

DEPARTMENT OF METALLURGICAL ENGINEERING
BANGLADESH UNIVERSITY OF ENGINEERING & TECHNOLOGY
DHAKA-1000
BANGLADESH

**A COMPARATIVE STUDY OF ION NITRIDING BEHAVIOR OF
STAINLESS STEELS.**

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



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MD. ZAHEDUL HUQ

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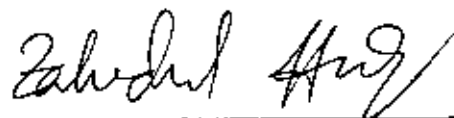
DECLARATION

This is to certify that this work has been carried out by the author under the supervision of Prof. A.S.W. Kurny, Department of Metallurgical Engineering, BUET, Dhaka and it has not been submitted elsewhere for the award of any other degree or diploma.

Countersigned




Supervisor



Author

The undersigned recommend to the Department of Metallurgical Engineering the acceptance of the thesis, " A COMPARATIVE STUDY OF ION NITRIDING BEHAVIOR OF STAINLESS STEELS", submitted by Md. Zahedul Huq, B. Sc. Engg. (Metallurgical) in partial fulfillment of the requirements for the degree of Master of Science in Engineering (Metallurgical).

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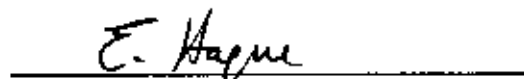
Prof. A.S.W. Kurny
Dept. of Metallurgical Engg.
BUET, Dhaka.

Chairman
(Supervisor)

2. 

Head
Dept. of Metallurgical Engg.
BUET, Dhaka.

Member

3. 

Prof. Ehsanul Haque
Dept. of Metallurgical Engg.
BUET, Dhaka.

Member

4. 

Dr. A. S. M. A. Haseeb
Assistant Professor
Dept. of Metallurgical Engg.
BUET, Dhaka.

Member

5. 

Prof. M. Ibrahim
Dr. Rashid Professor
BUET, Dhaka.

Member
(External)

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Department of Metallurgical Engg.
BUET, Dhaka.

The Author
May 1993

ABSTRACT

Stainless steels are well known for their good corrosion resistance, but the friction and wear characteristics of these materials can present problems in certain industrial and prosthetic environments. These difficulties can be offset considerably by enhancing the wear resistance of these steels through a surface nitriding process. This investigation on nitriding of stainless steels of the austenitic and the ferritic type was undertaken to determine the ion nitriding behavior of these steels. A smaller number of samples were also nitrided in ammonia gas atmospheres.

Ion nitriding of austenitic and ferritic types of stainless steels was carried out in 25%N₂:75%H₂ in the temperature range of 450⁰-500⁰C for a duration of 0.5 to 2 hours. Gas nitriding of the same steels was carried out in 100% ammonia gas in the temperature range of 450-550⁰C for a time period of 8 hours.

Microstructure of the nitrided case has been studied by using various etching reagents. A well defined nitrided layer was found to have formed on both types of stainless steels. No white layer could be detected on the samples after both ion and gas nitriding. Both types of nitriding showed an increase of case depth with

increasing treatment temperature. The higher case depth values were observed in ferritic stainless steel than in austenitic stainless steel. During ion nitriding surface hardness of ferritic stainless steel was found to increase upto 475⁰C and then decrease. While in austenitic stainless steels surface hardness values showed an increasing trend upto 500⁰C . On the otherhand in gas nitriding surface hardness values on both types of stainless steels showed an increase upto 550⁰C.

X-ray diffraction pattern showed the presence of CrN, γ' phases in the nitrided layer. X-ray pattern also showed an increase in lattice parameter of both nitrogen ferrite and nitrogen austenite phases, which has been attributed to the N₂ saturation. Formation of new phases and distortion of lattice parameters caused by the absorbed nitrogen are responsible for the increase in hardness.

Ion Nitriding in a mixture of N₂ and H₂ gases produced a nitrided layer similar to that formed during nitriding in ammonia. However ion nitriding has been found to be faster than nitriding in ammonia gas atmospheres.

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Chapter I

INTRODUCTION

1.1 Nitriding Processes

The production of hard surfaces on machine components with improved fatigue, wear and friction resistance, together with a tough ductile core is a persistent technological problem. Processes known as carburising, nitriding, cyaniding have been developed to attain this highly desirable combination of properties.

Nitriding is a well established commercial process for producing extremely hard wear resisting surfaces on low alloy steels. The main advantages of nitriding over case carburizing are (i) a far greater surface hardness is achieved (ii) the nitrided layer has a greater resistance to softening at elevated temperature (iii) because of the relatively low reaction temperatures (500-565°C), surface hardening in nitriding is achieved without any appreciable loss of strength within the previously tempered core and (iv) distortion and dimensional changes in the nitrided components are reduced to a minimum.

Nitriding is more complex, more costly and more time consuming process than the other surface hardening techniques. Even then it has received attention from both the scientific and the industrial communities due to the superior properties it offers. As a result numerous techniques of nitriding have developed. Of these nitriding in ammonia, in molten cyanide salts and in ionised gases have gained commercial importance.

