GAS NITRIDING OF SOME PLAIN CARBON AND ALLOY STEELS

A thesis submitted to the Department of Metallurgical Engineering, BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY, DHAKA, in partial fulfilment of the requirements for the degree of Master of Science in Engineering (Metallurgical).

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CERTIFICATE

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

Countersigned

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Signature of the author

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ABSTRACT

Gas nitriding of two different plain carbon steels, a low carbon aluminium steel, an 18-8 type austenitic stainless steel and an 18-4-1 type high speed steel has been carried out in 100% NH_3 gas atmosphere in the temperature range of 500°-580°C for time periods ranging from 8 to 24 hours. Microstructure of the nitrided case has been studied by using various etching reagents. It has been found that a white layer consisting of ε- and γ'- phases formed on plain carbon steels and in aluminium steel. Nitriding at 580°C produced a new phase in addition to the ε- and the γ'-phases in the white layer of the mild steel. The nitrided layer in the plain carbon steel and aluminium steel could not be revealed by etching. The morphology and growth kinetics of the white layer have also been studied. The white layer formed on the stainless steel has been found to be quite irregular; while in high speed steel this layer was absent. A well defined nitrided case has been found to occur in both stainless steel and high speed steel. No grain boundary phase and carburized layer have been observed in the steels investigated.

Microhardness surveys have shown that the hardness profile developed in plain carbon steels was quite shallow; in aluminium steel it was slightly steeper and in both stainless steel and high speed steel the profile was very steep. The maximum hardness developed under the conditions investigated has been found to be around 900, 975, 1420 and 1500 VHN in medium carbon steel, aluminium steel, stainless steel and high speed steel respectively.

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CHAPTER - 1
INTRODUCTION

1.1 The Nitriding Process

Nitriding is a thermochemical process of surface hardening which involves the diffusional addition of atomic nitrogen into the steel surface. The process is carried out by heating steel in the temperature range of 500° to 590°C in a medium which is capable of supplying nascent nitrogen to the steel surface. For any particular temperature, the nitriding period depends upon the desired depth of the nitrided case. When atomic nitrogen comes in contact with a heated steel surface the latter absorbs the former and nitrogen atoms take up positions in the interstitial voids of the iron lattice. In the presence of suitable alloying elements these atoms can precipitate in the metal to form a fine dispersion of alloy nitrides. Presence of these nitrides impart high hardness and wear resistance to the steel surface.

Nitriding has a number of distinct advantages over the other case hardening process such as the carburizing. The nitrided case has a far greater surface hardness and wear resistance. A characteristic feature of nitrided case is that it can retain its high hardness and wear resistance at relatively higher temperatures (600°- 650°C). This enables the nitrided articles to be used at higher operating temperatures. Since the nitriding process is carried out at a relatively low temperature, surface hardening is achieved without the loss of strength of the previously tempered core. The nitriding process does not involve any phase change in the matrix. As a consequence distortion and dimensional changes are reduced to a minimum. Nitriding also increases the fatigue limit and makes steel less sensitive to stress raisers. It also increases the corrosion resistance of steels particularly in atmospheric air, fresh water, superheated steam, gasoline, etc.

Three types of nitriding processes are in commercial use: (i) gas nitriding, (ii) liquid nitriding and (iii) ion nitriding. In gas nitriding, steel is heated in partially dissociated ammonia gas. When in contact with iron, ammonia is catalytically dissociated and the atomic nitrogen thus formed diffuses into the steel to form alloy nitrides.

The liquid nitriding or salt bath nitriding uses a molten cyanide-based salt bath as the nitriding medium. The bath usually consists of a mixture of sodium and potassium cyanides with an addition of a few percentages of sodium carbonate. During the process sodium cyanide (NaCN) in the bath reacts with atomospheric oxygen to form sodium cyanate (NaCNO) which in turn decomposes into sodium carbonate, carbon monoxide, and atomic nitrogen. The atomic nitrogen is immediately absorbed by the steel surface while carbon monoxide is converted into carbondioxide and active carbon which is also absorbed by iron. The salt bath process is suitable for nitriding small articles which require shallow case depths. A major disadvantage of liquid nitriding in conventional cyanide baths is that the salts used in the process are deadly poisonous and requires very special care during handling, storage and operation. Efforts are therefore being made throught the world to overcome this difficulty and as a result a number of modifications of the liquid nitriding technique have resulted. Recently a new process of liquid nitriding which uses raw materials other than the cyanides has been developed in the Department of Metallurgical Engineering, BUET, Dhaka (1,2,3).

Ion nitriding or glow discharge nitriding is a new development. In this process the component to be nitrided is made the cathode of an electric circuit. It is then subjected to glow discharge generated by applying a critical voltage in an atmosphere of N_2 and H_2 at a pressure of 1-10 torr. The gas molecules are positively ionized and accelerated to the workpiece. There they hit the surface with high kinetic energy which heats the surface thus eleminating the necessity of any external source of heating. The liberated nitrogen ions are then absorbed by the surface of the workpiece.

1.2 Gas Nitriding

Gas nitriding is the main commercial process of nitriding. Here pure ammonia or sometimes a mixture of ammonia and hydrogen is made to pass over the specimen kept at a temperature of 500° to 590°C. When ammonia comes in contact with the steel surface, the former is catalytically dissociated into molecular hydrogen and atomic nitrogen which is then dissolved in the interstices of iron lattice. The equation for nitriding in ammonia thus becomes

$$NH_3 \rightleftharpoons [N]_{Fe} + \frac{3}{2} H_2 \qquad \ldots \qquad (1)$$

There are two other possible reactions that can occur when ammonia reacts with iron at elevated temperatures. One such reaction is the solid solution of hydrogen.

$$NH_3 \rightleftharpoons \frac{1}{2} N_2 + 3 [H]_{Fe} \qquad \ldots \qquad (2)$$

But it is found that this reaction occurs only to a limited extent (4). The other possible reaction involves decomposition of ammonia to both molecular hydrogen and nitrogen.

$$NH_3 \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2 \qquad \ldots \qquad (3)$$

However this reaction is also suppressed at least upto a temperature of 600°C (5) when the flow rate of ammonia is high and the surface of the specimen is smooth.

The life of the active nitrogen is very short, so that a continuous flow of ammonia gas is to be maintained for all the time during nitriding. The total amount of nitrogen absorbed by the steel surface is very small, almost negligible compared to the total amount supplied during nitriding. Therefore the the flow rate of the gas has practically little effect on the process. In commercial practice the gas mixture is stirred in the furnace instead of flowing through the same. However it should be ensured that the metal surface is always exposed to the ammoniacal atmosphere for the absorption of active nitrogen.

1.3 The Iron-Nitrogen Phase Diagram

In the iron-nitrogen system (fig. 1.1) there are five stable phases viz. α-nitrogen ferrite, γ- nitrogen austenite, γ'- Fe_4N, ε- Fe_3N and ζ - Fe_2N. Two metastable phases namely α'- nitrogen martensite and α"- $Fe_{16}N_2$ also exist in this system. The nitrogen ferrite which has a bcc structure is similar to the carbon ferrite. Maximum solubility of nitrogen ferrite at the eutectoid temperature is 0.1 wt %. The face centered cubic nitrogen austenite (γ) is iso-structural with carbon austenite but has a wider range of homogeneity and exists down to 590°C (4,5).

The γ'- phase is stable between 5.29 and 5.71 wt% of nitrogen at the eutectoid temperature. The iron atoms of γ'- nitride form a face centered cubic lattice like austenite but the nitrogen atoms are fully ordered. These lattice parameter increases with nitrogen content from 3.783Å at 5.29% N to 3.793Å at 5.71% N (6). The nitrogen occupies about one quarter of the octahedral interstitial sites of the iron lattice. This phase is stable below 680°C.

The ε- phase is approximately between Fe_4N and Fe_2N with N-content ranging from 7.1 to 11.0 wt% at the eutectoid temperature. It has a close-packed hexagonal iron atom lattice. Tetragonal α''- $Fe_{16}N_2$ occurs as an intermediate precipitation during the tempering of nitrogen martensite or aging of supersaturated nitrogen ferrite.

1.4 Mechanism of Hardening of Nitrided Steels

Many theories have been proposed to explain the hardening caused by nitriding. Fry (7) originally thought that nitrogen hardening was due to the influence of nitrogen on the lattice spacing of iron. The insertion of interstitial nitrogen restores the original metal atom environment but produces a large anisotropic strain in the surrounding matrix. Many workers, on the other hand, believed that iron nitride formed was responsible for the high hardness of the nitrided case.

However it is now well established that hardening by nitriding follows the general mechanism of precipitation hardening. During nitriding, alloying elements such as Cr, Al, Mo, V etc. present in steel form very fine insoluble particles of the respective nitrides. These particles of submicroscopic size produce distortion of the iron lattice which is the prime reason of increase of hardness through nitriding. Elements like silicon and manganese also form nitrides; however, these are less effective in producing high hardness. The amount, size of the particles and interparticle spacing is important in determining the hardness. Since the size of the nitride particles formed is dependent on the time and temperature of nitriding, the maximum hardness obtainable in a given steel is also time and temperature dependent.

1.5 The Effect of Process Variables on the Nitriding Steels

The nitriding temperature, the nitriding time, the concentration of ammonia in the nitriding gas mixture, the alloying elements present in the metal and the prenitriding treatment of the metal are the main variables in the gas nitriding process.

Many workers (8,9,10) investigated the effect of these variables upon the nitrided case depth, maximum hardness, hardness profile and formation of surface iron nitrides. To relate these process variables Lightfoot and Jack (11) have proposed the following mathematical model

$$\xi^2 = \frac{2}{r} \cdot \frac{[N]}{[X]} \cdot D_N^\alpha . t \qquad \ldots \qquad (4)$$

Where

ξ = depth of the nitrided case

$[N]$ = surface nitrogen concentration, at. %

$[X]$ = original alloy concentration, at. %

t = nitriding time in seconds

r = the ratio of nitrogen to the alloying element in the nitride phase

D_N^α = the diffusivity of nitrogen in α- ferrite.

The above equation suggests that the nitrided case depth increases with the increase of nitriding time, the nitriding temperature which increases the nitrogen diffusivity, the surface nitrogen concentration by increasing the ammonia content in the gas mixture and decreases with increase of alloying elements.

Many investigators (10,11) have found that increasing the nitriding temperature leads to a shallower hardness profile. The effect of temperature on the maximum hardness has been investigated by Mridha (11) in some chromium bearing steels in the temperature range of 520-570°C. He observed that increase in the nitriding temperature had the effect of reducing the maximum hardness. This has been attributed to the precipitation of large nitride particles which are less effective in increasing the hardness. The hardness of the nitrided case of any material is dependent on the availability of alloying elements for the precipitation of fine nitride particles. It has already been shown that a decrease in the percentage of the nitride forming alloying elements leads to a greater nitrided depth, but this at the same time is followed by a reduced surface hardness. Not only the amount of alloying elements but also the nature of the alloying elements as depicted by the ease of nucleation of the alloy nitride precipitated and the strength of alloying element-nitrogen interaction determine the development of maximum hardness and the hardness profile.

1.6 Scope of the Present Work

In Bangladesh most of the spare parts essential for the machinaries in various industries are being imported from abroad. Recently a tendency has been observed to produce spares by using locally available material and technology. However most of such attempts are in failure due to the lack of the development of the required properties in the material used for their manufacture.

Many spares require some sort of surface treatment for their proper functioning and longer service life. Nitriding, one of the most successful commercial processes of surface hardening, can play an important role in this regard. However, nitralloys which are used in nitriding for obtaining the maximum benefit are not available in Bangladesh. A number of plain carbon structural steels are being produced locally. The main objective of this work is to evaluate the nitriding characteristics of these locally made mild and medium carbon steels. Some alloy steels such as stainless steel and high speed steel which are imported from abroad is also used in the present investigation. Experiments were also carried out on an aluminium alloyed steel produced in the Department.

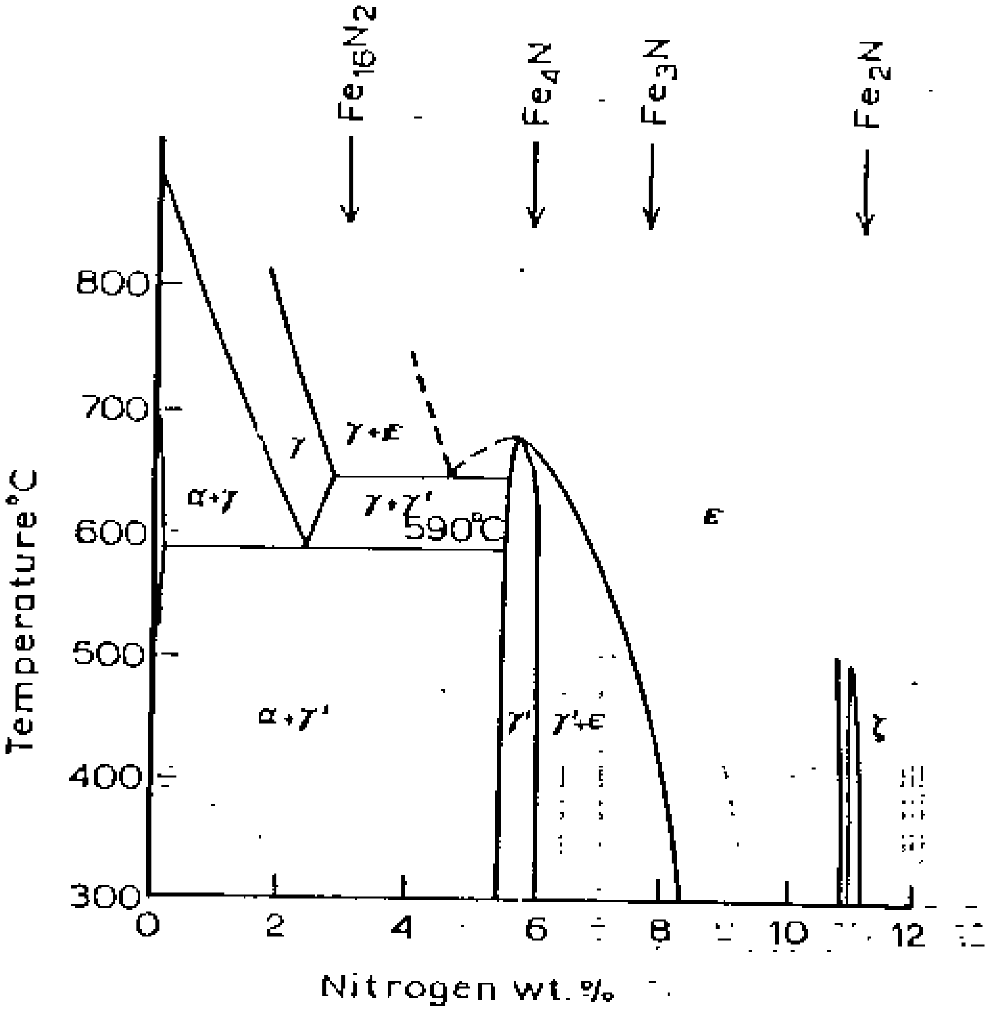


Fig. 1.1: Part of the equilibrium phase diagram for the Fe-N system.

CHAPTER - 2
MATERIALS AND METHODS

2.1 Materials Used

Mild steel was the principal material used in this investigation. For comparative study a medium carbon steel, an experimental low carbon aluminium steel produced in the Department of Metallurgical Engineering, BUET, an 18-8 type austenitic stainless steel and an 18-4-1 type high speed steel of commercial variety were also used. The composition of all these materials are given in table 2.1.

2.2 Preparation of Specimen for Nitriding

2.2.1 Mild Steel, Medium Carbon Steel and Aluminium Steel.

Hot-rolled rods of mild steel and medium carbon steel as procured from market were forged into thin strips of about 5mm thickness. The strips were cut into rectangular specimens of approximately 8 mmx15 mm size. The specimens were ground in a surface grinder to remove the oxide and the decarburized layers. These were then hardened by quenching in water from a temperature of 850°C, the holding time at the austenitizing temperature was 0.5 hr. An electrically-heated automatically-controlled muffle furnace was used for heating. After hardening, the specimens were tempered at 600°C for 1 hr. Following the tempering operation the scale and the decarburized layer were ground off using the surface grinder.

The specimens were then polished on fine emery papers. The polished specimens were etched for one minute in 10% nital to depassivate the surface (9). These were cleaned in soap solution followed by acetone. The specimens were then washed thoroghly in ethanol and dried by using a hot air blower. After all these treatments the mild steel samples were ready for nitriding.

The aluminium steel was made in an air induction furnace and the ingot was subsequently hot rolled to rods. These roads were reduced by hot forging to 5 mm thick strips which were then cut to dimensions similar to that of the plain carbon steel specimens. This material was austenitized and tempered as before and a surface finishing identical to that given to mild steel prior to the nitriding treatment was imparted to the specimens.

2.2.2 Stainless Steel and High Speed Steel.

Stainless steel in the austenitic state and high speed steel in the hardened state available in the market, were used for some selective experiments. Specimens were cut from both the varieties to the dimensions similar to those of the mild steel specimens. After grinding and polishing, the stainless steel specimens were pickled in 50% HCl at 70°C for one minute to dissolve any film of chromium oxide present on the surface. After pickling, these were cleaned in soap solution followed by aceton and washed thoroughly in ethanol and then dried in hot air.

The high speed steel specimens received the same treatments (e.g., grinding polishing, etching, cleaning, drying) as those for mild steel specimens prior to nitriding.

2.3 The Gas Nitriding Set Up

A laboratory model gas nitriding set up was used to carry out nitriding experiments. The set up has been designed and fabricated in the department of Metallurgical Engineering, BUET. The line diagram of the set-up is shown in figure 2.1. The main features of the set up are:

(i) The gas supply unit.

(ii) The nitriding chamber.

