas flow rate, the concentration of the carburizing gas inside the carburizing chamber was increased and a higher gas pressure was developed. Both the factors increased the carburizing rate.

The effective case depth of carburized and furnace cooled steels 1 to 3 for various carburizing periods with the gas flow rate of 12 ft$^3$/hr are presented in Table 3 and plotted in Figure 7 as a function of carburizing time. From Table 3 and Figure 7, it is evident that the effective case depth of all the steels increases with the increase in carburizing time. The reason for this is that as the carburizing time increases, carbon atoms get longer time to penetrate into a greater depth and provide a higher case depth.

Steel 1 is merely a plain carbon steel. This steel is used as a base steel to compare the carburizing behavior of the other two steels (steels 2 and 3) with small additions of niobium singly and in combination with nitrogen.

Figure 7 and Table 3 show that the microalloyed steels 2 and 3 produced lower case depth than the plain carbon steel 1. This indicates that the microalloying element niobium with or without nitrogen reduces the case depth.

The highest case depth in steel 1 is due to the much higher concentration of carbon at its surface which is clearly indicated by the presence of a thicker and feathery cementite network in its carburized case.
The formation of vanadium carbide reduces the solubility of carbon in austenite \(^{31}\) and hence decreases the carbon concentration of the surface of the steel specimen \(^{17}\). The much lower case depth in steel 2 with NbC than the base steel 1 indicates that the formation of niobium carbide also reduces the solubility of carbon in austenite resulting lower carbon concentration at the surface.

Steel 3 is basically steel 2 with nitrogen added to it. This steel produced lower case depth than steel 2. The lower case depth of steel 3 is also due to the lower concentration of carbon at its surface which is indicated from the presence of some thinner cementite network in the case of this steel. The lower concentration of carbon causing lower case depth in steel 3 may be due to the presence of nitrogen which is thought to decrease the solubility of carbon in austenite. Both the carbon and nitrogen dissolve in austenite making an interstitial solid solution. The atomic radius of nitrogen is much lower than that of carbon and thus, nitrogen in austenite accommodates more densely than carbon. As a result, carbon atom can not enter into the austenite cell of steel 3 as readily as in steel 2 and makes lower carbon solubility in austenite of steel 3 and thus retards the diffusion of carbon in austenite. The presence of nitrogen as Nb(C,N) is also thought to decrease the diffusion coefficient by increasing the activation energy. Consequently, a case depth lower than steel 2 is obtained in steel 3.
6.3. Prior Austenite Grain Size

Prior austenite grain size of steels 1 to 3 is plotted in Figure 8 as a function of carburizing time and presented in Table 4. Among the three steels, steel 1 is the base steel with which the prior austenite grain size of the microalloyed steels 2 and 3 are compared. Steel 1 is a plain carbon steel with no addition of alloying element. So it does not contain any second phase particles to inhibit austenite grain growth and thus, the austenite grain size of this steel increases rapidly as shown in Figure 8 with the increase in time at the carburizing temperature. Microalloyed steel 2 contains niobium which combines with carbon forming niobium carbide, NbC and steel 3 contains niobium in combination with nitrogen which form niobium carbonitride, Nb(C,N). These second phase particles pin the prior austenite grain boundaries and inhibit grain growth causing the steels to retain a fine grain size which is found to increase slightly during carburizing with successive longer holding time.

It is also evident from the experimental results that microalloyed steel 3 produced slightly finer austenite grains than steel 2. It has been reported that the temperatures for the precipitates in steels 2 and 3 to dissolve completely are 1135°C and 1162°C respectively. Therefore, it is expected that grain growth restriction in steel 3 will persist to a higher temperature than in steel 2. However, at the lower temperature of 950°C where the precipitates in these two steels were still effective as grain
growth inhibitors, steel 3 produces finer grain size than steel 2 suggesting that Nb(C,N) is more effective than NbC in controlling the grain growth of austenite. Bepari and Whiteman\textsuperscript{30} reported that the undissolved particles of Nb(C,N) in steel 3 are finer than the undissolved particles of NbC in steel 2. The greater effect of these Nb(C,N) particles than NbC particles in restricting grain growth is clearly due to their finer size.

For the lower carburizing period, the prior austenite grain size of steels 2 and 3 are very close to each other. With increase in carburizing time, the difference between the grain size of the two steels increases. This is thought to be due to the fact that Nb(C,N) particles coarsen less rapidly with increasing carburizing time because of their higher solution temperature than NbC particles.