During nitriding in ammonia gas, atoms of nitrogen are formed through the dissociation of ammonia at the metal surface, where they dissolve in the iron. Since nitriding is conducted at a temperature below the eutectoid temperature, the absorbed nitrogen begins to saturate α -iron at the surface of the workpiece. When maximum saturation of the α -phase (Fig. 1.1) for the given temperature is achieved, the next phase (γ') stable at the temperature begins to form. Upon further saturation with nitrogen, the ϵ -phase begins to form at the surface. Nitrides of alloying elements are obtained in the nitriding of alloy steels. Highly dispersed particles of these nitrides interlock the dislocations and thus result in a considerably increase the hardness of the nitrided layers¹.

A layer of compounds of nitrogen is obtained on the surface layers of nitrided steels. This layer is also known as white layer since it does not etch with the common reagent and therefore appears

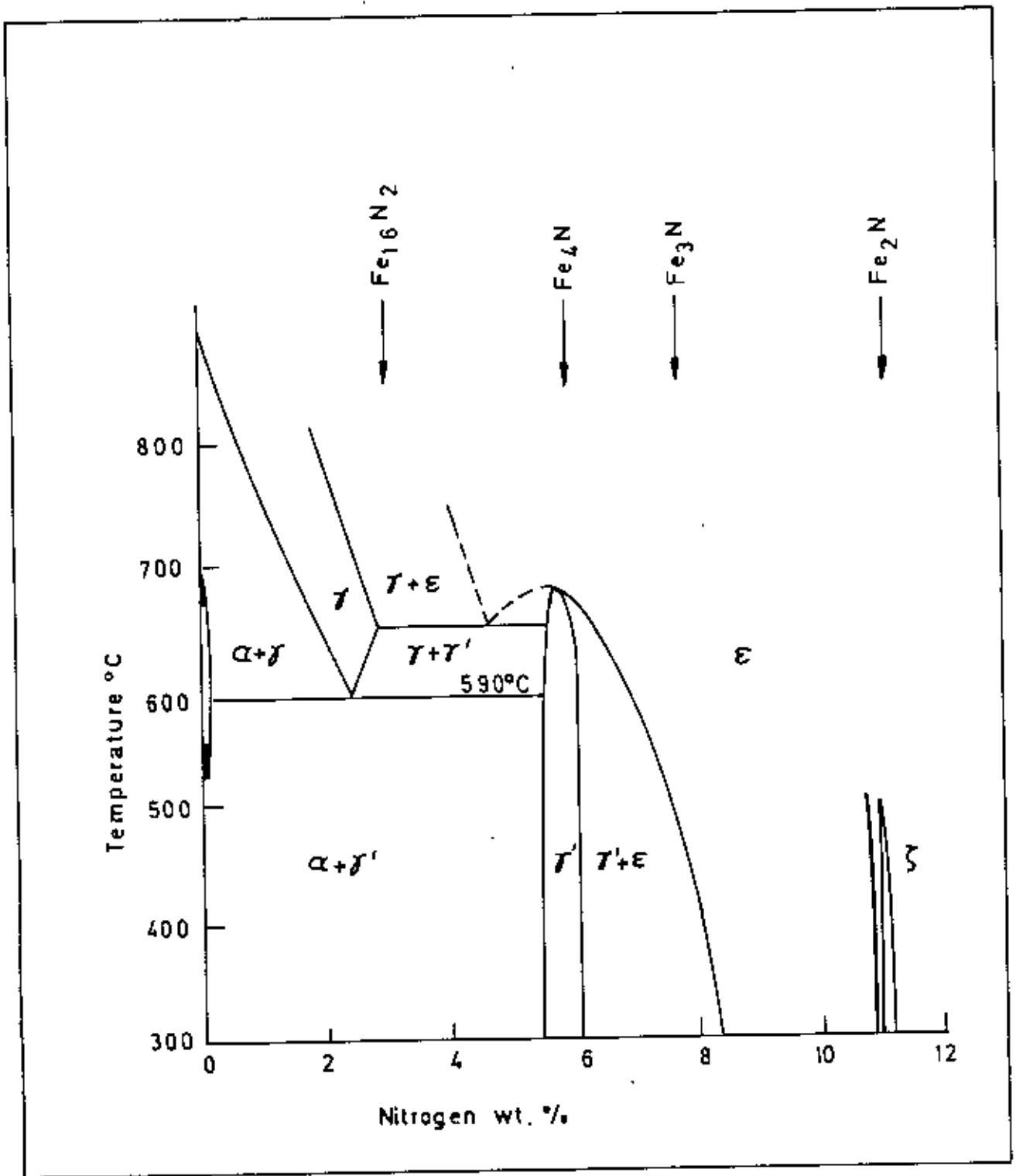


Fig. 1:1 Part of the equilibrium phase diagram for the Fe-N system

white under the microscope. The process of nitriding in ammonia provides very little control of the formation of this compound layer. In most cases a layer consisting of γ' nitride (face centered cubic) and ϵ -nitride (hexagonal) forms and due to the mismatch in structures, the white layer formed during gas nitriding is very brittle^{2, 3}.

Another conventional nitriding method involves heating in molten cyanides and is widely employed by the automotive industry. The salt bath produces a surface layer saturated with both nitrogen and carbon and gives excellent wear resistance. Unfortunately, salt baths are very toxic and environmentally hazardous, making disposal of the spent salts a great problem. Moreover, nitriding in molten salt baths depend, to a large extent, on the composition of the bath and since the composition of the bath changes continuously through oxidation, it is difficult to duplicate exactly the heat treatment conditions in most salt bath processes.