2.3.1 The Gas Supply Unit

The gas supply unit supplies the gases to the chamber where nitriding is carried out. The gases used in this set up are ammonia, hydrogen and nitrogen, which are available in cylinders. Ammonia gas coming out of the cylinder through a regulator goes to a constant pressure head capillary flow meter (10,12), Fig. 2.2. From the flow meter the ammonia gas enters into a purification train consisting of a drying tower containing pellets of potassium hydroxide as the drying agent. After leaving the drying unit the anhydrous ammonia gas goes directly to the nitriding chamber. The nitrogen cylinder supplies nitrogen gas which is used for initial purging of the nitriding chamber. Nitrogen coming out of the outlet of the regulator fitted to the cylinder passes through another capillary flow meter. Therefrom the gas enters into the nitriding chamber. Hydrogen gas from the cylinder, after passing through the purification trains (Fig. 2.1), enters into the furnace. In the present investigation nitriding was done in 100% NH_3. Hence hydrogen-gas was not used.

The flow rates of the gases are controlled by the capillary flow-meters (Fig. 2.2); control of flow rates is obtained by altering the head of vacuum pump oil in the bleeder tubes. Vacuum pump oil is used in the manometer and bubblers because of its low vapour pressure and comparative inertness to these gases.

2.3.2 The Nitriding Chamber

It consists of a horizontal alumina reaction tube at the middle of which is wound a nichrome wire heating element (Fig. 2.3). The coiled heating wire is covered with fireclay. The wound furnace tube is surrounded by a mild steel shell and the space between the shell and the tube is covered with refractory grogs. About 28 cm of the tube length remains outside the shell at both ends. The nichrome wire when connected to power supply provides a constant temperature hot zone of about 20 cm long. A chromel-alumel thermocouple is inserted into the fefractory lining to reach the middle position of the wound tube. Thermocouple is connected to an automatic temperature controller which controlles the temperature of the hot zone to about ± 5°C. Another chromel-alumel thermocouple in quartz glass tube is inserted into the hot zone through one end of the reaction tube. This thermocouple is connected to the display terminals of the above controller which also shows the hot zone temperature on a digital display.

The other end of the reaction tube is used for introducing the nitriding specimens to the hot zone. A port near this end of the tube is connected to the gas supply unit (Fig. 2.3). The same port is also connected to a vacuum pump of the rotary type so that the reaction tnbe could be evacuated prior to the nitriding rnn. Near the thermocouple end of the reaction tube a port for the exit of the exhaust gases is provided. This end is also connected to a mercury manometer. The exhaustion of air from the reaction tube prior to a nitriding run and any gas leak could be easly detected by this manometer. Copper cooling coils are provided near both ends of the furnace tube adjacent to the joints of the ground glass connections with the alumina tube to protect the sealing gum (Araldite) against heat while in operation.

2.4 The Nitriding Operation

After the preparation as described in section 2.2 the specimens were placed in a clean, dry porcelain boat. The boat was introduced into the reaction tube and placed in the hot zone. The tube was then sealed, evacuated and filled with nitrogen. After flushing the reaction tube with nitrogen for several times, ammonia gas was introduced into the tube and was allowed to flow. After half an hour, the power supply was switched on to heat the reaction tube and the controller was set for the desired temperature.

At the end of a predetermined time period, the power supply was switched off and the specimens were allowed to cool to room temperature in the reaction tube. Ammonia was allowed to flow into the reaction tube during the cooling period. This prevents any oxidation due to leakage of air. After cooling, the reaction tube was evacuated and then purged with nitrogen. The samples were then taken out.

2.5 Preparation of Specimen for Observation

To help preserve the edges and retain the flatness of the specimens during subsequent polishing of their mounted cross sections, the specimens were electroplated with nickel and copper. It has been found that with nickel plating alone, a problem was sometimes encountered in distinguishing compound zone of the nitrided specimen from the former. However, copper plating alone did not adhere firmly to the nitrided surface while nickel plating did. That is why the nitrided specimens were first electroplated with nickel for about 5 sec. and then with copper for 4.5 min.

The solution for nickel plating contains 320 gm/ litre $NiSO_4.6H_2O$, 50 gm/ litre $NiCl_2.6H_2O$ and 35 gm/ litre H_3BO_3. The current density was 0.05 amp/ cm^2 and the temperature $50^{o}C$. The copper plating solution contains 50 ml concentrated H_2SO_4 and 200 gm $CuSO_4.5H_2O$ made upto 1 litre with water. The current density and temperature were 0.01 amp/cm^2 and $20-50^{o}C$ respectively.

The nitrided specimens after electroplating were cut into two pieces at right angles to the nitrided surface by using a silicon carbide disc cutter with copious flow of water. One piece of each specimen was then mounted and polished by standard metallographic techniques. Optical microscopy and photomicrography were carried out by using a Shimudzu optical microscope. Microhardness measurements were carried out by using 25-100 gm load on polished and unetched specimen to obtain the hardness profiles. For measuring the microhardness of different nitrided zones, the specimens were lightly etched. The thickness of the various layers in the microstructure revealed on etching in different reagents were measured by using a micrometer eyepiece fitted to the Shimudzu.

TABLE 2.1

Chemical composition of the steels investigated

Material	% C	% Si	% Mn	%S	%P	% others
Mild steel	0.1	0.037	0.77	0.018	0.037	-
Medium carbon steel	0.55	0.17	1.26	0.07	0.03	-
Aluminium steel	0.04	0.4	0.25	-	-	N=0.0044 Al=0.85
High speed*(18-4-1 type) steel						
Stainless* steel (18-8 type)						

* According to suppliers-specification only.

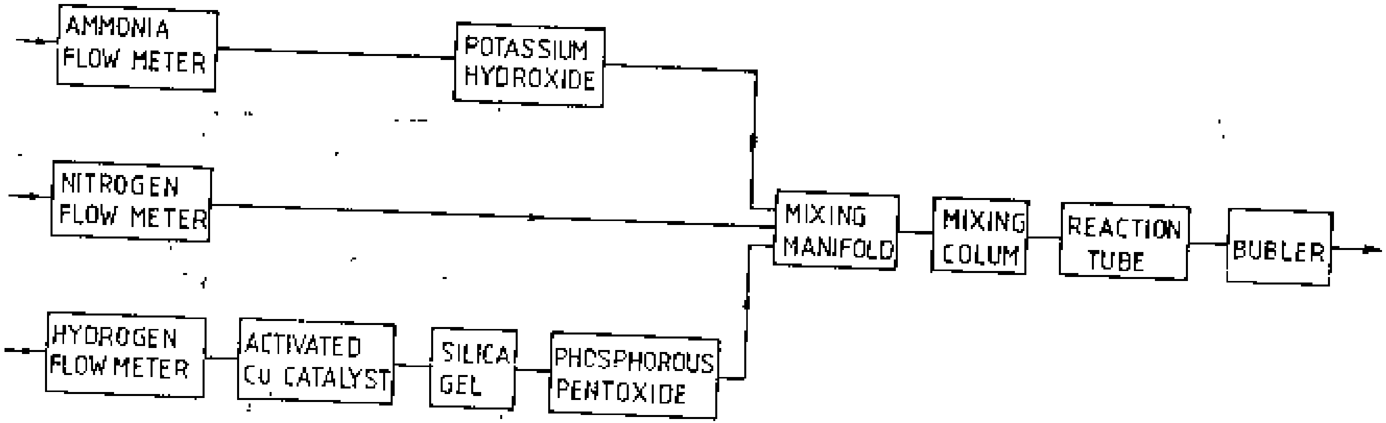


FIG. 21 LINE DIAGRAM OF THE NITRIDING APPARATUS.

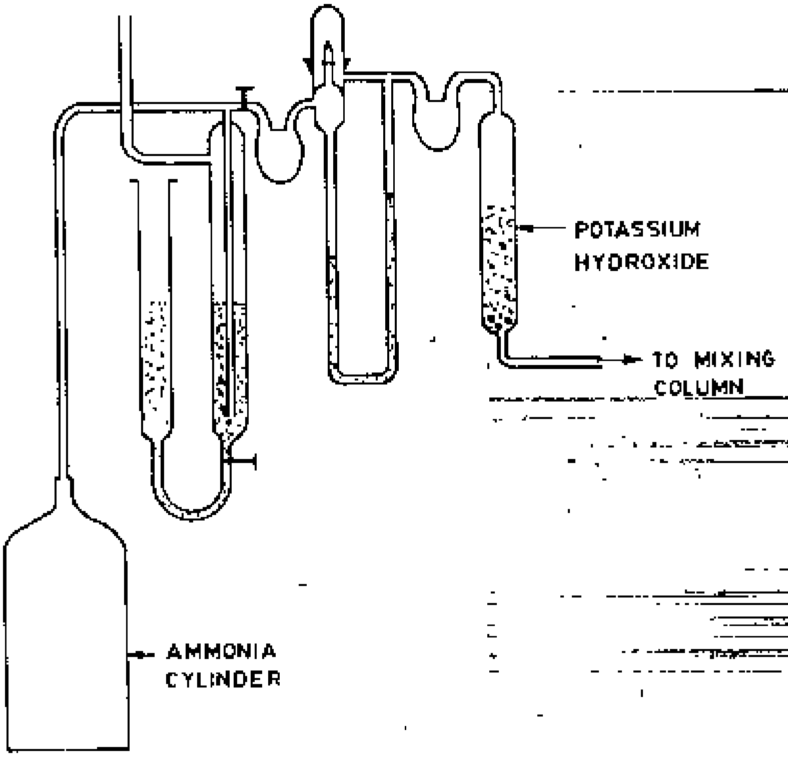


FIG 2.2 AMMONIA FLOWMETER WITH PURIFICATION TRAINS.

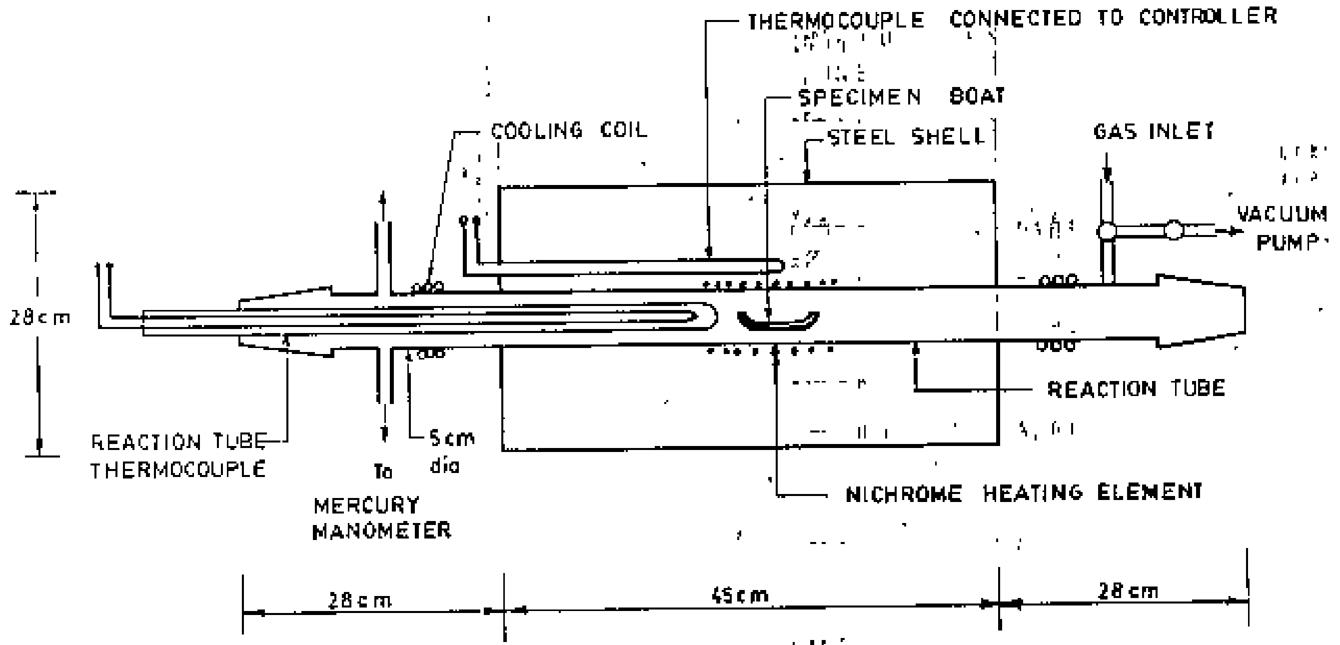


FIG. 2.3 NITRIDING FURNACE

CHAPTER - 3
RESULTS

3.1 Plain Carbon Steel

3.1.1 Detection and Identification of Different Zones

It is now well recognized that in the nitriding of steel in ammonia at least two layers or zones form. When etched in nital the outer most layer appears white under the microscope and hence this layer is known as the white layer. This layer consists of either γ'- phase (Fe_4N) or a mixture of γ'- and ϵ- phase (Fe_3N) depending on the nitriding condition. The recognition of the white layer as a mixture of compound of iron and nitrogen has led to its designation as the "compound zone". Beneath the compound zone is the internally nitrided zone or the nitrided layer where the nitrogen has mainly been incorporated into the existing-iron lattice as interstitial atom or as finely dispersed alloy-nitride precipitates. This layer is known as the nitrided layer. In all the commercial nitriding steels austenite grain boundary phase forms in the internally nitrided zone and this grain boundary phase has recently been identified as cementite (13). Ahead of the nitrided layer there occurs a carbon rich zone which has been designated as the carburized layer and this layer is inevitable in all the commercial nitriding steels nitrided under different process variables (10).

In plain carbon steel the compound zone forms under suitable nitriding condition. But the existence of different zones and the grain boundary phase has not yet been recognized. Actually the development of different nitrided structures/zones in plain carbon steels has not been thoroughly investigated and the growth morphology of the different phases of the compound zone is not definitely known. The present investigation seeks to distinguish the different nitrided zones by using some common etching reagents and to correlate these zones with hardness. Four well known etching reagents namely Oberhoffer's reagent, Villela's reagent, picral and nital were used to detect the different zones. Their chemical compositions are given in Table 3.1. None of these etching reagents revealed the nitrided layer, the grain boundary phase or the carburized layer in any of the specimens. But in all the reagents, white layer was revealed distinctly though they responded differently (Figs. 3.2 & 3.3). When etched in nital for a short time both the steels revealed a single layer compound zone (Fig. 3.1). A deeper etch in nital showed a two layer compound zone (Fig. 3.2a) on the mild steel specimen, the inner layer appeared to be very thin. While, the medium carbon steel specimen revealed a porous structure at the outermost portion and a relatively thick, dense structure at the inner side (Fig. 3.3a).

Etching in Villela's reagent revealed a detailed structure of the white layer (Fig. 3.2b) while in picral the layer appeared to be a two-layer zone (Fig. 3.3b). In Oberhoffer's reagent, the outermost layer of the compound zone in both the steels dissolved but the inner layer of this zone did not .

From this investigation it appears that under the present nitriding conditions the compound zone on both the mild and medium carbon steel specimens consists of two layers. Microhardness tests on these layers showed that the inner layer is harder than the outer layer (Table 3.2). It has already been mentioned that in all nitriding steels, nitrided in 100% NH_3, a compound layer consisting of ε- and γ'- phases forms. Mridha and Jack (14) have shown that Oberhoffer's reagent dissolves ε-phase but does not attack γ'- phase. It, therefore, appears that the two layers of the compound zone on the plain carbon steels are ε- and γ'- phases, the outermost phase that dissolved in Oberhoffer's reagent is the ε and the inner one that did not is the γ'- phase. Etching in Villela's reagent, picral, and Oberhoffer's reagent distinctly reveals the compound zone, the nitrided layer, the grain-boundary phase and the carburized layer in all commercial nitriding steels (14). But in the present investigation no other zones except the compound zone could be found in the nitrided plain carbon steel when etched in the above reagents. However, nital etch sometimes revealed a dark, ill-defined layer below the compound zone. This dark layer might represent the existence of the nitrided layer.

3.1.2 A New Phase in the White Layer

Under all the treatment conditions investigated, the medium carbon steel developed a white layer consisting of two phases.

In the mild steel nitrided at 500° and 540°C, there also formed a two-phase white layer. However, when the mild steel specimens were nitrided at 580°C a white layer consisting of three phases was obtained (Fig. 3.4). When deeply etched in nital the ε- phase appeared to be porous while the γ'- phase was a bright dense layer and the innermost new phase had columnar-grained structure (Figs. 3.4a & b). When etched in Oberhoffer's reagent the ε- phase dissolved as usual and the γ'- phase with the adjacent new phase etched differently (Fig. 3.4c), the new phase still showedthe columnar appearence. Microhardness tests were performed on all the phases of the compound zone and it was found that their hardness values were different. The innermost layer i.e., the new phase has a hardness of around 580 VHN while γ'- phase ε- phases have hardnesses of 500 and 400 VHN respectively.

Precipitation of some other particles, different from the componnd zone and the new phase, has also been noticed within the γ'- phase (Fig. 3.5(a)). From the hardness indentation marks in Fig. 3.5b it is also clear that the hardness of the particle is different from those of other phases in the compound zone. The particle has a hardness higher than that of ε but lower than that of either γ' or the new phase.

From these findings it can said that at 580°C, a compound zone consisting of 3 phases plus some other particles appearing occassionally in places forms on the mild steel.

3.1.3 Growth Morphology of the Compound Zone

Compound zones formed in mild steel under various nitriding conditions are shown in Fig. 3.6. From these figures it is evident that the thickness of the compound zone increases with the increase of nitriding time at any particular treatment temperature. These figures also show that for any particular nitriding time the thickness of the white layer increases with increase in nitriding temperature. At 500°C the white layer formed during nitriding appears to be quite dense (Figs. 3.6a, b,c), but at higher nitriding temperature the white layer is found to be porous (Figs. 3.6d,e,f,g,h). The porousness of the white layer is distinctly revealed by etching in nital (Fig. 3.7a). But when etched in Villela's reagent no such porous structure is revealed. Rather in Villela's reagent the minute details of the white layer i.e., the grains and the phase is revealed.

Microhardness values of the compound zones of the specimens nitrided at different temperature and time (shown in table 3.2) also show that at low temperature the white layer is harder; and its hardness decreases with increase of nitriding temperature as well as time.

3.1.4 Effect of Process Variables on the Compound Zone and its Phases

3.1.4.1 Compound Zone

The total thicknesses of the compound zone formed on mild steel and medium carbon steel under the present nitriding conditions are shown in Table 3.3 and 3.4 respectively. From the data presented in these tables it is clear that the thickness of the white layer increases with an increase in nitriding time as well as temperature. The graphical representation of the thickness values against the treatment time for mild steel specimens (Fig. 3.8) indicate that at all temperature the growth of the white layer is parabolic with nitriding time. A comparison of the above values also indicates that under the same nitriding condition the thickness of the compound zone is greater in mild steel than in medium carbon steel.