6.4. Hardness and Hardness Profiles

The graphical representations of VHN values against the distance from subsurface to core of the carburized steels 1 to 3 in the quenched and tempered (QT) condition are plotted in Figures 14 to 16 and those in the quenched, sub-zero treated and tempered (QST) condition are plotted in Figures 17 and 18. From Figures 14 to 18, it is clear that the hardness of the cases of the carburized steels 1 to 3 both in the QT and QST conditions do not remain constant throughout the cases. The hardness of the case near the surface is somewhat lower than that in the center of the case. This
lower hardness is due to the presence of retained austenite in the case near the surface. With the increase in distance from the surface towards the core, the content of low hardness constituent (retained austenite) decreases resulting higher hardness.

It is evident from Figures 14 to 16 that hardness profiles of steel 1 has a steeper slope from the case to the core than that of steels 2 and 3 and the steepness increases with carburizing time. This higher steepness in the hardness profiles at the interface between the carburized case and the core of plain carbon steel 1 is due to the higher concentration gradient. With the increase in carburizing time, the concentration gradient also increases and provides higher steepness in the hardness profiles. Between the two microalloyed steels, hardness profile of steel 2 has slightly steeper slope than that of steel 3. This is due to the fact that the concentration gradient from the case to the core of steel 2 is higher than steel 3.

From Figures 14 to 18, it has been found that the hardness profiles from the subsurface to the maximum hardness zone of carburized steels 1 to 3 in QT conditions have much steeper slopes than in QST conditions. These steeper slopes for carburized steels in QT conditions are due to the higher amount of retained austenite present in the case near the surface. Due to sub-zero treatment a substantial proportion of retained austenite has been transformed to martensite and thus, the extent of the low hardness region decreased.
The microhardness value at any point of the carburized steels 1 to 3 in QST conditions has been found always higher than that of QT conditions at the corresponding point for same carburizing period (Figures 14 to 18). The additional hardness in the case of the carburized steels in QST condition is due to the dual effect of sub-zero treatment. Sub-zero treatment substantially decreases the retained austenite content in the case and thus, increases the hardness. On the other hand, sub-zero treated steels suffer double quenching, one from 860°C to room temperature and another from room temperature to liquid nitrogen temperature. Due to this double quenching effect, carburized steels have much more residual stress in QST condition than in QT condition. This excess residual stress also provide additional hardness. In the core there is no retained austenite to be transformed to martensite. Here the increased hardness is thought to be due to the additional residual stress.

With increase in carburizing time, the core hardness of the carburized steels 1 to 3 both in the QT and QST conditions decreases. This decreasing tendency of the core hardness is believed to be due to the coarsening effect of ferrite net.

From Figures 14 to 18 and data presented in Tables 5 and 6 it is also clear that plain carbon steel 1 produced minimum case hardness and microalloyed steel 3 produced maximum case hardness while steel 2 produced case hardness in between 3 and 1. The higher hardness in the case of the microalloyed steels 2 and 3 is due to
the dual effect of the microalloying element alone or in combination with nitrogen. Niobium in solution increases the hardness of the martensite. On the other hand, steel 2 contains NbC precipitates and steel 3 contains Nb(C,N) precipitates. These undissolved particles NbC in steel 2 and Nb(C,N) in steel 3 impede the movement of the dislocations and hence produce further hardening effect in the steels. The undissolved particles of Nb(C,N) in steel 3 are finer than the undissolved particles of NbC in steel 2. These finer Nb(C,N) particles can impede the movement of the dislocations more effectively than comparatively coarser NbC particles in steel 2. As a result, Nb(C,N) particles contribute more to the increment of hardness producing higher hardness in steel 3 than steel 2.

From Figures 14 to 20 and Tables 5 and 6, it is clear that the maximum hardness of the carburized steels 1 to 3 both in QT and QST conditions increases with the increase in carburizing time. This hardness increasing tendency with carburizing time is due to the increasing carbon content of the martensite. The surface hardness of all the three steels decreases with the increase in carburizing time. This is because retained austenite content increases with the increase of carburizing time.