The first patent on ion nitriding was issued as early as in 1930⁴. Even then ion nitriding is a new process as far as its industrial applications are concerned. In the last few years the process has been getting increasing attention in all developed countries. An ion nitriding unit consists of a high voltage D.C. power supply, a control package for this power supply, and a gas mixing station where gases are blended in desired proportions. When the D.C.

circuit is completed, a level of 350 volts or greater is applied to a negatively charged workpiece, and the glow discharge state is achieved. The chamber in which ion nitriding is performed has no heating elements and therefore can not be considered to be a furnace.

The positive nitrogen ions produced by the application of a suitable D.C. voltage are attracted by the negatively connected workpiece and reaches the activated work surface instantly. This means that compared with conventional processing ion nitriding has 30 to 50 percent shorter cycle times². Ion nitriding can be performed at temperatures as low as 350⁰C and still achieve the required case depth and surface composition. Ion nitriding produces no toxic byproduct because it does not use any toxic gas. Another advantage of ion nitriding is the fact that the structure of the compound layer can be controlled precisely by manipulating the gas composition resulting in the formation of a monophasic layer which is inherently less brittle³. Gas and salt bath nitriding, by comparison, would have produced a mixed crystal structure that wear comparatively faster and therefore unsuitable for critical applications. Ion nitriding can reduce a manufacturers rejection rate. As for economics, ion nitriding compared to conventional processes has a utility cost saving of about 40 percent². It should be emphasized that ion nitriding is not limited to specific workpieces or sizes of workpieces. The process has been used to

treat pieces 50 feet long and has also handled articles as small as ball point pen tips.

Recent studies on ion nitriding behavior of special steels have indicated this process to be superior to the conventional nitriding processes in both the core properties and the surface hardness achieved^{1, 3, 4-7}.

A very thin film of chromium oxide forms very rapidly on stainless steels and therefore without pretreatment these steels usually do not respond to conventional nitriding in gaseous and liquid media. During ion nitriding ion bombardment effectively cleans the metal surface when the steel is in the nitriding atmosphere and ion nitriding can therefore be an effective technique of treating stainless steels. The activation energies for diffusion of the nitrided case are 47.1 Kcal/mole for ion nitriding and 143.5 kcal/mole for ammonia nitriding⁵. The large activation energy for ammonia nitriding may be related to the difficulty of infuaion of nitrogen into the chromium oxide film present on stainless steel during ammonia nitriding⁵.

1.2 Scope and Aim of the Present Work

The present work involves the study of the ion nitriding behavior of austenitic and ferritic stainless steels. These steels were ion nitrided in an atmosphere consisting of a mixture of 25%N₂ and 75%H₂. The effects were followed by optical metallography, microhardness measurements and x-ray metallography. Nitriding of these steels in ammonia gas atmosphere has also been done and a comparison of the results thus obtained has been attempted.

Chapter II

LITERATURE REVIEW

2.1 The Principles of Ion Nitriding

The principles of ion nitriding have been well published in recent years, particularly by Edenhofer⁵ and Jones et al.².

In this process, the work pieces to be ion nitrided are suspended or placed in the vacuum chamber in such a way that effective electrical isolation is provided. Together with the vacuum pump, the gas distribution system enables the vessels to be evacuated, filled with the appropriate treatment gas and maintained at the required vacuum, usually between 0.1 torr to 10 torr. A d.c. voltage which can be set to any value from about 100 volts to approximately 1500 volts is applied between the work piece to be ion nitrided and the wall of the chamber, the former being connected as the cathode and the latter as the anode. Under this potential difference the molecules and the atoms of the treatment

gas are excited and ionized, producing the typical luminous phenomenon known as the glow discharge. The positive ions of the treatment gas are accelerated towards the negatively connected work piece and hits its surface with tremendous kinetic energy. The release of this energy heats the work piece up and the ions are occluded into its surface. Thus the treatment chamber does not require a separate heating system.

Ion nitriding can be carried out either in pure nitrogen or in mixtures of nitrogen with hydrogen or suitable hydrocarbons. Gas consumption during processing is very modest due to the low pressure employed. The electrical units are equipped with current and voltage control elements as well as a high speed breaker system to control unstable discharge phenomena.

The temperature of the work piece is measured with the aid of thermocouple and regulated by means of a controller by varying the power output of the electric unit. The treatment temperature is, in most cases, set between 400° and 580°C depending on composition and structure of the material to be treated as well as the stress which the work piece will have to resist.

Treatment times vary from 10 minutes to a maximum of about 20 hours, depending on the grade of steel and the required depth of hardening.

2.2 Glow Discharge Fundamentals

The glow discharge used for plasma treatment occurs when an external voltage is applied between two electrodes, positioned within a gas mixture at some suitable partial pressure. The work piece to be plasma treated is connected to the negative electrode. The voltage source supplies a controlled variable voltage. A current limiting resistor permits the current to be independently controlled at any voltage level.

In the operation the space between the anode and the cathode is filled to some partial pressure with a gas mixture selected for the process. The glow discharge occurs when molecular elements in this gas mixture are ionized by collisions with electrons travelling from the work piece-cathode to the anode under the influence of the applied electrical voltage. Ionization of the low pressure gas mixture permits a sustained electrical current i.e. negative electrons flow from the work pieces to the anode and more importantly positive ions flow from the ionized gas mixture to the work pieces being treated.