3.1.4.2 ε-and γ'- Phases

The ε- and γ'- phases were detected in all the samples by etching technique. Subsequently their thicknesses were measured (Table 3.5 and Table 3.6) under the microscope fitted with a measuring eye piece.

From these tables it can be found that although the thickness of the white layer as a whole is greater in mild steel than in medium carbon steel, the thickness of the γ'- phase on mild steel is lower than that of the corresponding phase on medium carbon steel nitrided under similar treatment conditions. The thickness of the ε- phase on mild steel, on the other hand, is much higher than that of the same phase on medium carbon steel.

Table 3.5 and 3.6 also show that the thicknesses of both the ε-and γ'- phases on mild steel and medium carbon steels increase with nitriding time and temperature. The plots of thickness of the ε - phase formed on mild steel against nitriding time show that at all nitriding temperatures investigated, ε-phase grows parabolically with nitriding time (Fig. 3.9). The growth of the γ'- phase formed on mild steel at various temperature is also parabolic with time as is evident from Fig. 3.10.

The growth rates of the ε- and γ'- phases are presented in table 3.7 along with some published data. The table shows that although the growth rate of the γ'- phase is smaller in mild steel than in pure iron, the growth rate of the ε- phase is much higher in mild steel than in pure iron.

It has already been pointed out that a new phase appeared below the ε-phase on mild steel specimen nitrided at 580°C. This phase was conspicuously detected by etching reagent. The thickness of the new phase is found to increase with the increase of nitriding time (Table 3.8).

3.1.5 Development of Hardness Profile

When a specimen is nitrided, a variation of nitrogen concentration occurs from the surface to the centre of the specimen. Concentration of nitrogen is high at the surface and decreases towards the core of the specimen. Due to this variation of nitrogen concentration a hardness gradient exists in a nitrided case. Depending upon the (i) nitriding temperature, (ii) nitriding time, (iii) percentage of ammonia in the nitriding gas mixture, (iv) concentration of alloying elements in the metal and (v) the strength of solute-nitrogen interaction, the hardness profile of a nitrided steel may follow two extreme pattern. The profile may be very steep with a sharp line of demarcation between the nitrided case and the matrix. 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 of mild steel nitrided at various time and temperature have been plotted in Figs. 3.11, 3.12 and 3.13. The maximum hardness in this steel occurs at the white layer. Apparently, the hardness profiles seem to be very steep. However, a close observation reveals that the abrupt change in the slope of these profiles does not correspond to the transition from the nitrided case to the core. It actually represents the transition from the white layer to the internally nitrided zone. In fact it can be seen from these figures that the transition from the internally nitrided layer to the core is very gradual which means that the profiles are shallow. The same statements also apply to the hardness profiles of medium carbon steel which are shown in Fig. 3.14 and 3.15. It is observed from the above figures (Fig. 3.11 to 3.15) that in general, the case depth increases with the increase of nitriding time and temperature. The effect of temperature and time on the hardness profiles is found to be insignificant.

3.2 Aluminium Steel

3.2.1 Metallography

Nital etch clearly revealed the white layer on the nitrided aluminium steel. Figure 3.16 shows the micrograph of the aluminium steel nitrided at 540°C for 8 and 24 hours. It is seen from the micrographs that the white layer grows in thickness with nitriding time. The white layer on this steel is found to be denser as compared to that on the plain carbon steel. The thickness of this layer was found to be lower than that on either the mild or the medium carbon steels nitrided under the same treatment conditions. The growth morphology of this layer was also different. It is seen from the figures 3.16(b) and 3.17(a) that the white layer penetrates along the grain boundaries of this steel. When etched in nital the white layer seems to be a single-phase layer (Fig. 3.16). However, Oberhoffer's reagent revealed that it, actually, is a multiphase layer. On etching in Oberhoffer's reagent, the outer portion of this layer dissolved completely, a part of the inner portion also dissolved but most of this portion did not (Fig. 3.17(b)). This indicates that the white layer on aluminium steel nitrided under the present treatment conditions consists of ε on the outer portion and a mixture of ε and γ on the inner side.

In this steel neither the grain boundary phase nor the carburized layer was observed. The nitrided layer was also unresolved by either nital or Oberhoffer's reagent. However, hardness profiles indicate the existence of this layer.

3.2.2 Microhardness Test and Hardness Profile

It was found that in aluminium steel, too, the maximum hardness occured at the inner portion of the white layer. The maximum microhardness of the white layer on this steel obtained under the present nitriding conditions was around 900 VHN. Figures 3.18 and 3.19 show the hardness profiles of the aluminium steel nitrided at various temperature for different periods of time. A sudden drop in hardness at the interface between the white layer and the nitrided layer is evident from these figures. Nitriding at a lower temperature viz. at 500°C for both 8 and 24 hours did not develop any significant hardness in the nitrided layer. On nitriding at higher temperatures viz. at 540°C and 580°C, development of hardness in this zone is considerable. It is seen from these profiles that increase of the nitriding temperature increases the steepness of the hardness profile at the nitrided case matrix interface.

From the hardness profiles of the nitrided aluminium steel, the case depths were estimated and are given in table 3.9. It is to be noted that these depths include the thickness of both the white layer and the nitrided layer. From these values it is very much clear that the thickness of the nitrided case increases as the nitriding time as well as temperature increase.

3.3 Stainless Steel

Under the present nitriding conditions there developed a nitrided case on the stainless steel. When etched in nital or Villela's reagent the nitrided case was clearly revealed. Figure 3.20 shows the microstructures of stainless steel nitrided at 540°C for 24 and 46 hours. These micrographs show that on etching with nital or Villela's reagent, the nitrided case appears dark. A uniform white layer similar to that found on plain carbon steel or aluminium steel was not obtained on stainless steel. However, some irregular white precipitates were found on the outer portion of the nitrided case (Fig. 3.20(a)). Figure 3.20(b) shows the photomicrograph of the stainless steel nitrided for a longer time periods (46 hours). The white layer formed after 46 hours of nitriding is found to be quite thick although it is still discontinuous. The layer is also found to contain cracks. No carburized layer and grain boundary phase were observed in the nitrided stainless steel.

The case depths of the nitrided stainless steel samples were easily measured with a measuring eyepiece after etching the specimens with nital. The thickness values of the nitrided case formed under various nitriding conditions are shown in table 3.10. The values of the case depth squared were also ploted against nitriding time for samples nitrided at 540° and 580°C. These plots are shown in figure 3.21. The figure indicates that at both 540°C and 580°C the thickness of the nitrided case increases parabolically with time. From the slopes of the above plots the growth rates of the nitrided case on stainless steel were calculated and are shown in table 3.11 along with some published data on En19 steel. It is found that the growth rate of the nitrided case on the stainless steel increases with nitriding temperature. However, these values are much lower than the corresponding values for the commercial nitriding steel (En 19) nitrided under more of less similar nitriding conditions.

The hardness profiles of the stainless steel nitrided at different temperatures for various time periods are shown in figs. 3.22, 3.23 and 3.24. It is seen that under all the nitriding conditions the hardness versus distance curve assumed the form of a typically steep profile which is characterized by the abrupt drop in hardness at the nitrided case-core interface.

It is seen that the hardness of the nitrided case remains more or less constant throughout the case. Case hardness of the stainless steel nitrided under various conditions is given in table 3.12. From the table it is also evident that the hardness of the case depends on the nitriding temperature as well as time. It is found that at 500°C the maximum hardness is obtained after 24 hours of nitriding while at 580°C it is obtained only after 8 hours. The maximum hardness obtained at 500°C is higher than that obtained at 580°C. Nitriding at 500°C produces a maximum hardness of around 1400 VHN while that at 580°C produces about 1200 VHN.

3.4 High Speed Steel

Like the stainless steel this material also developed a well defined nitrided case. As can be seen from figure 3.25 that nital etches this case black. Within this case the original carbide precipitates (white spots) are also found. The so called white layer is not seen on this steel. However, evidence of the presence of a greyish layer on the outer portion of the nitrided case was observed. Broken pieces of this layer which is too brittle to spall during polishing were found in some places particularly at corners of the specimens. Either of the carburized layer or the grain boundary phase was not found in this steel.

Figure 3.26 shows the hardness profiles of high speed steel nitrided for 24 hours at 500°C and 540°C. It is seen from this figure that very steep hardness profiles developed in nitrided high speed steel. It is also found that the hardness of the nitrided case varies with distance from the surface. The hardness of the case is maximum near the surface and as the distance from the surface increases, the hardness of the case decreases. The decrease in hardness is found to be rapid for upto 100 µm, it then becomes gradual.

The maximum hardness of the nitrided case varies with treatment temperature. From the hardness profiles it is observed that nitriding at 540°C for 24 hours produced a maximum hardness of 1450 VHN while nitriding at 500°C for the same time period produced 1200 VHN. It was found that the base hardness of the high speed steel decreased considerably after nitriding. The base hardness of this steel was 500 VHN before nitriding; it became 300 VHN after the treatment. The thickness of the nitrided case was found to increase with time.

3.5 Surface Hardness and Maximum Hardness of the Nitrided Steel

Surface hardness of a nitrided case is very often loosely quoted in describing the hardness of a nitrided specimen. Generally commercial steels are nitrided in an environment where a compound zone consisting of ϵ and γ' forms to a thick layer. Below this layer lies the internally nitrided zone whose hardness is quite often found to be higher than that of the compound zone. It is, therefore, quite reasonable to assume that surface hardness may not be the proper representation of the hardness of a nitrided case. Attempts were made to see whether there is any relationship between the surface hardness and the maximum hardness of a nitrided steel. The medium carbon and the aluminium steel specimens were used for the purpose. After nitriding the microhardness was measured on the surface of these steel samples. Microhardness survey was also carried out on the mounted and polished cross sections of the same samples. The surface hardness along with the maximum hardness obtained on the cross section of these steels are shown in table 3.13. From the table it is evident that in the case of medium carbon steel, the surface hardness is always lower than the maximum hardness. It also shows that hardness difference is higher at higher nitriding temperature. In the case of aluminium steel the difference between the surface hardness and maximum hardness is insignificant.

3.6 Summary

A thick, well defined white layer developed on plain carbon steel. On mild steel nitrided at 500° and 540°C and medium carbon steel nitrided at 500°, 540° and 580°C the white layer consisted of ε-and γ'-phases. The white layer on mild steel nitrided at 580°C contained a new phase in addition to the ε- and γ'-phases. Nitriding at 580°C also produced a number of precipitates (which could not be identified) in the white layer of nitrided mild steel. The ε-phase which occured on the outer portion of the white layer was thicker and porous and its porousness was found to increase with nitriding time as well as temperature. The γ'-phase was thin and dense. The growth of the compound zone and its constituent phases was found to be parabolic with time. The total thickness of the white layer was found to be higher in mild steel than in medium carbon steel. However, the thickness of γ'-phase was lower and that of ε-phase was higher in mild steel. A non uniform, irregular dark etched layer was sometimes found to occur below the white layer. This black zone is thought to be part of the nitrided layer. No carburized layer and grain boundary phase could be detected in the plain carbon steels.

The maximum hardness of the nitrided case was found to occur in the white layer in both the mild and medium carbon steels. Development of hardness in the nitrided layer of these steels was negligible. The slope of the hardness profile was observed to be steep at the white layer-nitrided layer interface but quite shallow at the interface between the nitrided case and the core. White layer formed on medium carbon steel was found to be harder than that on mild steel.

Nitriding of aluminium steel produced a dense white layer which consisted of ε and γ'- phases. The layer was found to be thinner than that on the plain carbon steels. Below the white layer a zone with $Fe_{16}N_2$ precipitation was observed. Nither the carburized layer nor the grain boundary phase was found in this steel. In the aluminium steel too the maximum hardness of the nitrided case occured at the white layer. The white layer formed on aluminium steel was found to be harder than that on plain carbon steels. Development of hardness in the nitrided layer of aluminium steel was considerable when the nitriding temperature was 540° and 580°C. However, hardness developement, was not significant when nitriding temperature was 500°C. The hardness profile at the nitrided layer-matrix interface of the aluminium steel was found to be steeper than that of the plain carbon steels.

In nitrided stainless steel a quite irregular white layer was found. This layer was also observed to contain cracks. No white layer was found in high speed steel. However, evidence of the presence of a greyish layer on the outer portion of the nitrided case was observed. In both the stainless steel and high speed steel a well defined nitrided case developed. The case depth in the stainless steel was found to increase parabolically with time. The hardness profiles on these steels were found to be typically steep. The hardness developed on the nitrided case of these steels was quite high. The hardness of the case was found to vary with nitriding time as well as temperature.

TABLE 3.1

List of Etching Reagents

Reagent	Composition
Nital	2ml HNO_3 98 ml ethyl alchol
Picral	49 m picric acid 100 ml ethyl alcohol
Oberhoffer's reagent	1gm cupric chloride 30 gm ferric chloride 0.5 gm stannous chloride 50 ml Hcl 500 ml distilled water 500 ml ethyl alcohol
Villela's reagnet	1 gm picric acid 5 ml Hcl 100 ml ethyl alcohol

TABLE 3.2

Microhardness in VHN of γ'- and ε - phase in the compound zone of nitrided mild steel.

Temp. °C	8 hours		16 hours		24 hours	
	γ'	ε	γ'	ε	γ'	ε
500	-	590±25	-	580 ± 20	650 ±20	580 ±20
540	-	530±20	-	500 ±30	600 ±25	470 ±30
580	630	450±20	580±25	440 ±30	520 ±20	420 ±40

Table 3.3

Total thickness in μm of the compound zone of mild steel nitrided under different conditions

Nitriding temp. ^{0}C	Thickness of the compound zone, μm		
	8 hrs.	16 hrs.	24 hrs.
500	24	36.5	41
540	47.5	69	90
580	85	118.5	136

TABLE 3.4

Total thickness in µm of the compound zone of medium carbon steel nitrided under various conditions

Nitriding temp. ^{o}C	Thickness of the compound zone, µm		
	8 hrs.	16 hrs.	24 hrs
500	10.5	-	18
540	20	-	35
580	50	-	60

TABLE 3.5

Thickness of γ' and ε -phases of the compound zone of mild steel nitrided under different conditions.

Nitriding temp. $^{\circ}C$	Thickness of different phase of compound zone, μm					
	8 hrs.		16 hrs.		24 hrs.	
	γ'	ε	γ'	ε	γ'	ε
500	2	22	2.5	34	3	38
540	2.5	45	4	65	5	85
580	5	70	8	100	9	110

TABLE 3.6

Thickness of γ'- and ε-phase of the compound zone of medium carbon steel nitrided at different temperature and time.

	Thickness of different phases of the compound zone, μm			
Temp.	8 hrs.		24 hrs.	
^oC	γ'	ε	γ'	ε
500	2.5	8	4	14
540	5	15	8	27
580	15	35	20	40

TABLE 3.7

The growth rates of γ'- Fe_4N and ε-Fe_3N of 0.1% C steel nitrided at different temperature.

Nitriding temp. °C	Growth rate, cm^2/sec			
	Mild steel		Pure iron(8)	
	γ'	ε	γ'*	ε**
500	1.128×10^{-12}	1.87×10^{-10}	7.5×10^{-12}	52×10^{-12}
540	2.78×10^{-12}	8.33×10^{-10}		
580	8.68×10^{-12}	1.56×10^{-9}		

* Nitrided at 520°C in 30% NH_3

** Nitrided at 520°C in 80% NH_3

TABLE 3.8

Thickness of the new phase present in mild steel when nitrided at 580°C only.

Nitriding time, hr	Thickness, μm
8	10
16	10.5
24	17

TABLE 3.9

Case depth of aluminium steel nitrided under different condition.

Nitriding temp. ^{o}C	Case depth, μm	
	8 hr	24 hr
500	120	320
540	600	800
580	800	1200

TABLE 3.10

Thickness of nitrided case of stainless steel nitrided under various condition.

Nitriding temp. °C	Thickness, µm		
	8 hrs.	16 hrs	24 hrs.
500	15	90	-
540	100	140	170
580	105	155	180

TABLE 3.11

Growth rate of the nitrided layer of stainless steel at different temperatures.

Nitriding temp. ^{0}C	Growth rate, cm^2/sec	
	Stainless steel	En 19 (8)
540	3.125×10^{-9}	1.889×10^{-8}*
580	3.901×10^{-9}	3.148×10^{-8}**

* Nitrided at 520°C in 80% NH_3

** Nitrided at 570°C in 80% NH_3

TABLE 3.12

Case hardness of stainless steel nitrided under various condition

Temp.	Case hardness, VHN		
	8 hours	16 hours	24 hours
500	925	1200	1400
540	900	1200	1050
580	1200	1000	1100

TABLE 3.13

Relationship between the surface hardness and maximum hardness of medium carbon steel and aluminium steel.