It has been found that the surface hardness of all the carburized steels both in the QT and QST conditions is lower than the maximum hardness obtained in the carburized case (Tables 5 and 6). The explanation for this is that the surface of the carburized
steels in both the heat treatment conditions contain certain amount of retained austenite along with tempered martensite. During surface hardness measurement by Rockwell hardness testing machine, the indentor sinks into the region containing both retained austenite and martensite. Consequently, an average hardness of the two phases (retained austenite and martensite) is obtained.

It is also evident from Tables 5 and 6 that the difference between the maximum hardness and surface hardness of all the steels in both the QT and QST conditions increases with the increase of carburizing time. The surface hardness of all the steels in both the heat treatment conditions is found to decrease due to the presence of increased amount of retained austenite at the surface while the maximum hardness in both the heat treatment conditions increases due to increasing carbon content of martensite with the increase of carburizing time. Thus, the difference between surface hardness and maximum hardness increases with the increase in carburizing time.

Among the three steels microalloyed steel 2 produced the highest core hardness and plain carbon steel 1 produced the minimum while steel 3 showed core hardness in between 2 and 1. The higher hardness in the core of the microalloyed steels 2 and 3 is due to the presence of niobium in the solid solution in low carbon martensite and as NbC and Nb(C,N) in steels 2 and 3 respectively. Steel 1 has no alloying element and thus, showed minimum core hardness. According to the metallographic result (Figure 12) steel
3 produced more ferrite net in the core along with low carbon martensite than that in steel 2. Lower core hardness of steel 3 than steel 2 may be due to the presence of higher amount of ferrite net which is thought to be caused by the presence of nitrogen with niobium in it.

6.5. **Effect of Sub-Zero Treatment on Retained Austenite**

It has been found from Table 8 and micrographs presented in Figures 11 and 13 that in the cases of steels 1 to 3 carburized for 4 hours in QST condition has much lower retained austenite content than in QT condition. The explanation for this is that during carburizing the carbon content in the case near the surface exceeded 0.65 percent. Carbon content in a carbon steel higher than 0.65 percent shifts the $M_f$ temperature to below room temperature and all the austenite can not transform to martensite when quenched in 10 percent brine. The higher percentage of retained austenite found in the case of carburized steels in QT condition thus indicates clearly that the $M_f$ temperature is much below the temperature of the quenching medium used. When the carburized and quenched specimens were immersed in liquid nitrogen in order to cool the specimens much below the $M_f$ temperature, a substantial amount of the retained austenite was transformed to martensite resulting lower retained austenite content in the case.

X-ray diffractrometry results (Table 8) also revealed that for retained austenite transformation sub-zero treatment is most
effective for steel 1 and least effective for steel 3. The reason for this is that steel 1 has no alloying element to retard the retained austenite transformation to martensite. In steel 2 microalloying element niobium retards the austenite transformation making the sub-zero treatment less effective than that in plain carbon steel 1. Steel 3 is essentially steel 2 containing nitrogen in combination with niobium, where the nitrogen may further retard the austenite transformation.

From the X-ray metallographic results (Table 8), it is clear that there was still some retained austenite in the case of all the steels after sub-zero treatment. This is due to the fact that for 100 percent retained austenite transformation, several cycles of sub-zero treatment followed by tempering is required. But in this experiment only one cycle was performed.

6.6. Wear Resistance

According to the experimental results presented in Table 9, it is evident that carburized steel 1 both in QT and QST conditions showed lower wear resistance than that of steels 2 and 3 under identical conditions. Steel 1 has no second phase particles and contains higher amount of retained austenite in the carburized case than steels 2 and 3 both in the QT and QST conditions (Table 8). This higher retained austenite content in steel 1 reduces its wear resistance. The higher surface hardness of steels 2 and 3 along with lower retained austenite content increases the wear resistance
of the case. Moreover, the presence of NbC in steel 2 and Nb(C.N) in steel 3 further increase the wear resistance of the case of the steels. This effect of niobium in wear resistance is also supported by Fiset et al.\textsuperscript{13}

It has also been observed from Table 9 that steel 3 showed slightly higher wear resistance than that of steel 2. This increased wear resistance may be due to higher surface hardness and finer Nb(C.N) particles in the hardened case of steel 3.

Table 9 showed that wear rate of all the carburized steels 1 to 3 in the QT condition is always higher than that in the QST condition. This is due to the fact that during sub-zero treatment a considerable amount of retained austenite was transformed to martensite. The lower percentage of retained austenite in the case gives lower wear rate.