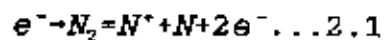
After the gas has become ionized by electrons leaving the surface of the work piece, the newly formed positive ions are accelerated towards the work piece where they combine with the chemical elements of the work surface. If the low pressure gas mixture is

predominantly nitrogen, the work surface can be nitrided by these nitrogen ions. If the gas mixture is a hydrocarbon, the work surface can be carburized.

2.3 Ion Nitriding Chemistry

Plasma treating in a partial pressure of nitrogen has been called glow discharge nitriding, ion nitriding, and plasma nitriding. There are four chemical reactions at a work surface that are believed⁹ to be important when a plasma is used as the source for atomic nitrogen as shown in Fig.2.1

1. Production of ionized and neutral nitrogen atoms by energetic electrons.



2. Sputtering of Fe and contaminants from the work surface by these ionized nitrogen atoms. The impact of nitrogen ions on the work surface dislodges contamination that can then be removed by the pumping system. This effect, called sputter cleaning, removes a significant barrier to nitrogen diffusion through the work surface into the core.

N^+ - work surface = sputtered Fe and sputtered contamination

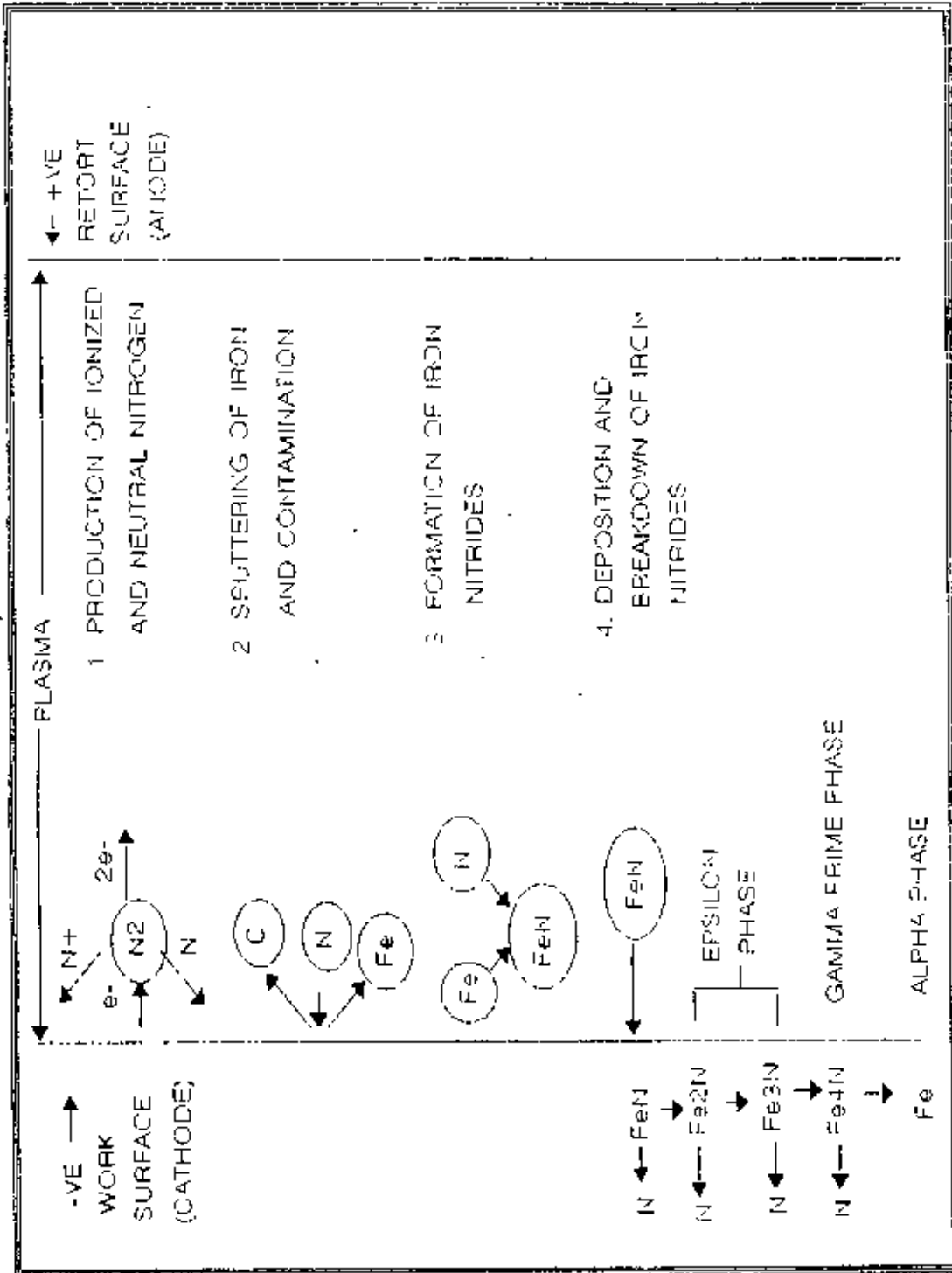
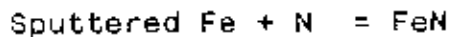
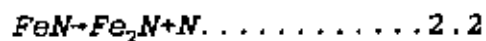


FIG 2.1 SURFACE REACTIONS DURING ION NITRIDING

3. Formation of iron nitrides by the sputtered iron atoms and neutral nitrogen atoms. Although the predominant mechanism of plasma nitriding involves this reaction of iron atoms with nitrogen atoms in the gas phase near the work surface, and then their redeposition on the surface as a chemical compound, there is evidence that sputtering is not the only reaction mechanism. It can be shown that nitriding takes place even when the energy in the plasma is not high enough to cause sputtering.