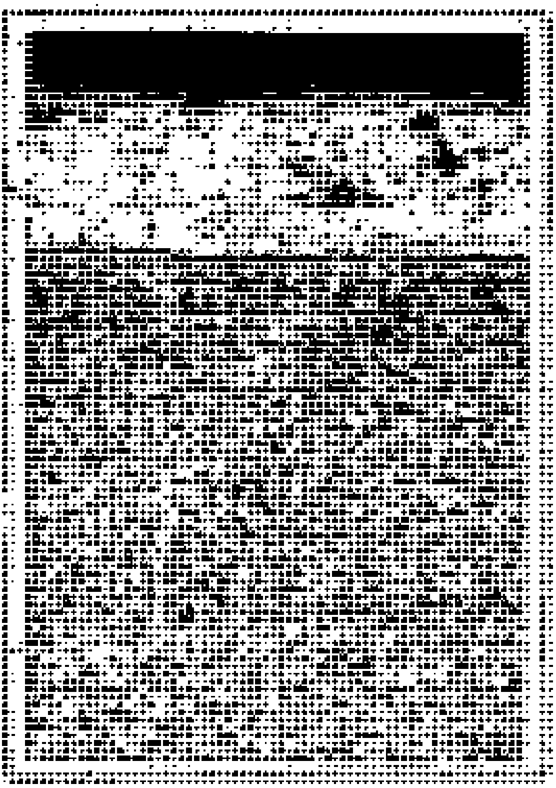
Material	Nitriding temp. °C	Nitriding times hr.	Surface Hardness VHN	Maximum Hardness VHN
Medium carbon steel	500	8	445	509
		24	460	509
	540	8	385	701
		24	350	766
Aluminium steel	500	8	760	766
		24	850	891
	540	8	770	800
		24	770	841

Fig. 3.1: Optical micrographs showing the compound zone and the variation of its thickness on different plain carbon steels

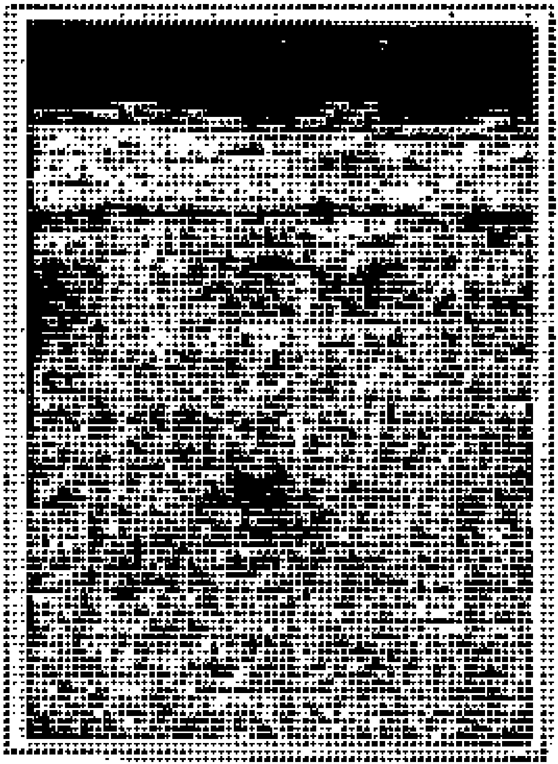
a. mild steel nitrided at 580°C for 24 hours in 100% NH_3

b. medium carbon steel nitrided at 580°C for 24 hours in 100% NH_3.

[illegible]



(a)



(b)

2004

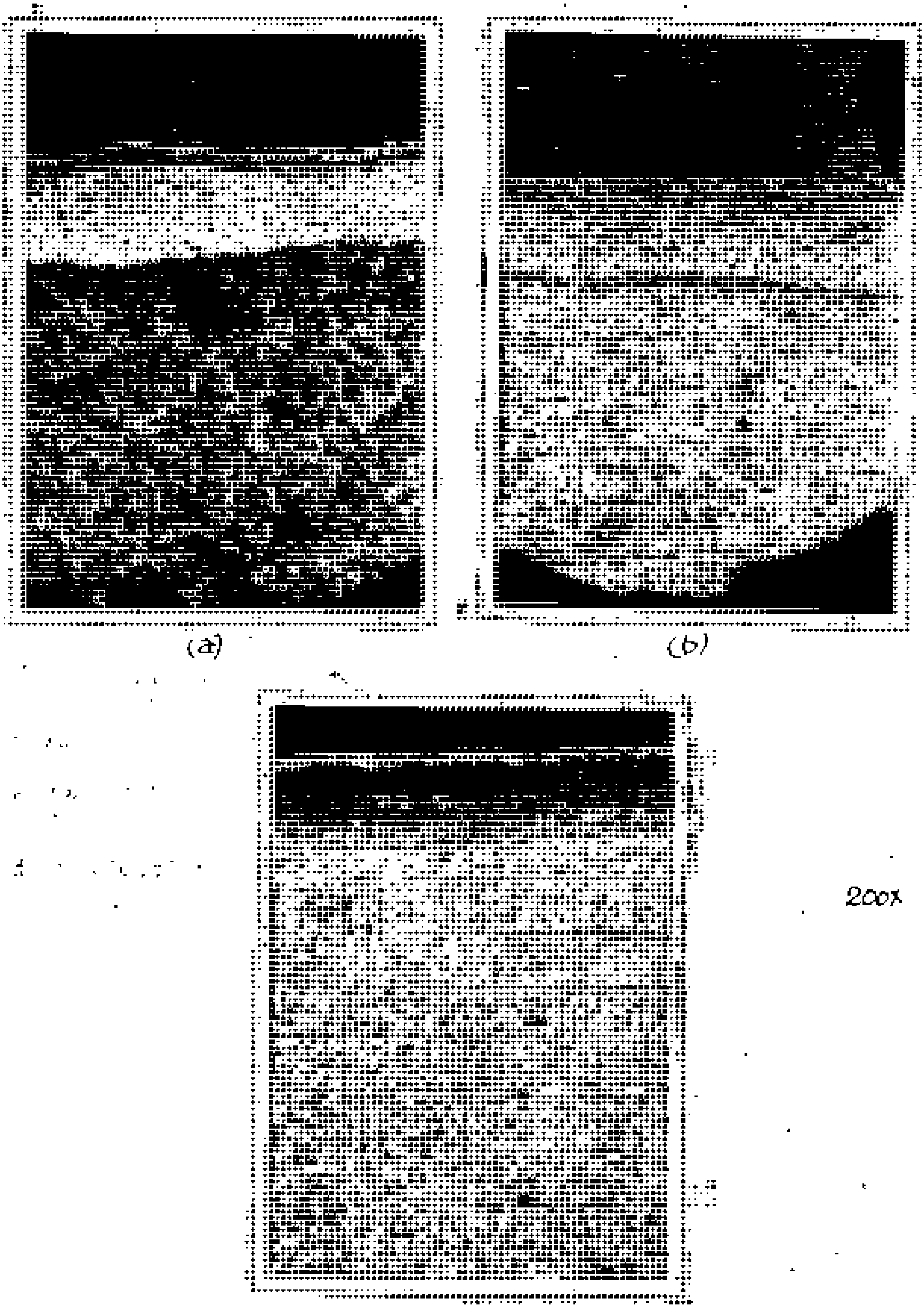
Fig. 3.2: Microstructures of compound zone of mild steel revealed by different etchants

a) nital reveals the boundary between ε- and γ'-pha

b) Villela's reagent also distinguishes ε- and γ-phase

c) Oberhoffer's reagent dissolves the outer ε-phase.

[illegible]



(a)

(b)

(c)

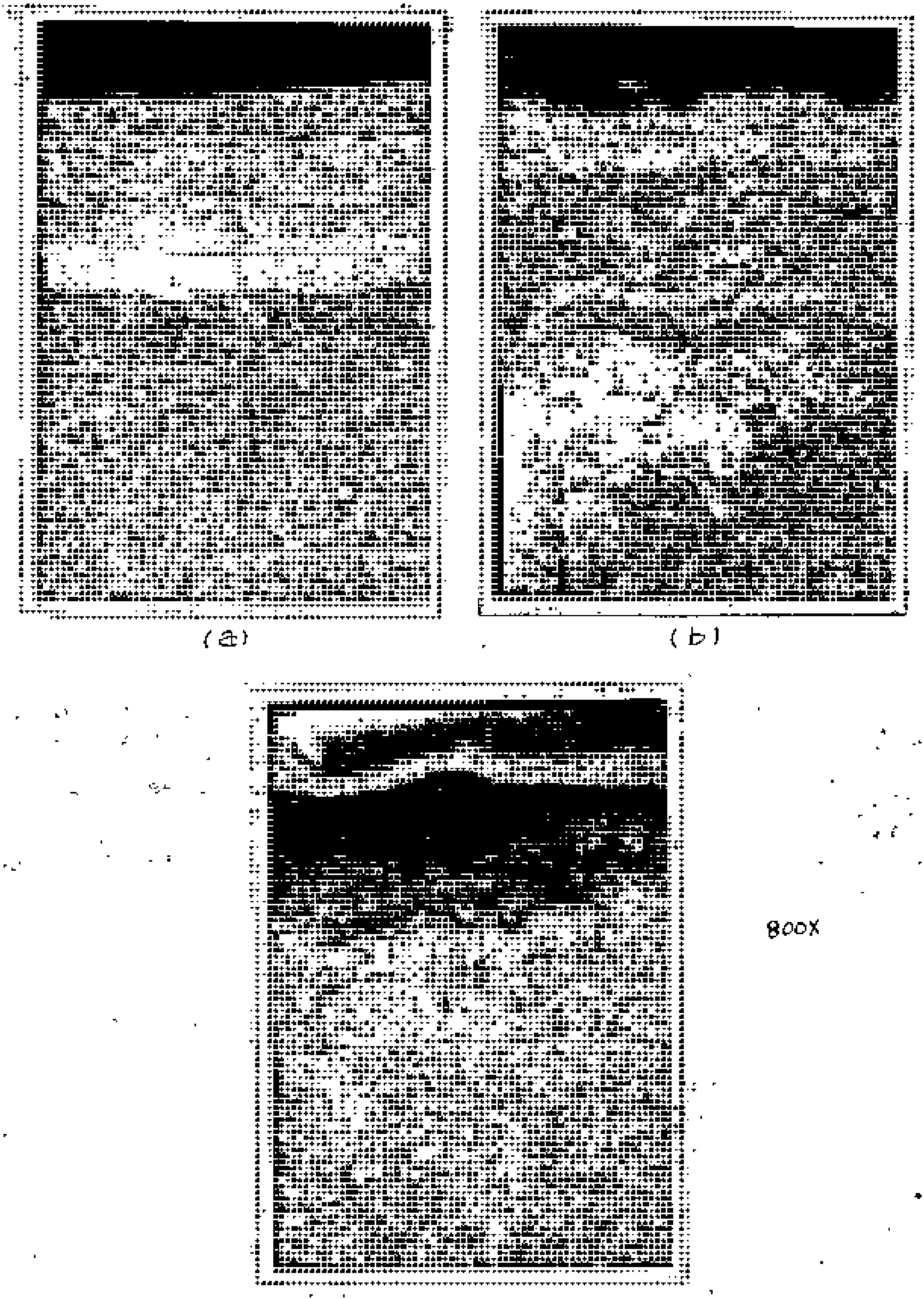
200x

Fig. 3.3: Optical micrographs showing the compound zone of medium carbon steel as revealed by different etchants

a) nital differentiates outer, porous ε-phase from inner, dense γ'-phase

b) picral also distiguishes ε- and γ'- phase but less distinctly

c) Oberhoffer's reagent dissolves ε completly and leaves γ' unattacked.



(a)

(b)

(c)

800X

Fig. 3.4: Optical micrographs showing the new phase (columnar grains) at the inner side of the white layer formed at 580°C.

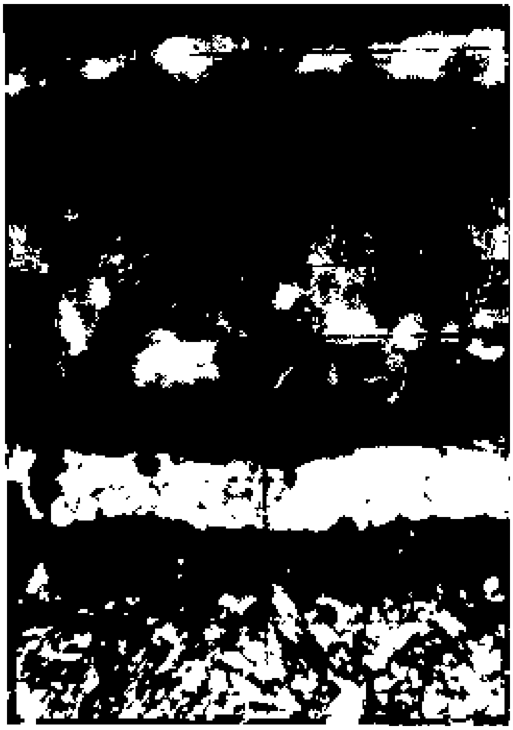
a) for 8 hours, etched in nital

b) for 24 hours, etched in nital

c) for 24 hours, etched in Oberhoffer's reagent and then nital.

(a)

(b)

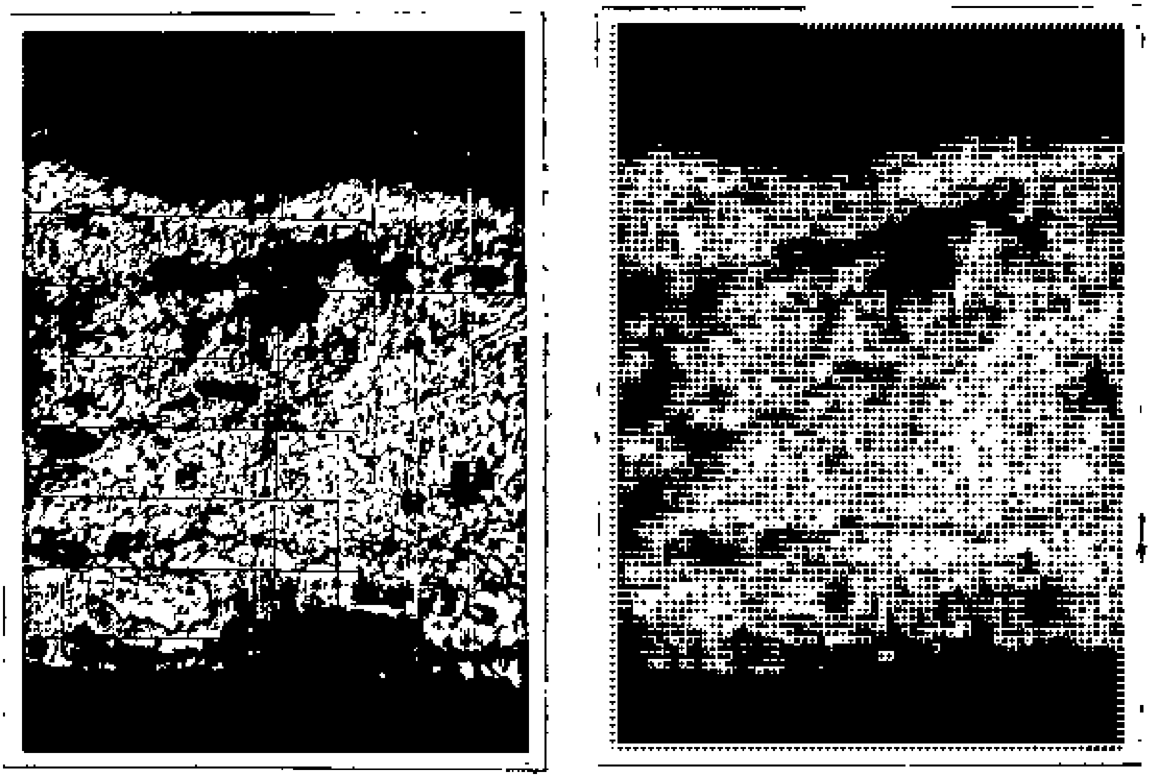


(c)

400X

Fig. 3.5: a) Optical micrograph showing the entraped new particle in the white layer of mild nitrided at 580°C for 24 hours.

b) Same as above but with hardness indentation marks.



(a) (b)

800X

3·5

Fig. 3.6: Optical micrographs showing the variation of thickness and porousness of compound zone formed on mild steel at different nitriding time and temperature(nital etched).

a) nitrided at 500°C for 8 hours

b) nitrided at 500°C for 16 hours

c) nitrided at 500°C for 24 hours

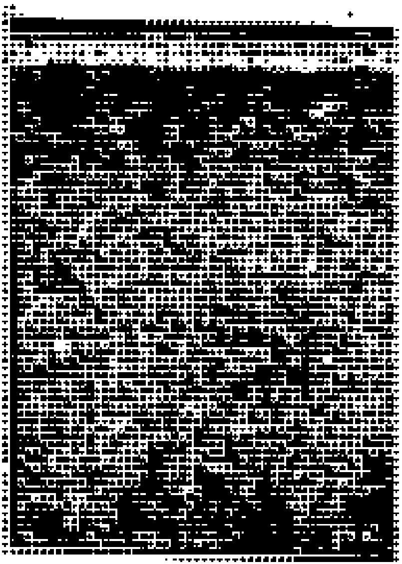
d) nitrided at 540°C for 8 hours

e) nitrided at 540°C for 16 hours

f) nitrided at 540°C for 24 hours

g) nitrided at 580°C for 8 hours

h) nitrided at 580°C for 16 hours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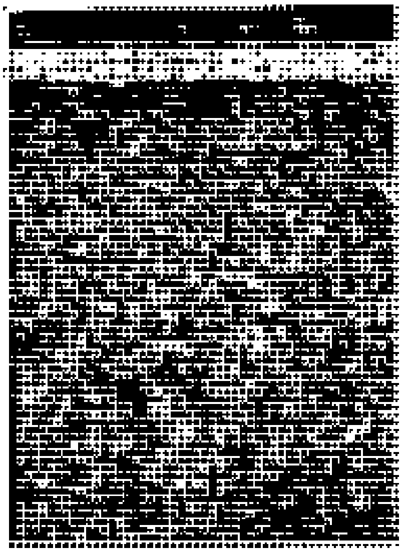
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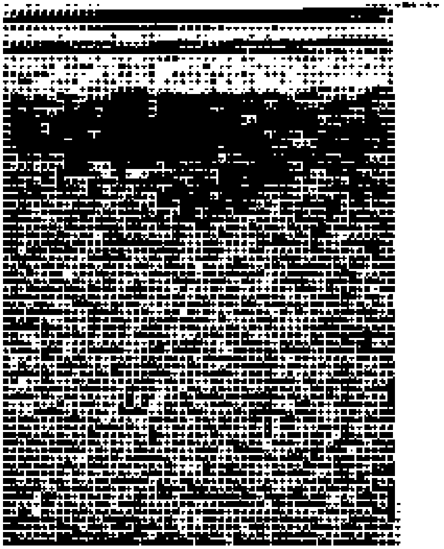
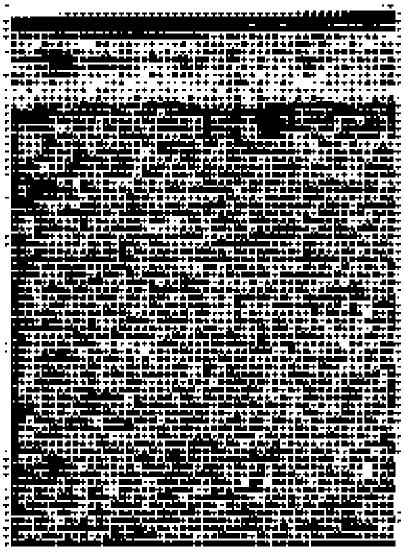
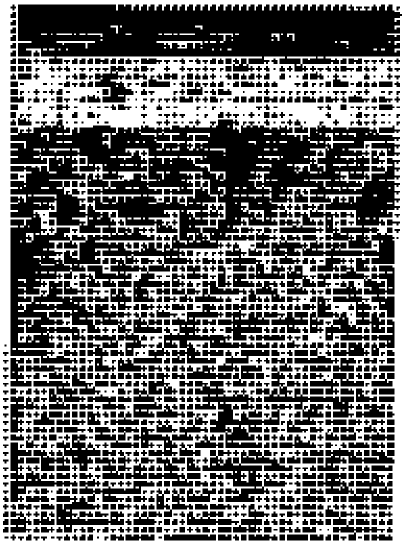
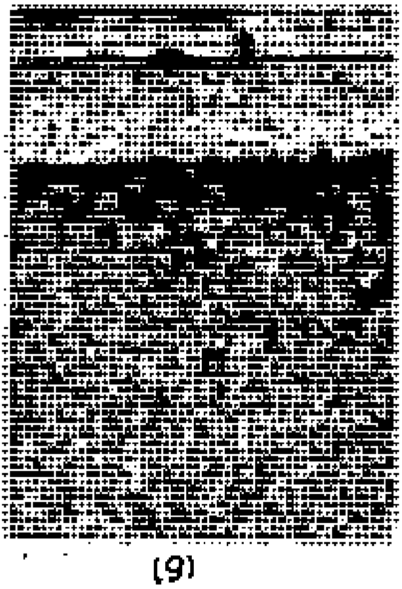
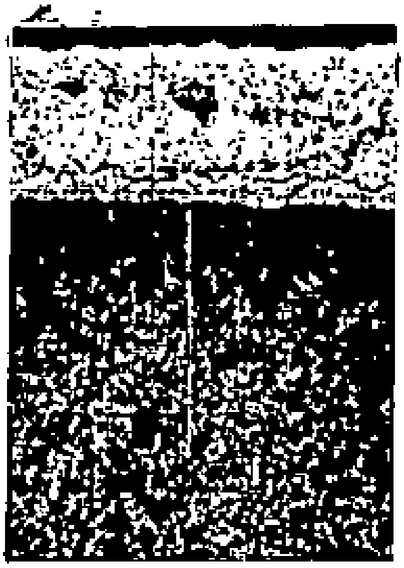