Wear rate increases with the increase in carburizing time for all the steels both in the QT and QST conditions (Table 9). The reason for this is that with the increase in carburizing time, the carbon concentration in the cases also increases. With the increased carbon concentration an increased amount of retained austenite is obtained in all the steels both in the QT and QST conditions. This increased amount of retained austenite which is detrimental to wear resistance causes higher wear rate.

6.7. **Toughness**

It has been found from Table 10 that the impact energy
absorbed in the base steel 1 is the highest and that in steel 2 is the lowest while steel 3 showed toughness slightly higher than steel 2. This indicates that microalloying element niobium with or without nitrogen is detrimental to the toughness of the core of low carbon steels in the carburized, hardened and tempered condition. The coarse low carbon martensite found in steel 1 lowers the impact energy absorbed to such an extent that it is still much higher than those caused NbC or Nb(C,N) particles in steels 2 and 3 respectively.

Steel 2 produced finer low carbon martensite than steel 1. But it contains NbC precipitates. NbC precipitates impair the toughness of the annealed and normalized low carbon steel. The much lower impact energy absorbed of steel 2 is clearly due to the presence of NbC precipitates.

The impact energy absorbed of steel 3 is higher than that of steel 2 and lower than that of steel 1. Moreover, this steel showed finer martensite formed from the finer austenite grains produced by Nb(C,N) precipitates. The better toughness of this steel than that of steel 1 and 2 are clearly due to Nb(C,N) particles present in it.

The small amount of ferrite net present in the above steels have some effect on energy absorbed but this is considered negligible.
7.1. Conclusions Drawn from the Present Work

1. Microalloying element niobium with or without nitrogen reduces the case depth of the carburized steels. Niobium with nitrogen is more effective than niobium in reducing the case depth.

2. The undissolved particles of niobium carbide, NbC and niobium carbonitride, Nb(C,N) inhibit the grain growth of austenite of the carburized cases of low carbon steels. But Nb(C,N) is more effective than NbC in reducing the grain growth of austenite.

3. Niobium reduces the amount of retained austenite in cases of carburized and hardened steels with or without sub-zero treatment. Niobium with nitrogen is more effective than niobium in reducing the amount of retained austenite.

4. Sub-zero treatment reduces substantially the amount of retained austenite in the carburized and hardened cases of
low carbon steels containing niobium alone or in combination with nitrogen.

5. Niobium sluggishes the retained austenite transformation to martensite during sub-zero treatment. In presence of nitrogen, this sluggishing effect of niobium becomes enhanced.

6. Niobium alone or in combination with nitrogen produces fine martensite. Niobium with nitrogen is more effective than niobium without nitrogen in refining the size of martensite.

7. Niobium improves the surface hardness and maximum hardness of the carburized cases of low carbon steels under all the heat treatment conditions employed. Niobium in combination with nitrogen is more effective than niobium to improve the surface hardness and maximum hardness.

8. Niobium with or without nitrogen increases the core hardness of low carbon steels. In increasing the core hardness, niobium singly is more effective than niobium with nitrogen.

9. Sub-zero treatment increases the case and core hardness of the carburized low carbon steels in the hardened and tempered condition.
10. Under all the heat treatment conditions, surface hardness of the carburized plain carbon and niobium steels is always lower than the maximum hardness.

11. Microalloying element niobium improves the wear resistance of the low carbon steels. Niobium in combination with nitrogen is more effective than niobium to improve the wear resistance.

12. Sub-zero treatment improves the wear resistance of the carburized, hardened and tempered cases of low carbon steels containing niobium singly or in combination with nitrogen.

14. As the retained austenite content of the carburized case of low carbon steels with or without niobium increases, wear resistance of the case decreases.

15. Niobium with or without nitrogen is harmful for the toughness of low carbon steels in the carburized and hardened condition. Niobium in combination with nitrogen is less detrimental to toughness than niobium alone.
7.2. **Suggestions for Further Work**

1. A further modification in the arrangement of the automatic temperature controlling system for simultaneous control of gas and air flow as per requirement should be carried out.

2. A high temperature tempering of the carburized and hardened steels may be carried out to show the variations of hardness with tempering temperature and the results thus obtained may be compared with those of low temperature tempering with shorter duration.

3. A study on the effect of number of cycles of sub-zero treatment should be carried out on the carburized and hardened steels in order to convert 100 percent retained austenite to martensite and to have a detailed information about the subsequent effect on properties.