4. Deposition and breakdown of FeN on the work surface. The FeN produced from these chemical reactions is unstable and under the influence of the continuing ion bombardment from the plasma, it breaks down progressively into the epsilon phase ($\text{Fe}_{2.3}\text{N}$), and into the gamma prime phase (Fe_3N) forming an iron/nitrogen compound zone. At each stage of the breakdown, atomic nitrogen is released either to the plasma or to the work surface for diffusion inward and for the formation of an alloy nitride diffusion zone.



The use of nitrogen for surface treating metals is an established technology. Although the nonreactive nature of nitrogen has made it an important protective atmosphere, its dissociation makes it highly reactive and able to participate in surface treatments to produce high hardness, wear resistance, and corrosion resistance. Hochman¹⁰ has summarized the properties of some typical nitrides.

Nitride	Properties and applications
AlN	Very refractory with good thermal shock resistance and a low coefficient of thermal expansion; very effective as a hardening agent in nitrided steels.
α -BN	Excellent refractory with good electrical resistance; a very good solid lubricant often called "white graphite". Used to contain some highly corrosive acid solutions.
β -BN	Very hard and often used as a diamond substitute; used in the composition of heat-resistant alloys; has excellent potential in tribological applications.
Cr and Fe Nitrides	Very good hardness and wear resistance particularly effective as hardening agents in nitrided steels.

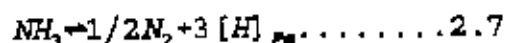
TiN and Ti ₂ N	Good high-temperature materials with thermal shock resistance; good abrasive and tribological materials; very good corrosion resistance.
Si ₃ N ₄	Very good high temperature properties and oxidation resistance. Also it has potential as an electronic material and a high temperature tribological material.

2.4 Gas Nitriding

Gas nitriding is the most widely used 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 525 to 570⁰c. When ammonia comes in contact with the steel surface, the former is catalytically dissociated into hydrogen and nitrogen which is then dissolved in the interstices of iron lattice. The equation for nitriding in ammonia thus becomes

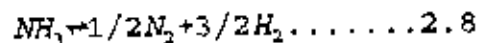


There are two other possible reactions that can occur when ammonia reacts with iron at elevated temperatures. One such reaction is the solid solution of hydrogen.



But it is found that this reaction occurs only to a limited

extent¹¹. The other possible reaction involves decomposition of ammonia to both molecular hydrogen and nitrogen.



However this reaction is also suppressed at least up to a temperature of 600°C when the flow rate of ammonia is high and surface of the specimen is smooth¹².

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 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.

2.5 The Iron-Nitrogen Phase Diagram

In the iron-nitrogen phase system (Fig. 1.1) there are five stable phases viz. α -nitrogen ferrite, γ -nitrogen austenite, γ' -Fe₄N, ϵ -Fe₃N and δ -Fe₂N. Two metastable phases namely α' -nitrogen martensite and α'' -Fe₁₆N₂ also exist in the 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 is iso-structural with carbon austenite but has a wider range of homogeneity and exists down to 590°C.

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 fcc lattice like austenite but the nitrogen atoms are fully ordered. These lattice parameter increases with nitrogen content from 3.783 Å at 5.29% N to 3.793 Å at 5.71% N¹³. 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 Fe₄N and Fe₂N with nitrogen content ranging from 7.1 to 11.0 wt% at the eutectoid temperature. It has a close-packed hexagonal iron atom lattice. Tetragonal ϵ -Fe₁₆N₂ forms as an intermediate precipitation during the tempering of nitrogen martensite or aging of supersaturated nitrogen ferrite.

2.6 Mechanism of Hardening of Nitrided Steels

Many theories have been proposed to explain the hardening caused by nitriding. Fry¹⁴ 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 workers¹⁵, 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, Mo, V, Al 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.

2.7 Advantages of The Ion Nitriding Method Over Gas Nitriding

Ion-nitriding offers several advantages over both of the better known methods of gas and salt bath nitriding. Some are in the area of improved environmental conformance and ease of operation and others relate to increased output and the production of a better

final product. These will now be outlined in greater detail.

At present time there is more concern than there has been in the past about both the influence of a process on the environment and the comfort and welfare of workers in the area. In ion nitriding, mixtures of N_2 and H_2 are used at reduced pressures. The quantities of gas required are very small, so that the gas phase of ion nitriding in general is inexpensive and not hazardous or undesirable for the operators. Gas nitriding on the other hand, consumes large quantities of ammonia gas, releases a considerable quantity of raw gas to the atmosphere, and as a result creates many problems in proper handling and disposal of the gas.

In general, the parts and the work area for ion nitriding must of necessity be clean, which again contributes to a desirable work area for the operators.

The parameters which require control and measurement are temperature, pressure, current and voltage, and these all lend themselves to rather simple modern electronic equipment, so that the process is easily controlled and parameters are easily repeatable. In the ion nitriding treatment chamber, only the work piece is heated. The case of the chamber is held near room temperature by water cooling. This reduces the thermal inertia as compared with conventional furnaces and improves the working

environment.