(c)


(d)


(e)


(f)


(g)


(h)

200X

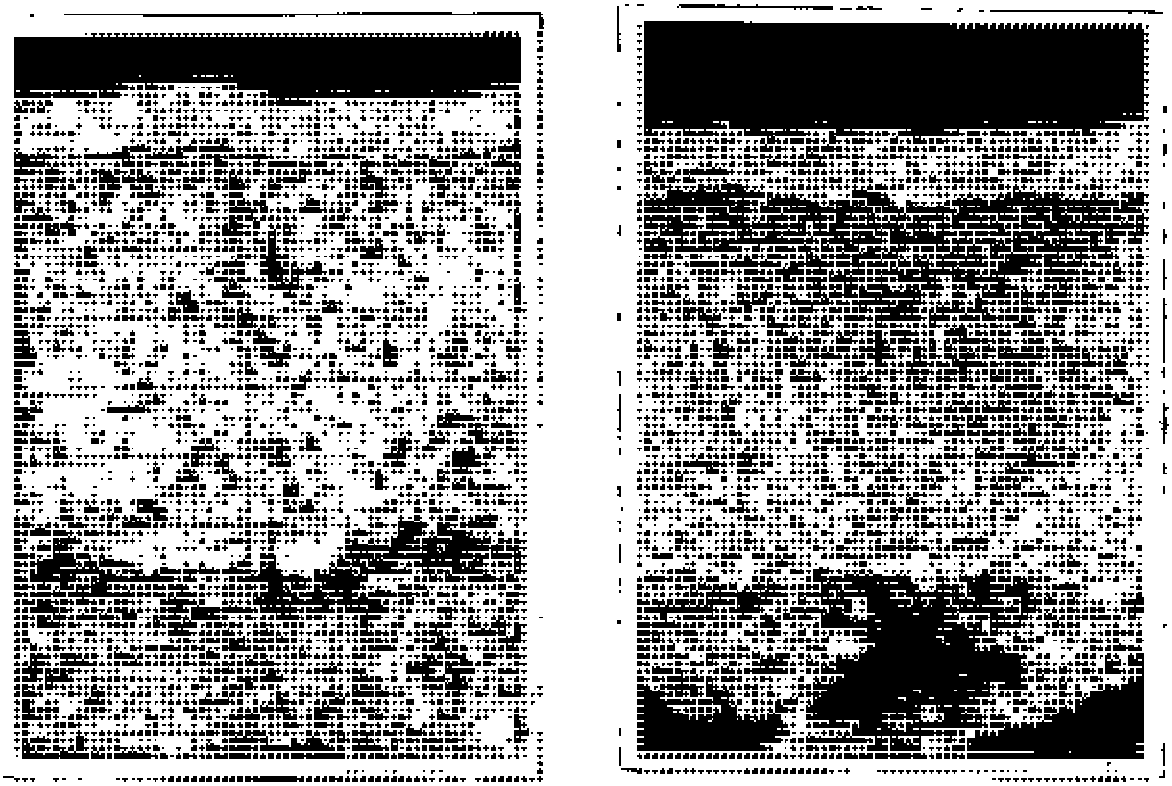
2.4

Fig. 3.7: Porousness of white layer is distinctly shown by

a) nital, but not by

b) Villela's reagent

Both specimens were nitrided at 540°C for 24 hours.



(a) (b)

800X

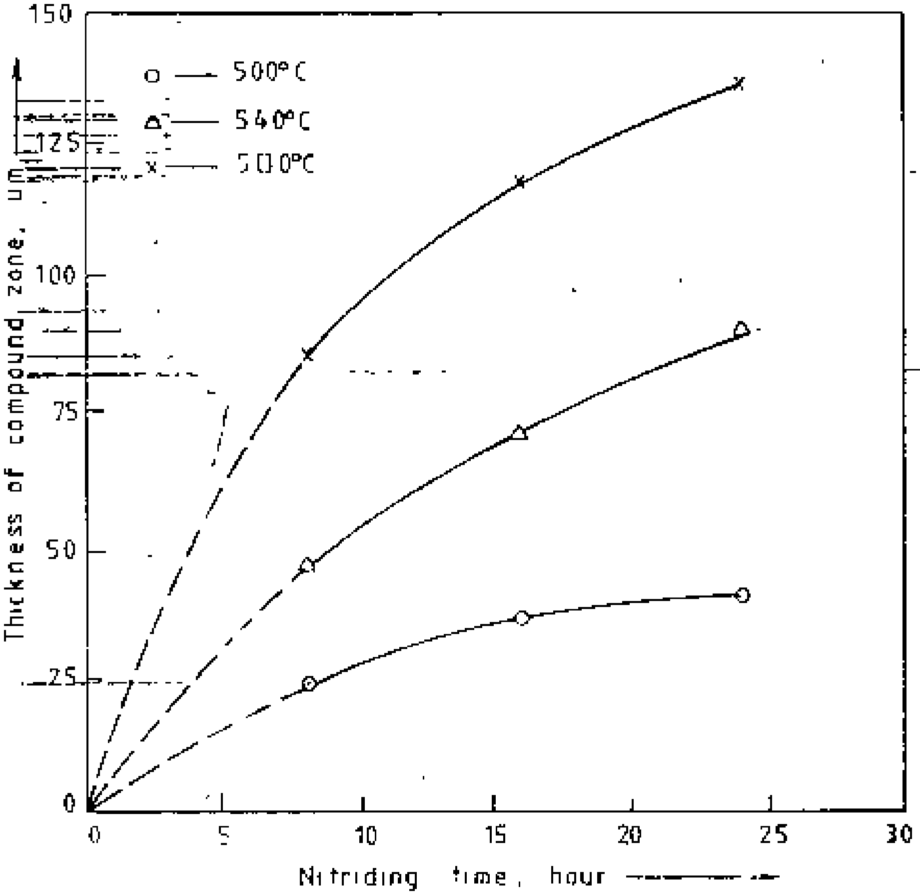


Fig 3 8 Variation of thickness of compound zone of mild steel with nitriding time at different temperature.

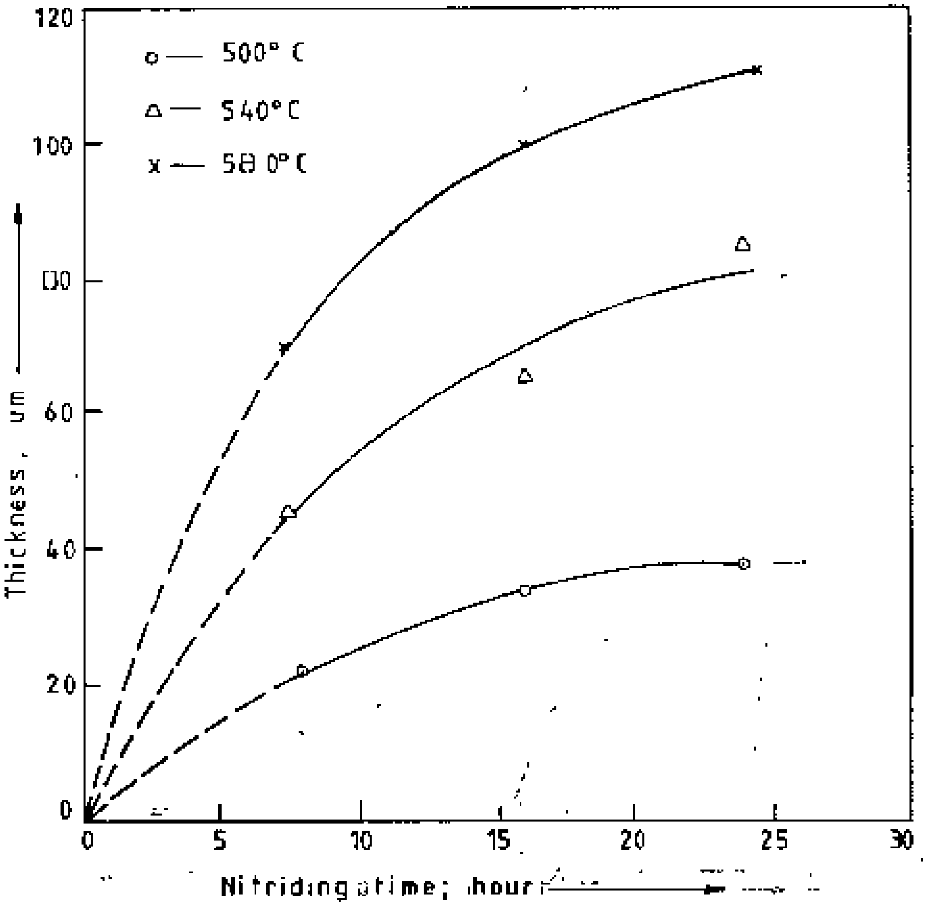


Fig. 3.9 Variation of thickness of ε-Fe$_3$N of the compound zone of mild steel with nitriding time at different temperatures.

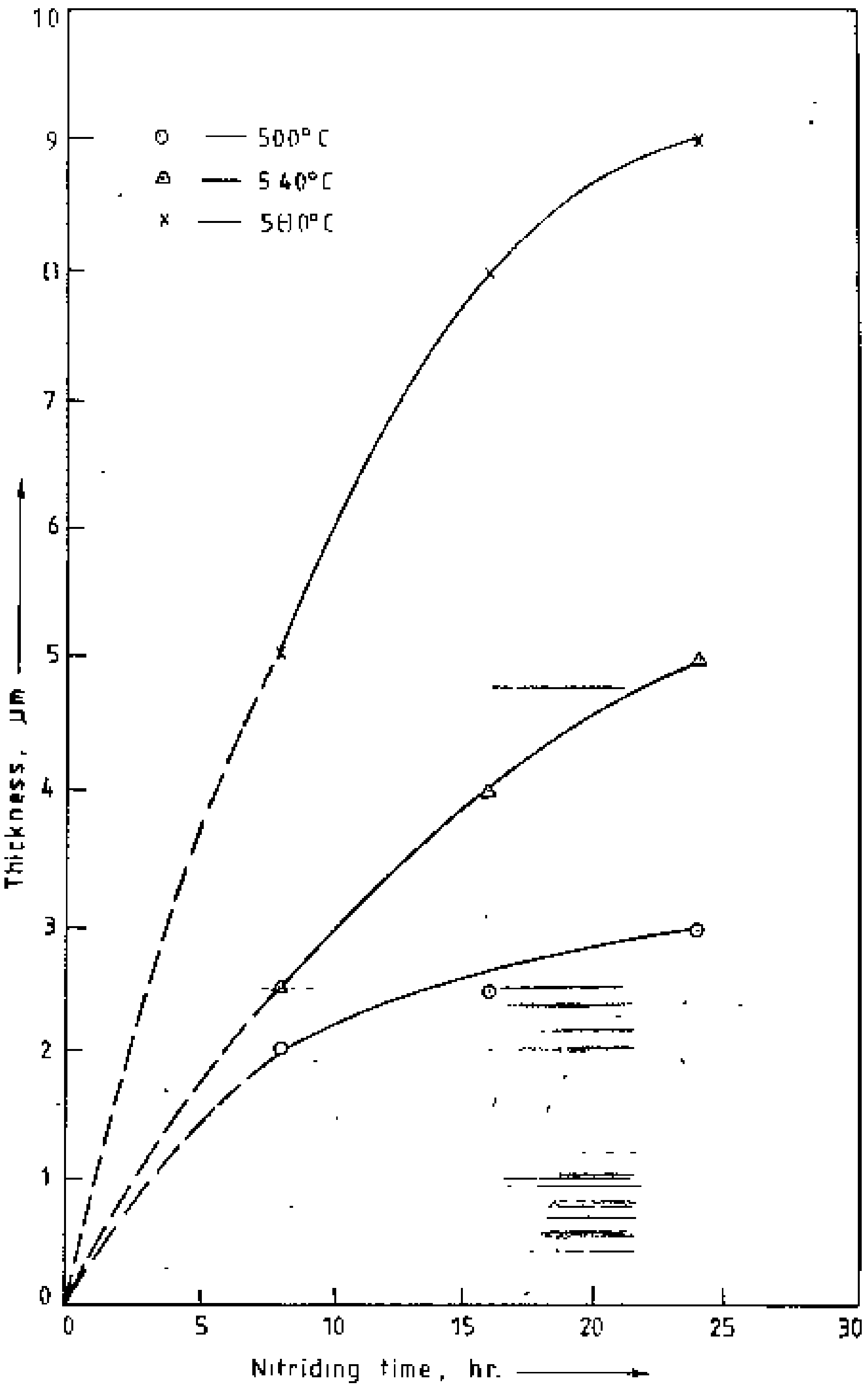


Fig. 3.10 Variation of thickness of γ'-Fe$_4$N of the compound zone of mild steel with nitriding time at different temperatures

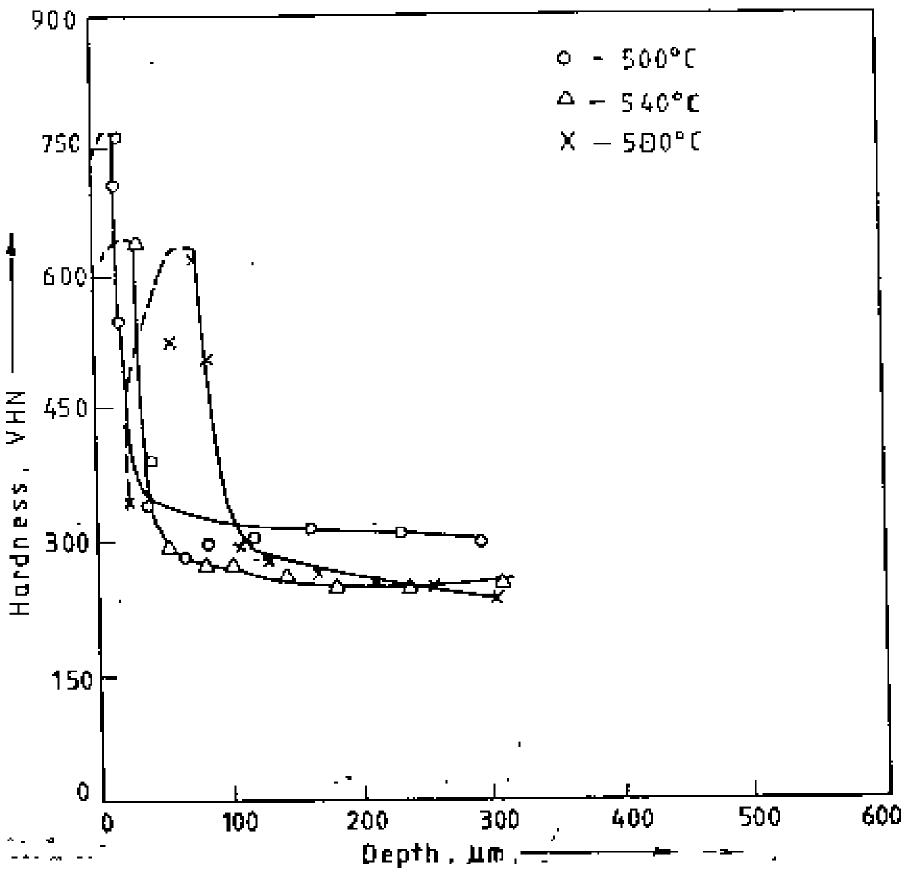


Fig. 3.11 - Hardness profiles of mild steel nitrided for 8 hours in 100% NH_3 at different temperatures