4. A detailed X-ray diffraction study should be performed to know the effect of each cycle of sub-zero treatment on the extent of conversion of retained austenite to martensite.

6. A systematic study on hardenability, tensile and fatigue properties of the steels should be performed in order to have a complete understanding of the behavior of the carburized low alloy steels.
7. Service behavior of the carburized niobium microalloyed steels should be investigated.

8. For detailed information on the precipitate morphology electron microscopic study should be carried out.
REFERENCES

1. Seminar, Department of Chemical Engineering, Bangladesh University of Engineering and Technology, Dhaka, Natural Resources and Industrial Prospects in Bangladesh, 1972, p.B-2.


17. Haque, M.N. and Bepari, M.M.A., a paper to be published.


Table 1
Composition of steels 1 to 3 in weight percent.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Nb</th>
<th>N</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.07</td>
<td>0.22</td>
<td>0.55</td>
<td></td>
<td>0.002</td>
<td>0.012</td>
<td>0.010</td>
</tr>
<tr>
<td>2</td>
<td>0.07</td>
<td>0.23</td>
<td>0.58</td>
<td>0.04</td>
<td>0.001</td>
<td>0.015</td>
<td>0.016</td>
</tr>
<tr>
<td>3</td>
<td>0.07</td>
<td>0.24</td>
<td>0.58</td>
<td>0.04</td>
<td>0.02</td>
<td>0.011</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 2
The effective case depth of steels 1 to 3 carburized for 1 hour at different gas flow rates and cooled slowly in the furnace.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Case depth, micrometer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6 ft³/hr</td>
</tr>
<tr>
<td>1</td>
<td>510</td>
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<tr>
<td>2</td>
<td>430</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
</tr>
</tbody>
</table>
Table 3
The effective case depth of steels 1 to 3 carburized for different periods of time and cooled slowly in the furnace.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Case depth, micrometer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/2 hr</td>
</tr>
<tr>
<td>1</td>
<td>550</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
</tr>
<tr>
<td>3</td>
<td>415</td>
</tr>
</tbody>
</table>

Table 4
The prior austenite grain size of the case of steels 1 to 3 carburized for different periods of time and cooled slowly in the furnace.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Austenite grain size, micrometer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/2 hr</td>
</tr>
<tr>
<td>1</td>
<td>101</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
</tr>
</tbody>
</table>
Table 5
Relationship between surface hardness, maximum hardness and core hardness of steels 1 to 3 without sub-zero treatment.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Carburizing time, hour</th>
<th>Surface Hardness</th>
<th>Maximum Hardness</th>
<th>Core Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rc</td>
<td>VHN</td>
<td>VHN</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>59</td>
<td>725</td>
<td>810</td>
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<td></td>
<td>2</td>
<td>52</td>
<td>580</td>
<td>850</td>
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<tr>
<td>2</td>
<td>1</td>
<td>60</td>
<td>735</td>
<td>824</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>55</td>
<td>620</td>
<td>880</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>51</td>
<td>560</td>
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<td>1</td>
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<td></td>
<td>2</td>
<td>58</td>
<td>700</td>
<td>920</td>
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<td></td>
<td>4</td>
<td>53</td>
<td>590</td>
<td>1010</td>
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</table>
Table 6
Relationship between surface hardness, maximum hardness and core hardness of steels 1 to 3 with sub-zero treatment.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Carburizing time, hour</th>
<th>Surface Hardness</th>
<th>Maximum Hardness</th>
<th>Core Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Rc</td>
<td>VHN</td>
<td>VHN</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>61</td>
<td>750</td>
<td>880</td>
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<td></td>
<td>4</td>
<td>59</td>
<td>725</td>
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<td>2</td>
<td>64</td>
<td>875</td>
<td>960</td>
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<td></td>
<td>4</td>
<td>63</td>
<td>850</td>
<td>1035</td>
</tr>
</tbody>
</table>

Table 7
Operating condition of the X-ray Diffractometer.