The penetration rates of nitrogen in ion nitriding have been universally found to be faster than conventional gas nitriding. The so called 'white layer' is thinner in ion nitriding, and therefore much less likely to spall off. There are several parameters which control the amount of white layer formed, the contributors being gas composition, current density and temperature of nitriding.

A major advantage of ion nitriding in terms of cost of operation and time saving in handling is the use of mechanical masking. The glow is unable to penetrate a spacing less than the so-called cathode dark space at a particular pressure. In general this means that masks which fit the work piece with a clearance of about 1/32 inch will adequately mask the enclosed area. By using a low-carbon steel, the mask becomes a part of the work piece and hence heats up uniformly in the glow which then tends to minimize any distortion in the work piece¹⁴. In cases where a hole in a work piece requires masking where the bottom of the hole may be larger than the entrance, a layer of fine iron particles may be used if it is desirable to have the glow cover the area, or a layer of silicon dioxide may be used if no heating is desired⁸. At the completion of the process, the masked areas will appear as bright and shiny as when they were first placed in the vacuum system.

It is generally accepted that the source of fatigue fracture of a work piece is initiated at the case-core transition area. On this basis there should be little difference in the fatigue characteristics of an ion-nitrided and gas nitrided work piece. For nitralloy, this appears to be true, but for AISI 4340 and 4140 there is about 25% improvement in fatigue resistance when ion nitriding has been done¹⁴.

It is generally accepted (16-18) that nitriding is performed at process temperature from 500-575°C. The high end of this temperature range is set by the requirement for ferritic steels that the transition temperature should not be exceeded. The lower limit has probably been established by the dissociation conditions required in gas furnaces. A particular advantage of ion-nitriding is the fact that even at low temperatures of between 350° and 450°C nitrogen saturation of the surface is possible. The white layer formation decreases with decreasing temperature while the reverse is true for gas nitriding¹⁶.

These advantages have lead to the following applications¹⁹:

1. As a substitute for chrome plating for the corrosion protection of shock absorber rods. The ion nitriding operation is pollution free and can be completed in one-third the time required for plating.

2. As a substitute for carburizing and carbonitriding the synchronizer ring in automotive gear boxes. These gears manufactured from chrome-alloy steels were gas carbonitrided to eliminate burring in operation, but growth during heat treatment caused dimensional tolerance problems that caused a high number of rejects. This problem was solved by ion-nitriding.

3. As a substitute for salt bath treatment for rocker arms cam followers. Air pollution and salt disposal problems were eliminated with use of ion nitriding.

Chapter III

EXPERIMENTAL TECHNIQUES

3.1 Materials

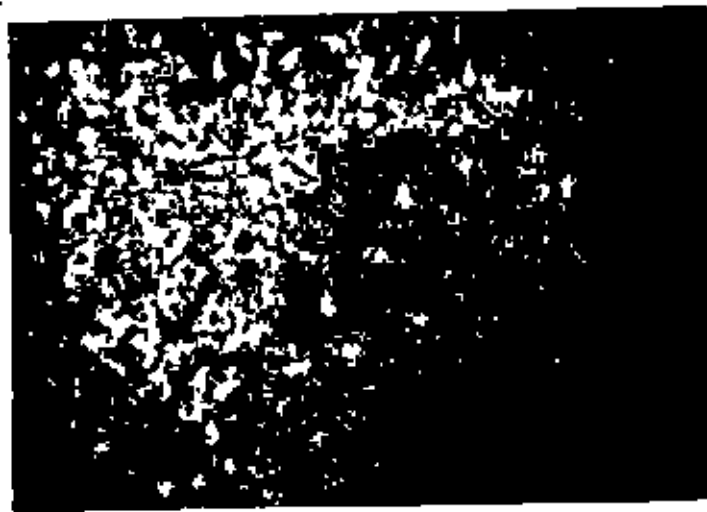
Commercial varieties of austenitic and ferritic stainless steels were used in this investigation. The chemical composition, and microstructure of these materials are given in Table 3.1, and Fig.3.1 respectively.

3.2 Preparation of Specimen For Nitriding

Austenitic and ferritic stainless steels available in the local market were used for these experiments. Discs 3 mm thick and 22 mm in diameter, were used for nitriding. Before ion nitriding the specimens were mechanically polished with abrasive paper and degreased in acetone. The samples used for gas nitriding 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

Table 3.1: Chemical composition of the steels investigated.

Material	%Cr	%Ni
Austenitic stainless steel 304 type	18	8
Ferritic stainless steel 434 type	11.5	-



(a)



(b)

Fig:3.1

- a. Microstructure of ferritic stainless steel before nitriding (etchant: picral-HCl).
- b. Microstructure of austenitic stainless steel before nitriding (etchant: villela's reagent).

cleaned in soap solution followed by cleaning in acetone and washed thoroughly in ethanol and then dried in hot air.

3.3 Nitriding Apparatus

3.3.1 The Ion Nitriding Set-up

Ion nitriding was carried out in a laboratory model ion nitriding set-up. The apparatus was designed and fabricated in the Department of Metallurgical Engineering, BUET. The ion nitriding apparatus consists of a vacuum chamber with a vacuum pumping system, a high voltage D.C. supply, and a gas supply system (Fig.3.2).