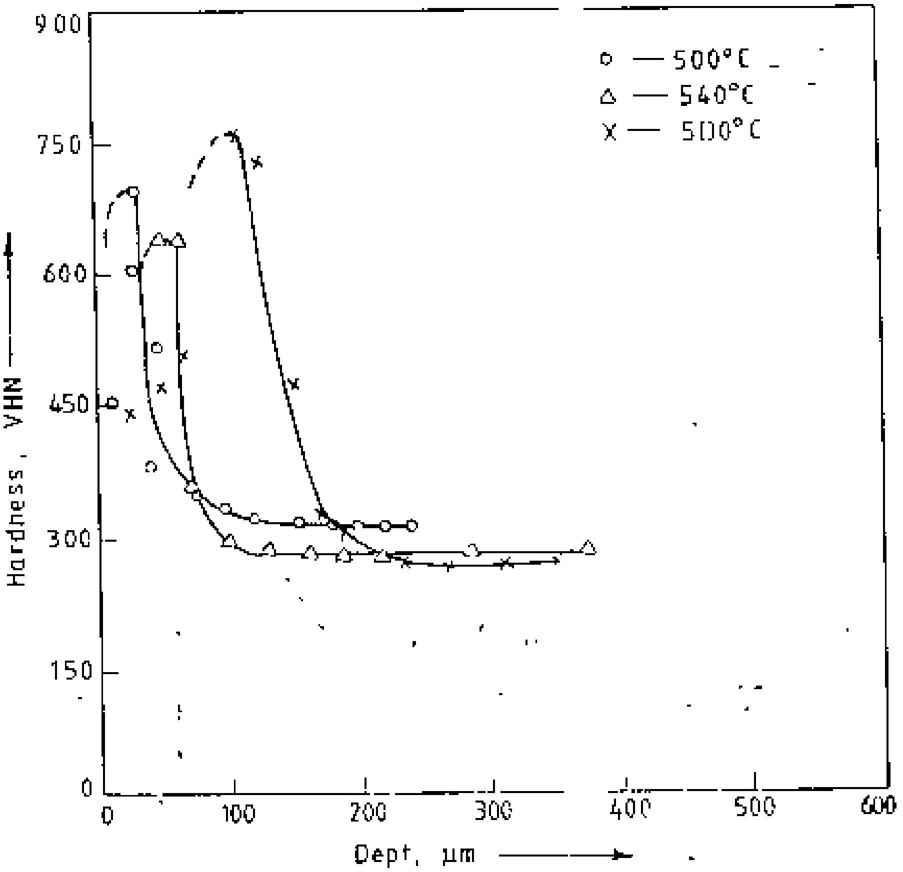


Fig. 3.12 : Hardness profile of mild steel nitrided for 16 hours at different temperatures

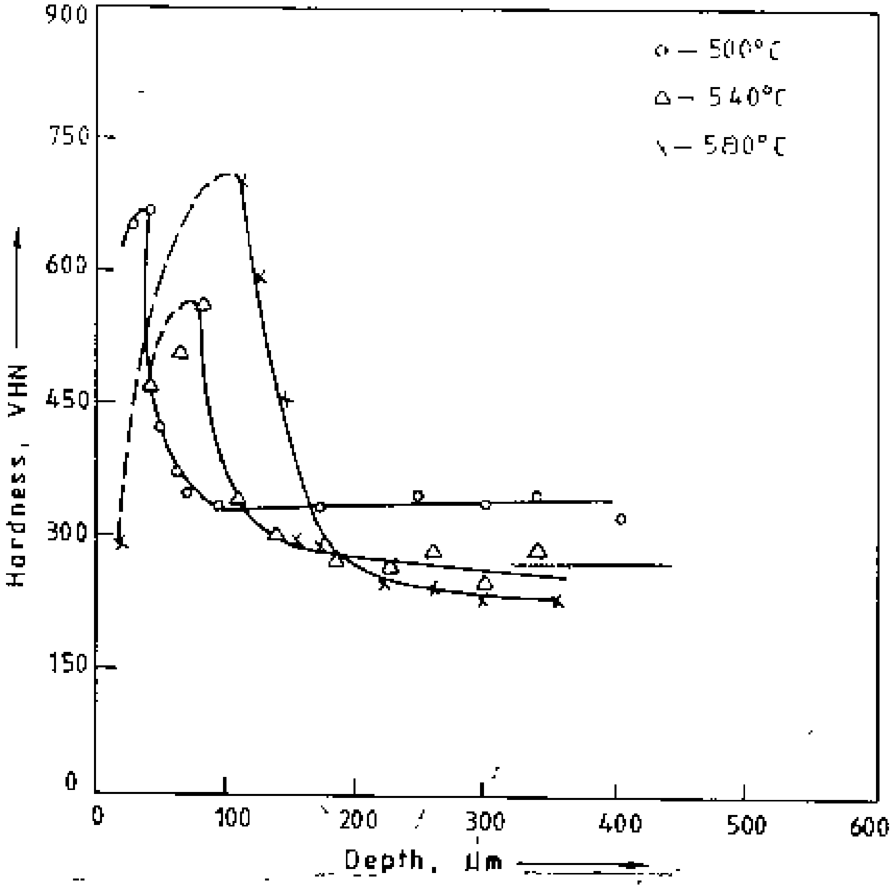


Fig. 3.13 Hardness profiles of mild steel nitrided for 24 hours at different temperatures.

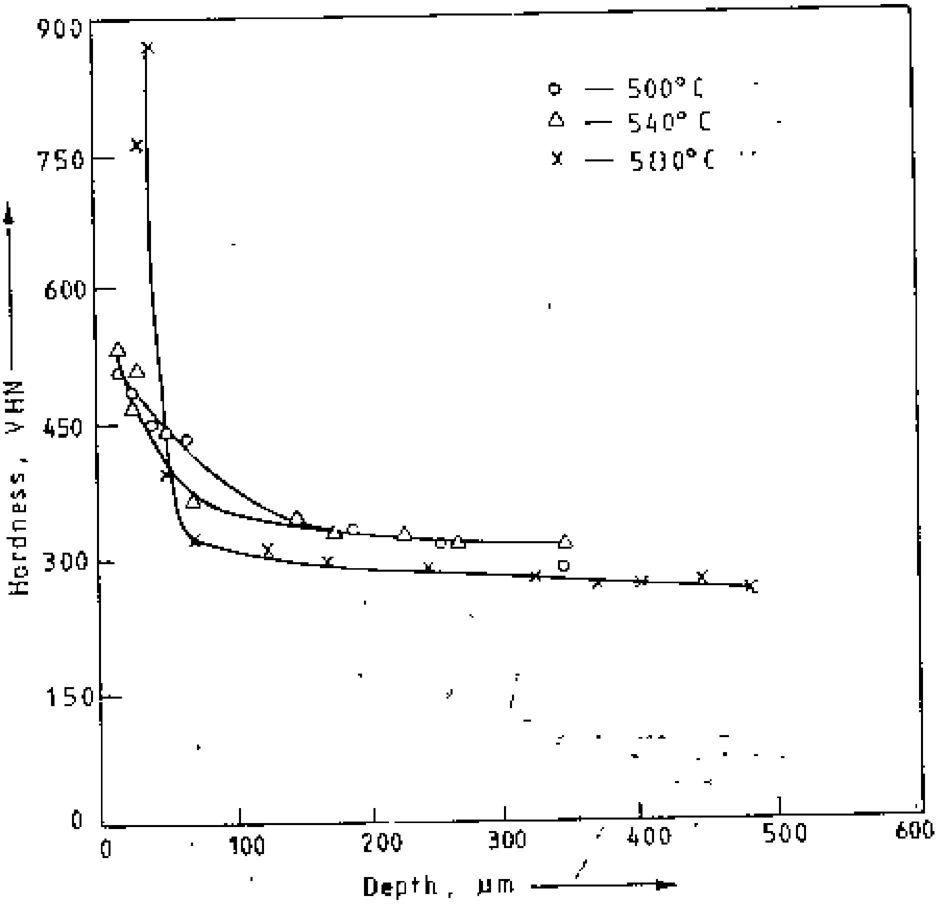


Fig. 3.14 Hardness profiles of medium carbon steel nitrided for 8 hours

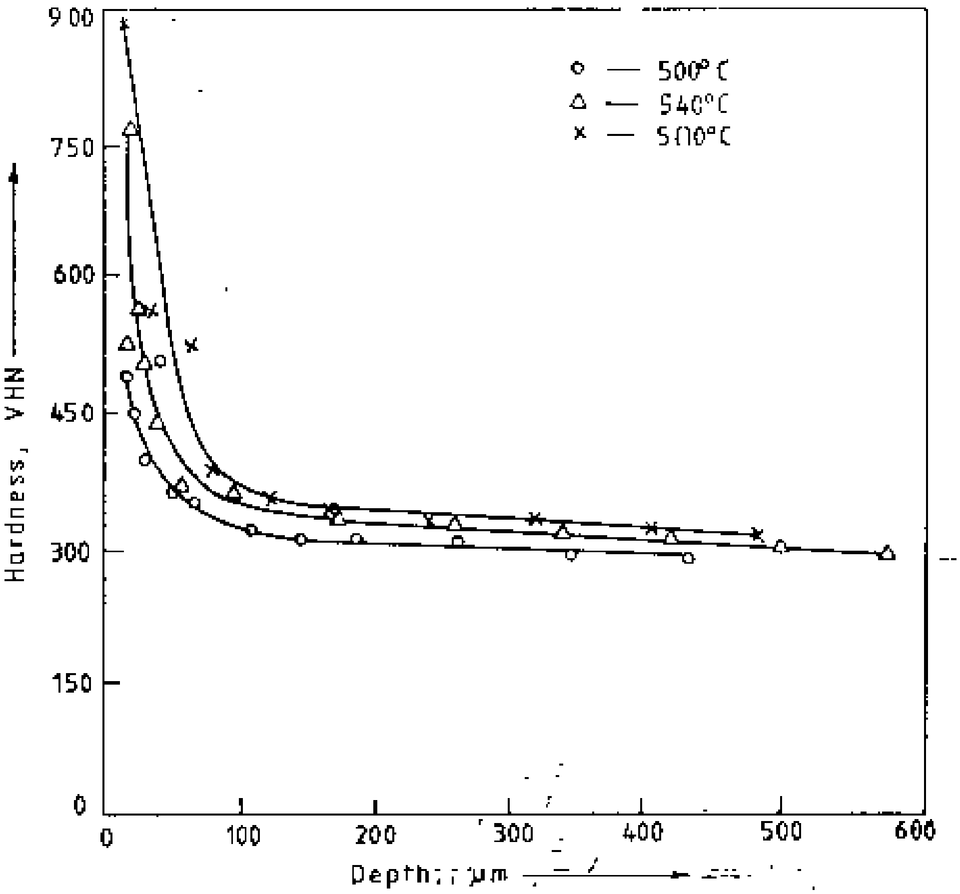


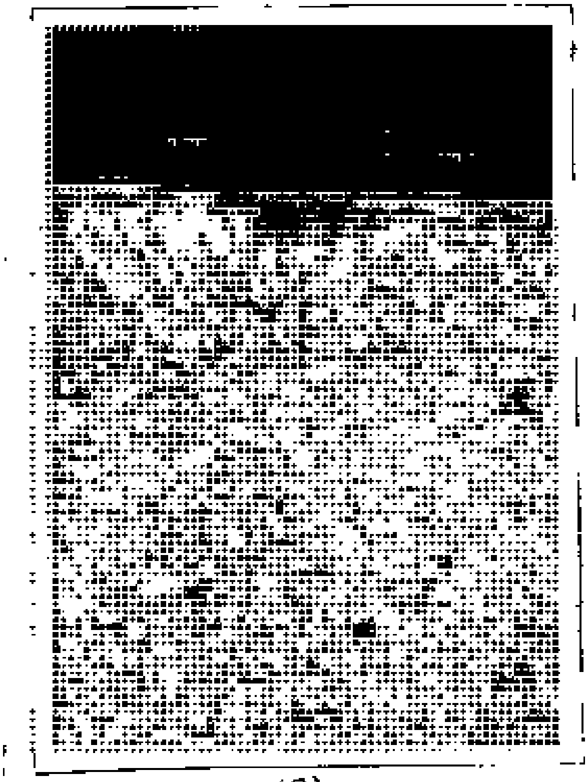
Fig. 3.15 Hardness profiles of medium carbon steel nitrided for 24 hours at different temperatures.

Fig. 3.16: Microstructure of Aluminium steel nitrided at 540°C for

a) 8 hours

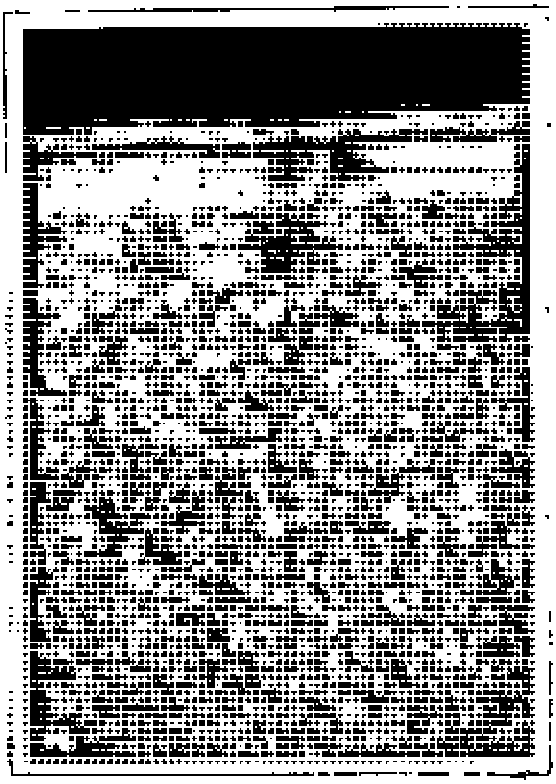
b) 24 hours

Showing the white layer and $Fe_{16}N_2$ needles.



(a)

800X



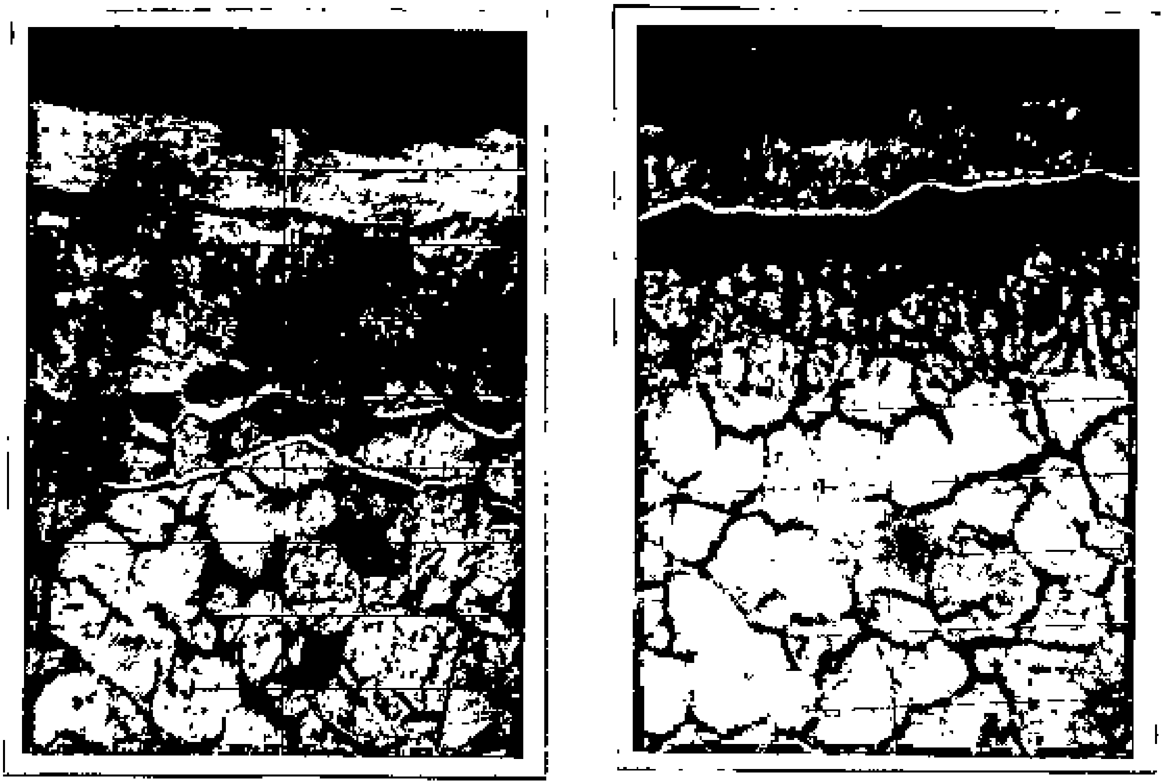
(b)

200X

Fig. 3.17 : Microstructures of compound zone of Aluminium steel nitrided at 580°C for 24 hours revealed by different etchants

a) etched in nital

b) etched in Oberhoffer's reagent.



(a) (b)

800X

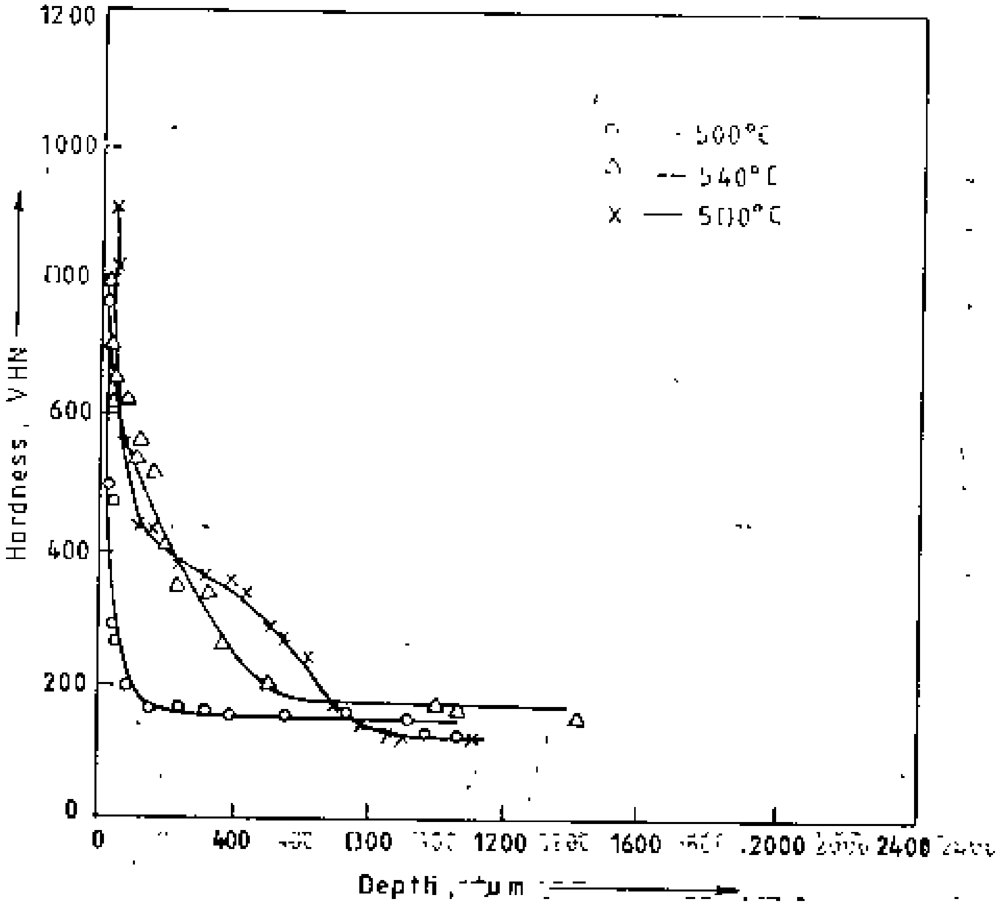


Fig. 3.18 Hardness profiles of aluminium steel nitrided for 8 hours at different temperatures.