- Radiation: CuKα
- Voltage: 30 kV
- Current: 10 mA
- Scan Rate: 20/min
- Chart Speed: 10 mm/min
- Scale Factor: 1000 cps
Table 8
X-ray diffractometry results of steels 1 to 3 carburized for 4 hours and heat treated.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Retained Austenite Content, pct</th>
<th>Retained Austenite Recovery, pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT</td>
<td>QST</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>27.0</td>
<td>10.6</td>
</tr>
<tr>
<td>2</td>
<td>22.0</td>
<td>10.0</td>
</tr>
<tr>
<td>3</td>
<td>21.2</td>
<td>10.1</td>
</tr>
</tbody>
</table>

Table 9
Weight loss due to wear and wear rate of steels 1 to 3 carburized and heat treated.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Carburizing Time, hrs</th>
<th>Weight Loss, mg</th>
<th>Wear Rate, mg/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT</td>
<td>QST</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>4.70</td>
<td>4.20</td>
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<td></td>
<td>4</td>
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<tr>
<td></td>
<td>4</td>
<td>4.80</td>
<td>3.40</td>
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<td>3</td>
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<td>2.90</td>
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<tr>
<td></td>
<td>4</td>
<td>4.50</td>
<td>3.25</td>
</tr>
</tbody>
</table>
**Table 10**

Impact energy absorbed of steels 1 to 3.

<table>
<thead>
<tr>
<th>Steel No</th>
<th>Impact Energy Absorbed, Ft-lbs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>180</td>
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<tr>
<td>2</td>
<td>152</td>
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<td>168</td>
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</tbody>
</table>
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APPENDIX

DETERMINATION OF RETAINED AUSTENITE CONTENT BY X-RAY DIFFRACTION TECHNIQUE

The retained austenite content in the carburized case of steels 1 to 3 was determined by X-ray diffraction using direct comparison technique and various information explained by B.D. Cullity in the Text 'Elements of X-ray Diffraction'.

Calculation of R for Martensite

Plane for the strongest peak = 110
Lattice parameter a = 2.87 X 10^{-10} m
2\Theta = 45.6^0
Volume v = (2.87)^3 X 10^{-30} = 23.64 X 10^{-30}
(1/v)^2 = 1.78 X 10^{57}
sin\Theta/\lambda = 0.251
f = 17 (appx) (Appendix 12)
|F|^2 = 4f^2 = 4 X 17 X 17
   = 1156
P = 12 (Appendix 13)
e^{-2M} = 0.95 (Table 4.20)
(1 + cos^22\Theta)/sin^2\Theta.cos\Theta = 10.75
R_H = (1/v)^2 [ |F|^2 P \{ (1 + cos^2 2\Theta)/sin^2\Theta.cos\Theta\} \ e^{-2M}]
   = 1.78 X 10^{57} X 1156 X 12 X 10.75 X 0.95
   = 252168.68 X 10^{57}

Calculation of R for Austenite

Plane for the strongest peak = 200
Lattice parameter a = 3.58 X 10^{-10} m
2\Theta = 50^0
Volume v = (3.58)^3 X 10^{-30} = 45.88 X 10^{-30}
(1/v)^2 = 4.75 X 10^{56}
\[ \sin \theta / \lambda = 0.27 \]
\[ f = 17.25 \text{ (appx)} \]
\[ |P|^2 = 16 \quad r^2 = 16 \times 21 \times 21 \]
\[ = 4761 \]
\[ P = 6 \]
\[ e^{-2K} = 0.98 \]
\[ (1 + \cos^2 2\theta) / \sin^2 \theta \cdot \cos \theta = 8.73 \]
\[ R_A = (1/v)^2 \left[ |P|^2 \cdot P \cdot \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cdot \cos \theta} \right) \right] e^{-2K} \]
\[ = 4.75 \times 10^{16} \times 4761 \times 6 \times 8.73 \times 0.94 \]
\[ = 1113487 \times 10^{16} \]
\[ R_A / R_K = 0.44 \]

Carburized, Quenched and Tempered Specimens

\[ I_A = 21 \]
\[ I_K = 170 \]
\[ I_A / I_K = R_A C_A / R_K C_K \]
\[ C_M = 3.56 \cdot C_A \]
\[ C_N + C_A = 1 \]
\[ C_A = 0.2192 \]
\[ C_N = 0.7807 \]
Martensite content = 78 percent
Austenite content = 22 percent

Carburized, Quenched, Sub-zero treated and Tempered Specimens

\[ I_A = 11 \]
\[ I_K = 225 \]
\[ I_A / I_K = R_A C_A / R_K C_K \]
\[ C_M = 9.0996 \cdot C_A \]
\[ C_N + C_A = 1 \]
\[ C_A = 0.0996 \]
\[ C_N = 0.9003 \]
Martensite content = 90 percent
Austenite content = 10 percent