The vacuum chamber, where nitriding actually took place is shown in Fig.3.3. A 400 mm long and 80 mm internal diameter pyrex glass tube was used in the fabrication of this chamber. Two stainless steel flanges, with circular grooves for seating the glass tube were fixed to the ends of the glass tube with epoxy resin (araldite). The top flange contains a tapered hole through which a PTFE rod was press-fitted. A hole at the centre of this PTFE cork allows the anode to extend outside the chamber. The top flange was also provided with a port for introducing the treatment gas. The bottom flange contains a 70 mm diameter hole in the centre. This flange is secured to the base plate through allen screws. An O-ring seal has

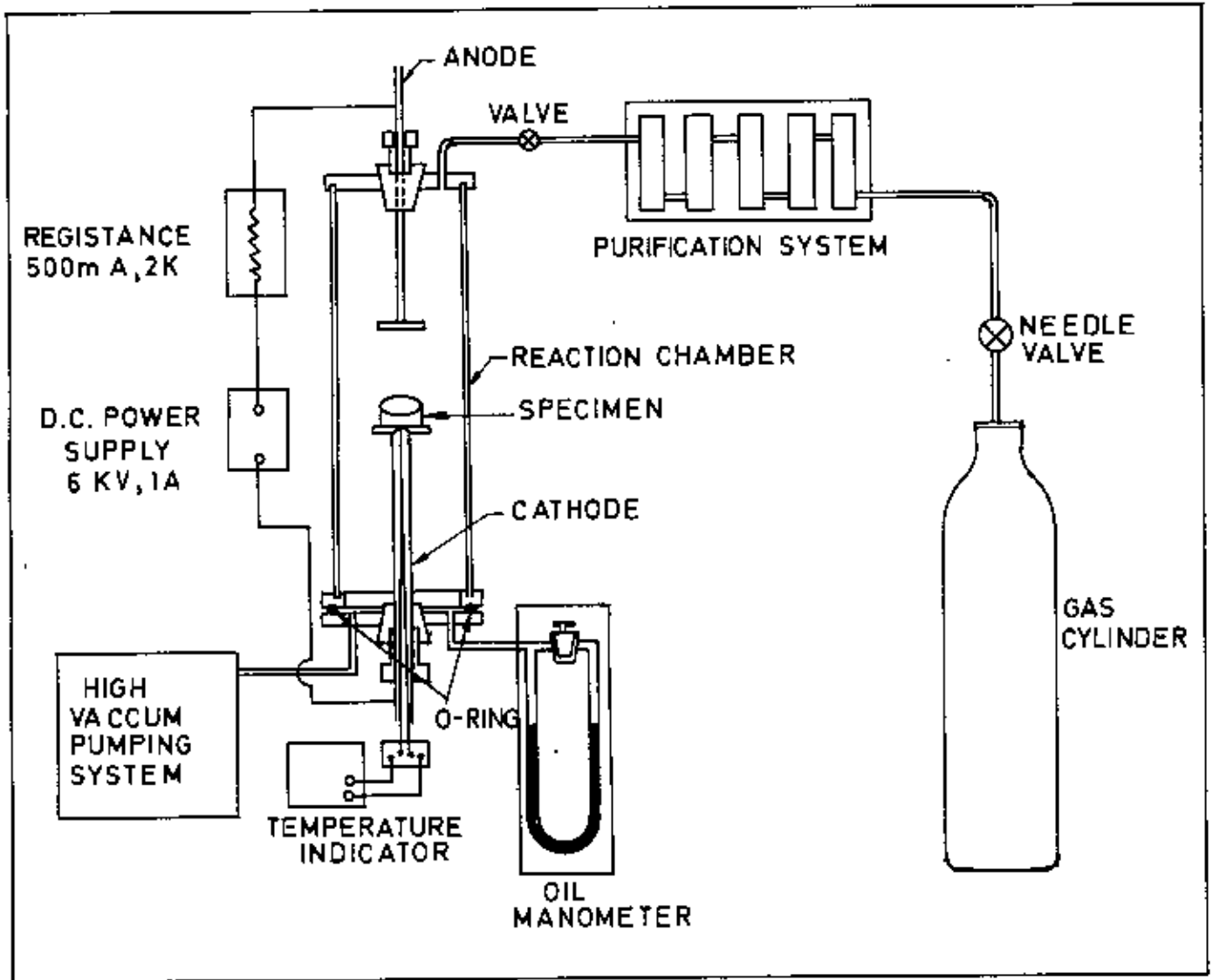


FIG. 3.2 EXPERIMENTAL SETUP FOR ION NITRIDING

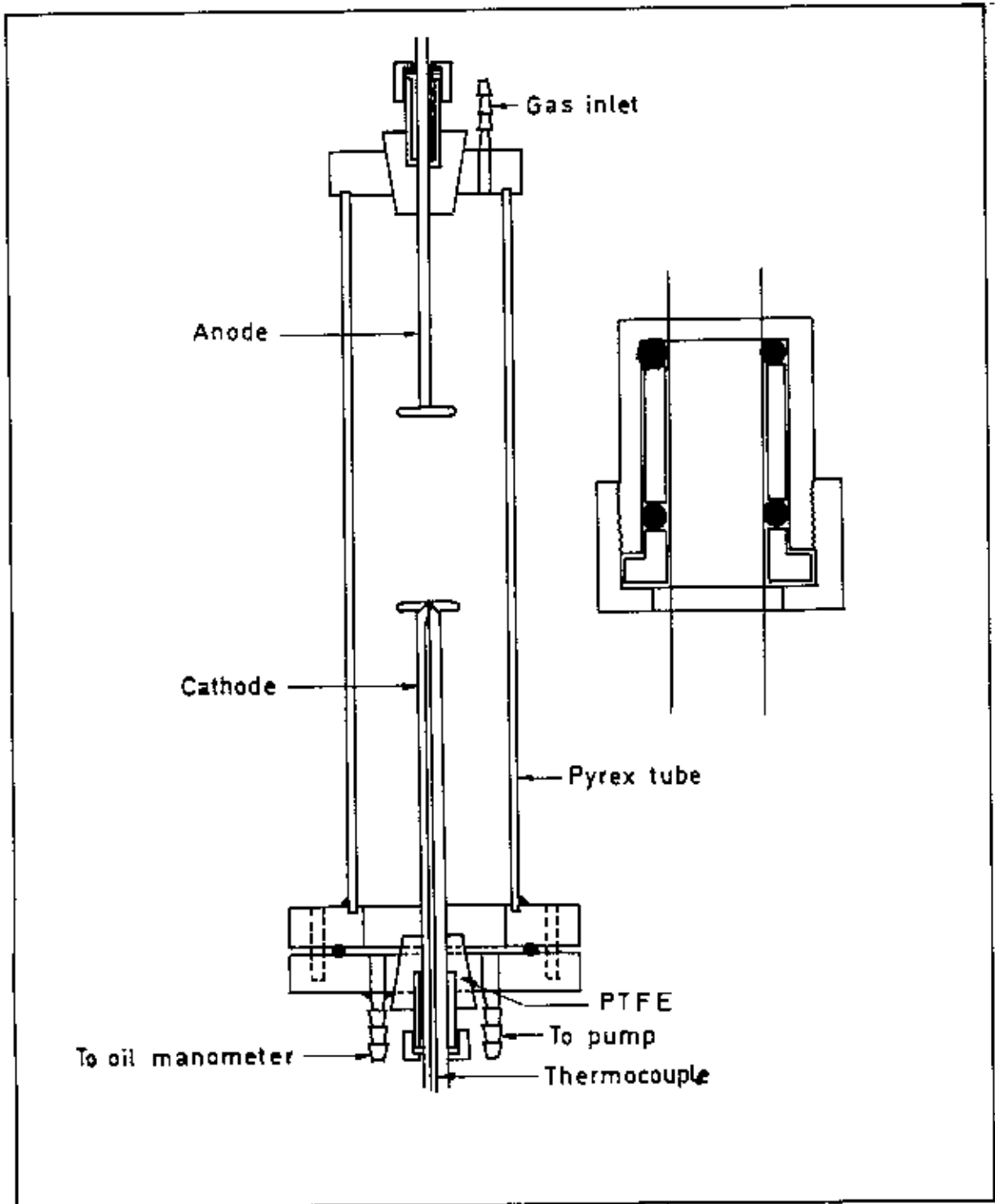


FIG. 3.3 THE VACUUM CHAMBER

been used to seal the opening between the bottom flange and the base plate. The entire chamber can be lifted off from the base-plate to introduce or to remove samples. The base-plate is made of nickel plated mild steel. This plate has a tapered hole at the centre and a PTFE cork was press fitted into this hole. The cathode inserted through a central hole in the PTFE cork, extends beyond the chamber. A stainless steel tube was silver brazed to a stainless steel disc to form the cathode. The edges of both the anode and the cathode were rounded off to prevent concentration of the discharge and consequently turning into an arc discharge. A protected chromel alumel thermocouple was introduced through the tube making the cathode and embedded in the steel disc. The ends of the thermocouple were connected to a temperature-indicator. The base plate is provided with two ports, one of them being connected to the vacuum pumping system and the other to an oil manometer used for the measurement of pressure inside the working chamber.