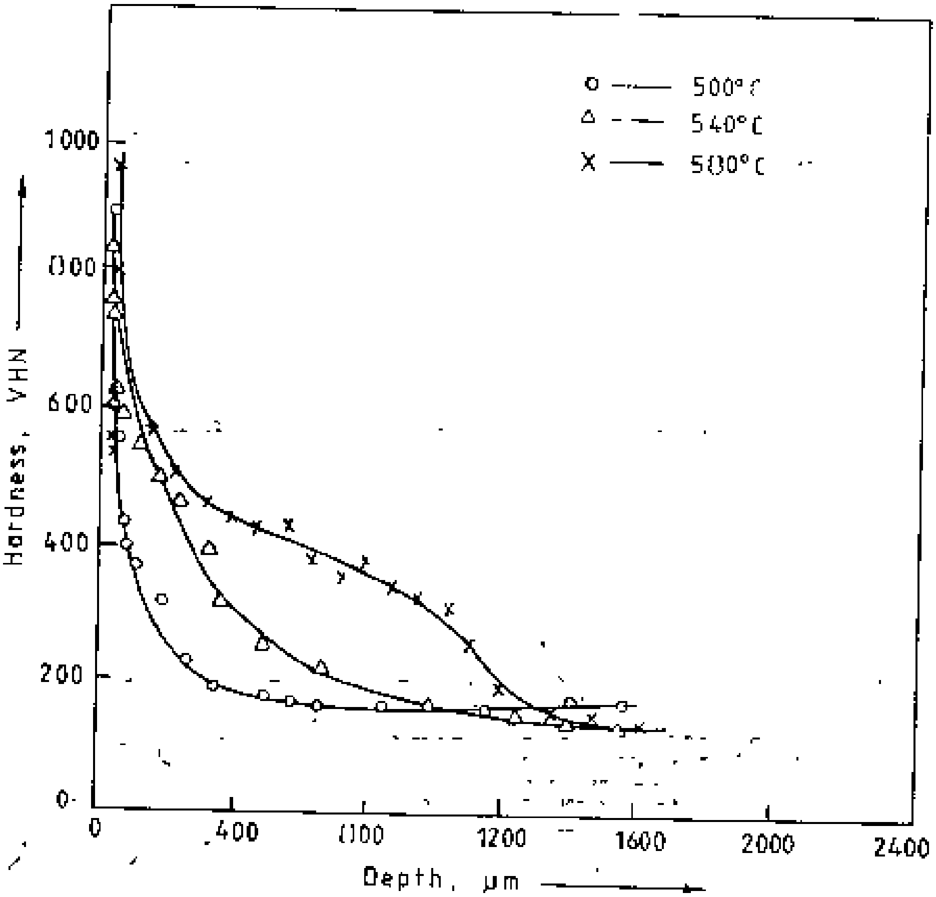


Fig 3.19 Hardness profiles of aluminium steel nitrided for 24 hours at different temperatures.

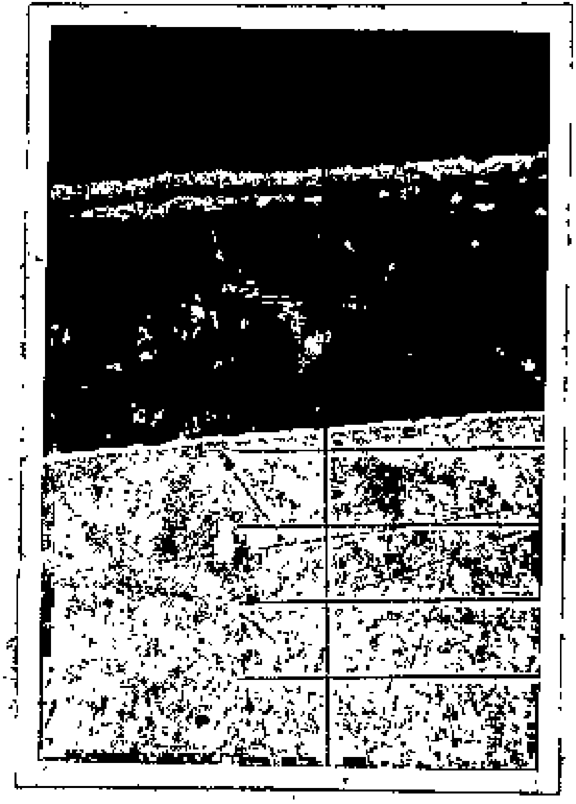
Fig. 3.20: Microstructures of stainless steel

a) nitrided at 540°C for 24 hours

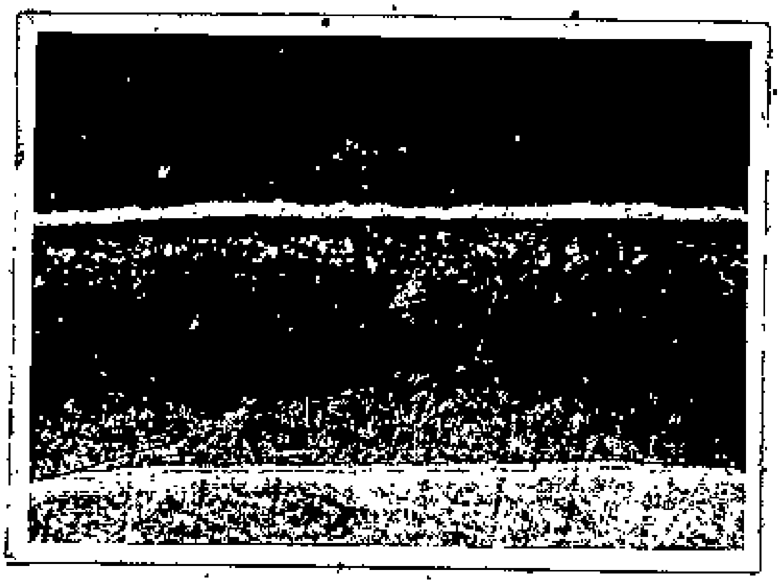
i) etched in nital

ii) etched in Villela's reagent, both show a well defined nitrided case with a quite irregular white layer at the outer portion.

b) nitrided at 540°C for 46 hours, shows an uneven but somewhat continuous white layer containing cracks (situated at corner of the specimen).



(a)(i) 200X



(a)(ii) 200X

?

(b) 800X

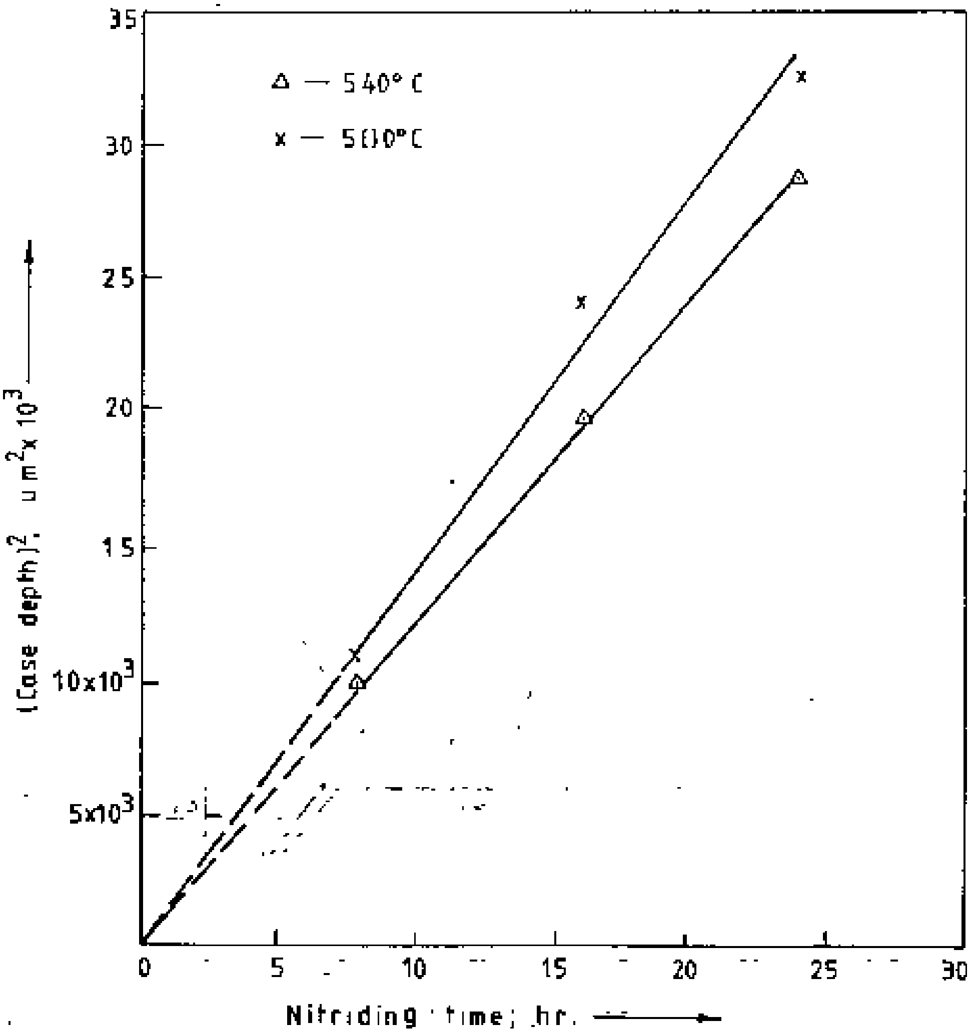


Fig 3.21 Showing the relationship between the case depth squared and the nitriding time for stainless steel nitrided at different temperatures.

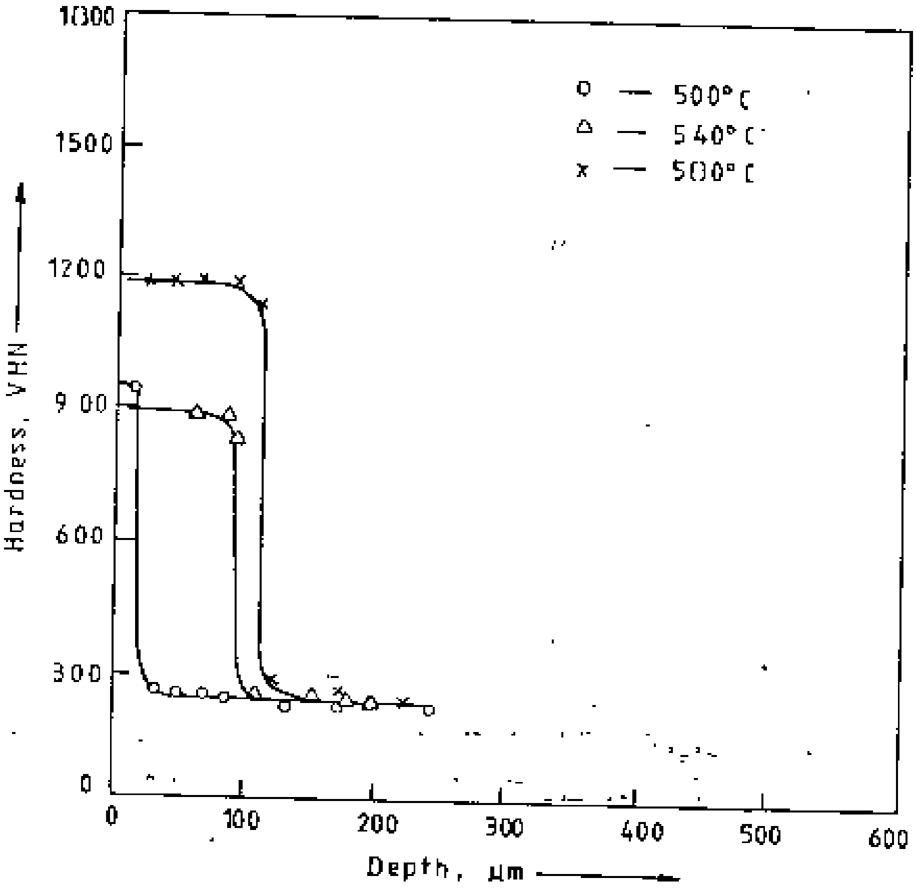


Fig. 3.22 Hardness profile of stainless steel nitrided for 8 hours at different temperatures

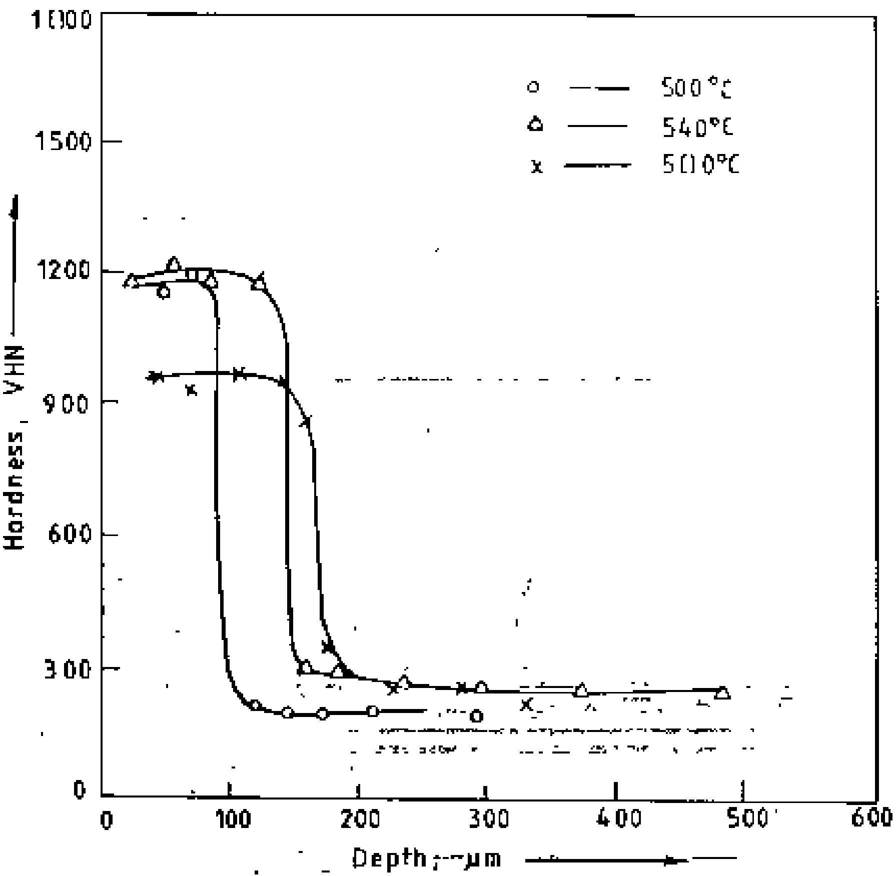


Fig. 3 23 Hardness profile of stainless steel nitrided for 16 hours at different temperatures

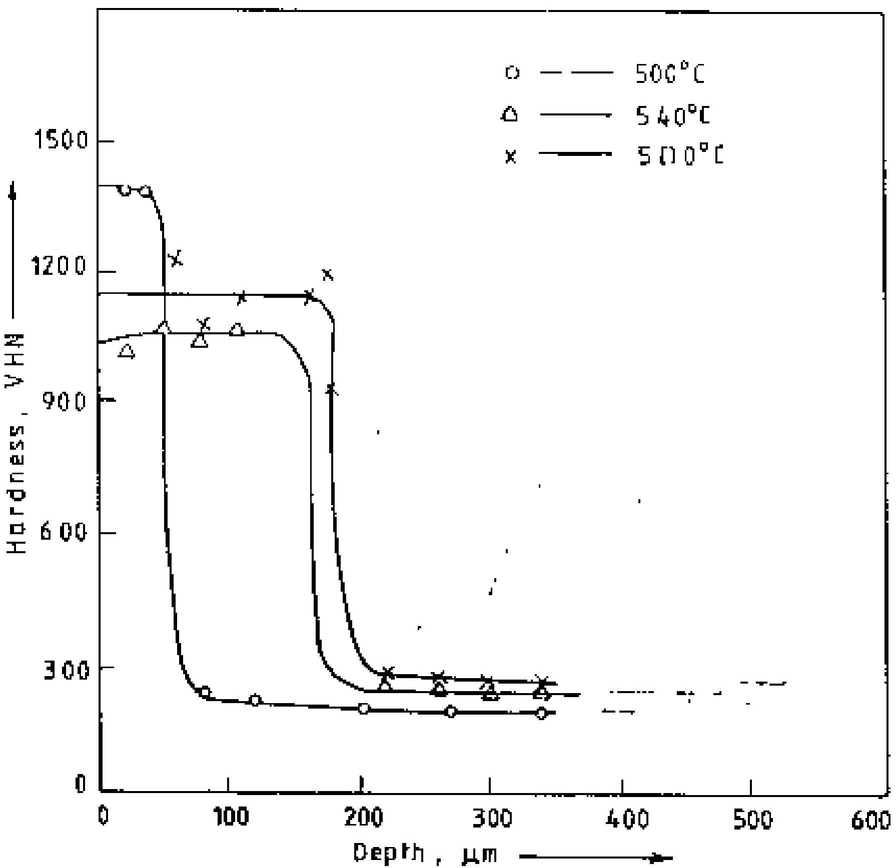
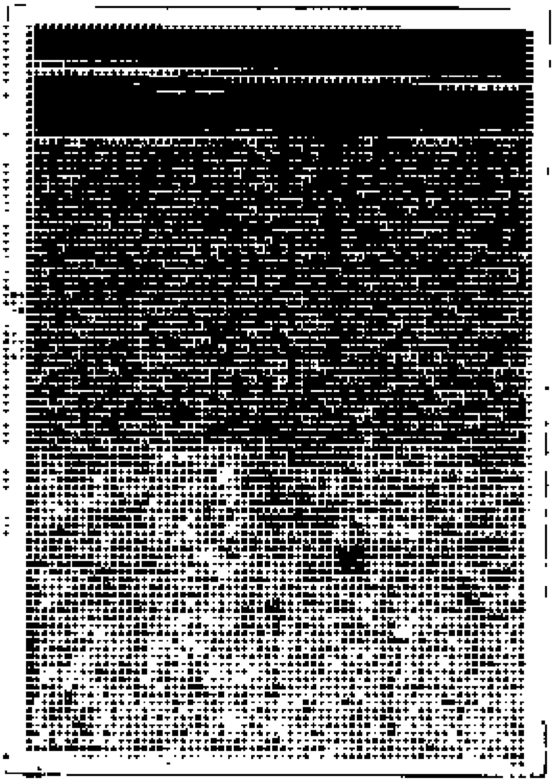


Fig 3.24 Hardness profiles of stainless steel nitrided for 24 hours at various temperatures.

Fig. 3.25 : Nitrided case revealed by nital in high speed steel nitrided at 540°C for 24 hours.



200X

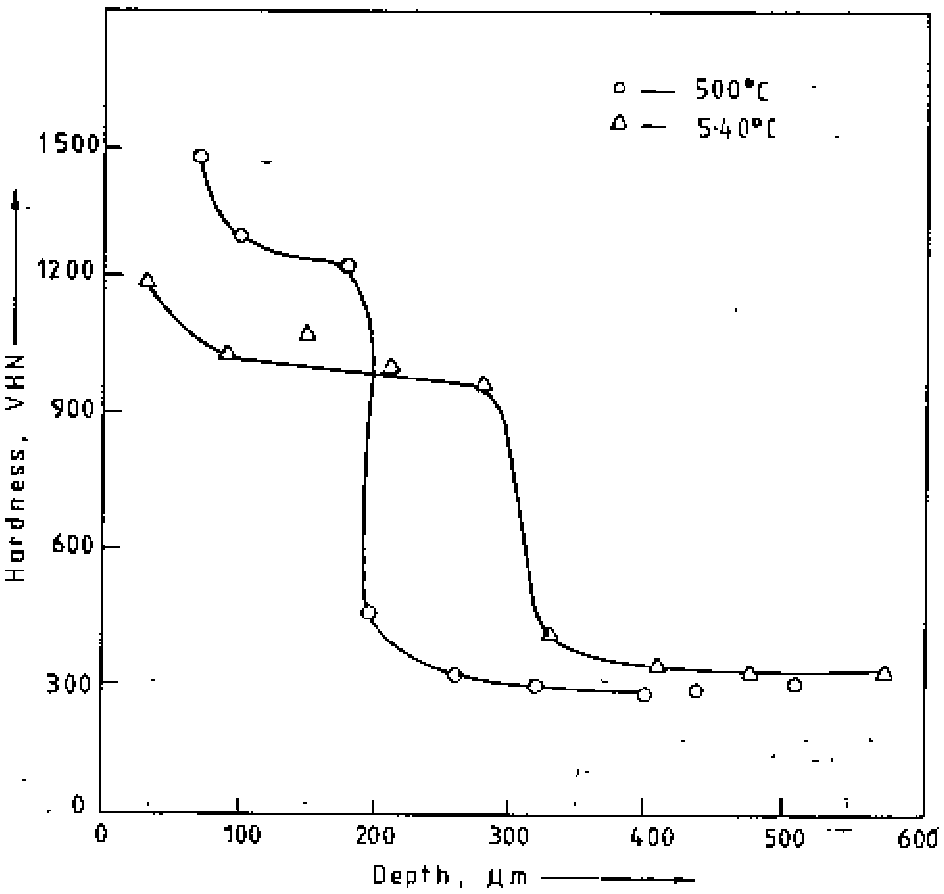


Fig. 3.26 Hardness profiles of high speed steel nitrided for 24 hours at different temperatures

CHAPTER - 4
DISCUSSION

4.1 Compound Zone

A regular, continuous compound zone or white layer forms on the plain carbon steel and the aluminium steel. In stainless steel an irregular compound zone, which appears at places, forms under the present nitriding conditions. No white layer can be found on the high speed steel. These observations are quite in conformity with the fact that the presence of alloying elements particularly, the nitride formers hinder the formation of the compound zone. Aluminium steel contains only a small percentage of aluminium. Hence in this steel hindrance to the formation of the white layer is relatively small. In stainless steel the amount of the nitride former i.e., chromium is quite high, about 18%. Hence in this steel formation of white layer is more difficult. High speed steel contains still larger amount of the nitride former, nominally 18% tungsten plus 4% chromium plus 1% vanadium and in this steel white layer does not form at all under the present nitriding conditions.

The morphology of the white layer is also found to be different on different steels. In plain carbon steel the outer portion of the white layer i.e., the e-phase is found to be quite porous. Porousness of this phase is found to increase with the increase of nitriding temperature as well as time.

The white layer formed on the stainless steel is quite irregular, only a few grains appear at places. However, the white layer formed after 46 hour-nitriding is somewhat continuous especially at the corner of the specimen and is relatively thick. This layer is also found to contain cracks. Billion and Hendry (15) nitrided AISI 316L stainless steel and have shown that cracks developed in the white layer of austenitic stainless steel if the former consist predominantly of γ'. This is because the unit cell dimension of the γ'- phase is longer than that of the austenite form which it forms. The white layer consisting mainly of γ'- phase thus grows in compression but when the layer grows to a considerable thickness stress relaxation occurs at the free surface. A stress gradient is therefore established across the white layer and this results in a bending force that tends to lift the layer upward and causes cracking. In the present investigation, it is believed that the white layer formed on AISI 304 stainless steel consists predominantly of γ'. The occurance of γ' as the predominant phase in the white layer is due to the presence of considerable amount of nickel in this steel. Because it has been found (15) that nickel stabilizes γ'- phase in the white layer.

It is found that at all nitriding temperature and time the total thickness of the white layer formed on the mild steel containing 0.1% carbon is higher than that formed on the medium carbon steel containing 0.44%C. Recently Haque (16) has shown that keeping the percentage of all other elements in steel constant, increasing carbon content increases the total thickness of the white layer. But in the present investigation total thickness of the white layer is found to be lower in steel containing higher amount of carbon. This apparent anomaly is thought to be due to the presence of variable percentages of other elements particularly manganese and silicon in these steels. The percentages of manganese and silicon in mild steel are 0.77 and 0.037 whereas in medium carbon steel these are 1.26 and 0.17 respectively. So it seems that higher percentages of these elements are responsible for the lower value of the total white layer thickness in medium carbon steel. Further, the measurement and comparison of the thickness of the constituent phases in the white layer of the two steels show that the thickness of ε is lower and that of γ' is higher in the medium carbon steel. The thickness of γ' in the medium carbon steel nitrided at a higher tempeature for a longer time period is quite high which is not expected as far as the fe-N or fe-N-Cm system is concerned; because the γ'- phase is stable only within a narrow range of composition. Billon and Hendry(15) have found that nickel, when present in steel, dissolves in γ' thus stabilizing it. So, analogously, it is thought that the presence of higher amount of manganese and silicon in medium carbon steel stabilizes the γ'- phase and increases its thickness. This implies that manganese and silicon help decrease the thickness of the ε - phase to a far greater extent such that the total thickness of the white layer in the medium carbon steel is lower. However, investigation need to be carried out to confirm this explanation. The growth of the white layer as a whole as well as the individual phase in it are found to be parabolic with time which implies that their growth is diffusion controlled.

4.2 Different Nitrided Zones

It has been established that when a commercial nitriding steel is nitrided, a compound zone, a nitrided layer, a grain boundary phase within the nitrided layer and a carburized layer form (13). Below the compound zone lies the nitrided layer in which alloy nitride precipitates of submicroscopic sizes are present. It has been found that the alloying elements such as chromium in a nitralloy remain as carbides in the quenched and tempered state. During nitriding, when nitrogen reaches these alloy-carbides, the latter decompose and precipitates of alloy nitrides form, and set the carbon free. A part of this carbon leaves the steel through the surface (17), a part precipitates as cementite at the prior austenite grain boundaries in the nitrided layer and the rest is found to migrate and form the carburized layer ahead of the nitriding front.

In the present investigation no grain boundary phase and carburized layer are found in the nitrided plain carbon steels. This is what is expected. In plain carbon steel no stronger nitride formers like chromium, molybdenum etc. are present. So mostly iron nitride is formed in the nitrided layer. On entering the steel, nitrogen finds enough free iron atoms to form iron nitride and thus the carbon which is present as the iron carbide in the quenched and tempered plain carbon steels remainsundisturbed. No carbon is, therefore, allowed to form the grain boundary phase or carburized layer. Although in the plain carbon steel there are some silicon and manganese, which are very weak nitride former, these can not contribute to the formation of the grain boundary phase and the carburized layer; because silicon and most of the manganese remain in solution in the quenched and tempered plain carbon steel and hence can form nitride without disturbing carbon.

It has already been stated that in a nitrided nitralloy the nitrided layer, which occurs below the white layer, is actually a zone with enhanced precipitation of alloy nitrides e.g., chromium-, aluminium-, molybdenum- nitrides etc. In the plain carbon steel, which contains no strong nitride former, the region below the white layer contains precipitate of iron nitride and possibly some manganese and silicon-nitride.

Neither of the etchants used in the present study could reveal this region clearly. However, nital etches shows a dark region below the white layer. This dark region which is actually a part of the nitrided layer is believed to be nitrogen-pearlite.

The absence of the grain boundary phase and the carburized layer in the aluminium steel can be explained in the following manner. Aluminium is not a carbide former, it remains in the quenched and tempered steel in solid solution. So, during nitriding the formation of aluminium nitride in the nitrided layer does not involve liberation of carbon for forming the grain boundary phase and the carburized layer. In the aluminium steel the percentage of carbon is very low. As a result water quench could not produce martensite in this steel. So, in the quenched and tempered state this steel consists mostly of ferrite. During furnace cooling after nitriding, the super saturated nitrogen ferrite below the white layer decomposes. As a result of this decomposition the metastable nitride, $Fe_{16}N_2$ forms which was found to appear in the microstructure of the nitrided aluminium steel as precipitates with the characteristic needle shape.

In stainless steel a large amount of chromium is present. Nitriding of such a steel containing a high percentage of nitride former proceeds by the advance of a hard, sharply defined nitrided case because all the available nitride former at the nitriding front must be consumed before nitrogen can go deeper into the steel. On etching the nitrided case is clearly revealed. No grain boundary phase and carburized layer are found in this steel. Although a small amount of chromium is used up in precipitating carbon as chromium carbide during nitriding, the temperature of which being within the sensitizing range, considerable amount chromium still remains in solution. The chromium in solution can form nitride as long as nitrogen is available, so there is no need for the dissociation of chromium carbide to supply chromium for the formation of chromium nitride. Thus no carbon is set free for producing the grain boundary phase and the carburized layer. The growth of the nitrided case is found to be parabolic with time. This is quite in agreement with the nitriding model suggested by Light foot and Jack (11). The growth rate of the nitrided case in stainless steel is found to be lower than that of the nitrided layer in nitralloys. This is expected, because according to the above model thickness of the case decreases as the amount of alloying element increases. High speed steel is higly alloyed with strong nitride former. So, it is natural that this steel, like the stainless steel, develops a hard, sharply defined nitrided case. In the quenched and tempered condition only a fraction of the alloying elements remains as carbide and the rest which remains in solution can directly form the nitrides without disturbing the carbon. So it is logical that this steel does not form the grain boundary phase and the carburized layer.

4.3 Precipitation of a New Phase

The formation of a new phase below the γ' phase of the compound zone has already been detected and described in section 3.1.2. This phase formes in mild steel when nitrided at 580°C and it is harder than the γ' and ε of the white layer. The thickness of this layer increases with nitriding time (Table 3.8). This phase can easily be detected by using etching technique. The reason for the formation of this new phase in this steel is not known. No information is available regarding the precipitation of such phase in any steel. It is assumed on the basis of the information of Hudson and Perry (18) that this phase may be austenite. In medium carbon steel having 0.55% carbon nitrided under the same condition this phase was absent. With higher percentage of carbon the austenite precipitation is reported (19) to be the easier. Hence the new phase in 0.1% carbon steel may not be the austenite phase.

4.4 Development of Hardness and Hardness Profile

It has already been described that a compound zone forms on the plain carbon steel and below this zone is the zone containing nitrogen saturated ferrite mixed with pearlite/carbide. So there is little possibility of developing higher hardness below the white layer. The high hardness region on these steels, therefore, would be the compound zone. The compound zone of the medium carbon steel is harder than the mild steel. This is because higher amount of carbide is incorporated in the compound zone of the medium carbon steel. Of course, the compounds of manganese also contribute to the high hardness of this zone. Although the hardness versus penetration distance curve in plain carbon steel is very steep at the white layer-nitrided layer interface, the curve is shallow at the interface between the nitrided layer and the core. This is quite reasonable; because in these steels there is no strong nitride former as a consequence of which high hardness is not developed in the nitrided layer. In aluminium steel the white layer is harder than that of the mild steel. It is thought to be due to the presence of alloy nitrides in this compound zone. Below the white layer there is a high hardness region; however, its hardness is lower than that of the white layer. The higher hardness of this region as compared to that in the plain carbon steel is due to the formation of aluminium nitride. The higher steepness of the hardness profile at the interface between the nitrided layer and the core in this steel is also due to the presence of aluminium nitride in the nitrided layer. It is found that the development of hardness in this nitrided layer formed at a lower temperature e.g. 500°C is poor. However, at higher temperatures e.g. 540° and 580°C development of hardness is considerable. This, it is believed, is due to the fact that nucleation of aluminium nitride is difficult at lower temperatures.

In stainless steel, a steep hardness gradient developed under all nitriding condition. This is likely to happen. Because the amount of chromium in stainless steel is quite high, so there is a sufficiently strong interaction between nitrogen and chromium and the nucleation of chromium nitride is easy at the temperatures used in the present investigation. As a result the nitriding reaction in stainless steel proceed by the formation of a hard uniform subscale and this subscale advances into the material developing the steep hardness profile. It is found that the hardness developed in this steel is considerably higher than that developed in a commercial nitralloy. The maximum hardness developed in stainless steel in the present investigation is 1400 VHN whereas the maximum hardness of the nitrided case of a conventional nitralloy is usually 1000-1100 VHN. The total amount of nitride former in stainless steel is considerably higher-than that in a nitralloy. Therefore, the volume fraction of the nitride particles which are responsible for increased hardness is higher in the nitrided case of stainless steel. This is the reason of increased hardness of the nitrided case of this steel. It can also be found that the hardness of the nitrided case depends on the nitriding temperature as well as time. At lower nitriding temperatures maximum hardness is obtained after a longer time period while at higher temperatures it is obtained after a shorter nitriding time. This is logical. Because maximum hardness is obtained when the nitride particles reaches a critical size. At lower nitriding temperatures it takes time for the particles to grow to the critical size whereas at higher nitriding temperature critical size is reached at the earlier stage of nitriding.

It is found that surface hardness of the nitrided medium carbon steel is lower than the maximum hardness obtained in the nitrided case. The explanation of this difference in hardness lies in the fact that at the surface occurs the porous and softer ε-phase. Below the ε-phase is the dense and harder γ' phase on which the maximum hardness occurs. So when the surface hardness is measured, the indentor sinks into the ε-phase and indicates its hardness. The difference between the maximum hardness and the surface-hardness increases with the increase of nitriding temperature. This is because the porosity and softness of ε phase increases with temperature. In aluminium steel the maximum hardness and the surface hardness are nearly the same. The reason is that in this steel the white layer on which the maximum hardness occurs is quite dense and have nearly the same-hardness across its cross section.

From the above discussion on the surface hardness versus maximum hardness, it may be concluded that surface hardness may sometimes give a fallacious result particularly on samples having a thick and porous phase at the surface. The surface hardness of a nitrided sample thus may not be the maximum hardness value that develops through nitriding. In order to get the maximum hardness of a nitrided specimen one should measure the hardness along the cross section and not on the surface. It should be noted that the porous phase of the compound zone is very often brittle and it spalls in no time in service leaving a harder surface beneath it.

4.5 Implication of Nitriding of Locally Available Steels

Large number of spare parts of many of the industries in Bangladesh are at present being imported. Attempts have been made by various concerns to manufacture these spares using local material and technology. It has been reported that many spares can be fabricated with the local know-how but due to the scarcity of proper material and heat treatment know-how, these spares can be used for a shorter period as compared to that of the imported ones. The only surface treatment the manufacturers usually apply to their spares is curburizing followed by hardening. The maximum hardness that can be attained by such a treatment on plain carbon steel is around 750 VHN. But by nitriding one can achieve a hardness of upto 900 VHN in plain carbon steel. So if spares are required with high hardness and wear resistance , steel w higher carbon can be used after nitriding treatment. For a still higher hardness, stainless steels can be used after nitriding, which develops a hardness value as high as 1400 VHN.

In most of the workshops high speed steel is used as a cutting tool and it has been shown in the present investigation that by applying nitriding treatment, the surface hardness can be increased to a value which is double to that of the hardened state. There is, therefore, a scope to increase the service life of high speed tools through nitriding treatment.

CHAPTER - 5

5.1 Suggestions for Future Work

1. The new phase and other precipitates that form in the white layer of mild steel nitrided at 580°C should be identified and the conditions under which they form should be establised.
2. Effect of silicon and manganese on the nitrided case particularly on the white layer of the plain carbon steel should be systematically studied.
3. Service behaviour of nitrided tool steel should be investigated.

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