The pumping system consists of an oil diffusion pump backed by a rotary pump. With these pumps the chamber could be evacuated to an ultimate pressure of 1×10^{-3} torr.

The power supply used (0-6 kv d.c., 1 A) was capable of providing the required voltage and current for the generation of the glow discharge and for the attainment of the nitriding temperature. This was provided with a means of continuous regulation of the voltage.

The circuit diagram of the power supply is shown in Fig.3.4.

Numerous investigators have recommended the use of a mixture of nitrogen and hydrogen for ion nitriding. Hudis²⁰ observed that nitriding is faster in nitrogen-hydrogen mixture than in pure nitrogen. Jones And Martins²¹ indicated that hydrogen in the treatment gas cleans the workpiece surface and accelerate the rate of nitriding. Soccorsy and Ebinhara³ observed that after initial cleaning of the substrate, hydrogen reacted with the nitrogen to form ammonia, limiting the growth of the nitrided layer. On the basis of these observations it was decided to use a mixture of 25N₂:75H₂ throughout this study. Gas mixture of this composition were prepared and supplied by the Bangladesh Oxygen Limited. The gas dispensing system consists of the cylinder containing the treatment gas fitted with a regulator. The gas mixture flowing out of the flowmeter were made to enter into the nitriding chamber. A needle type valve between the flowmeter and the chamber was used to control the flow rate of the gas mixture.

3.3.2. The Gas Nitriding Set-up

A laboratory model gas nitriding set-up was used to carryout nitriding experiments. The set-up has been designed and fabricated in the department of Metallurgical Engineering, BUET. The main feature of the set-up are the gas supply unit and the nitriding chamber (Fig. 3.5).

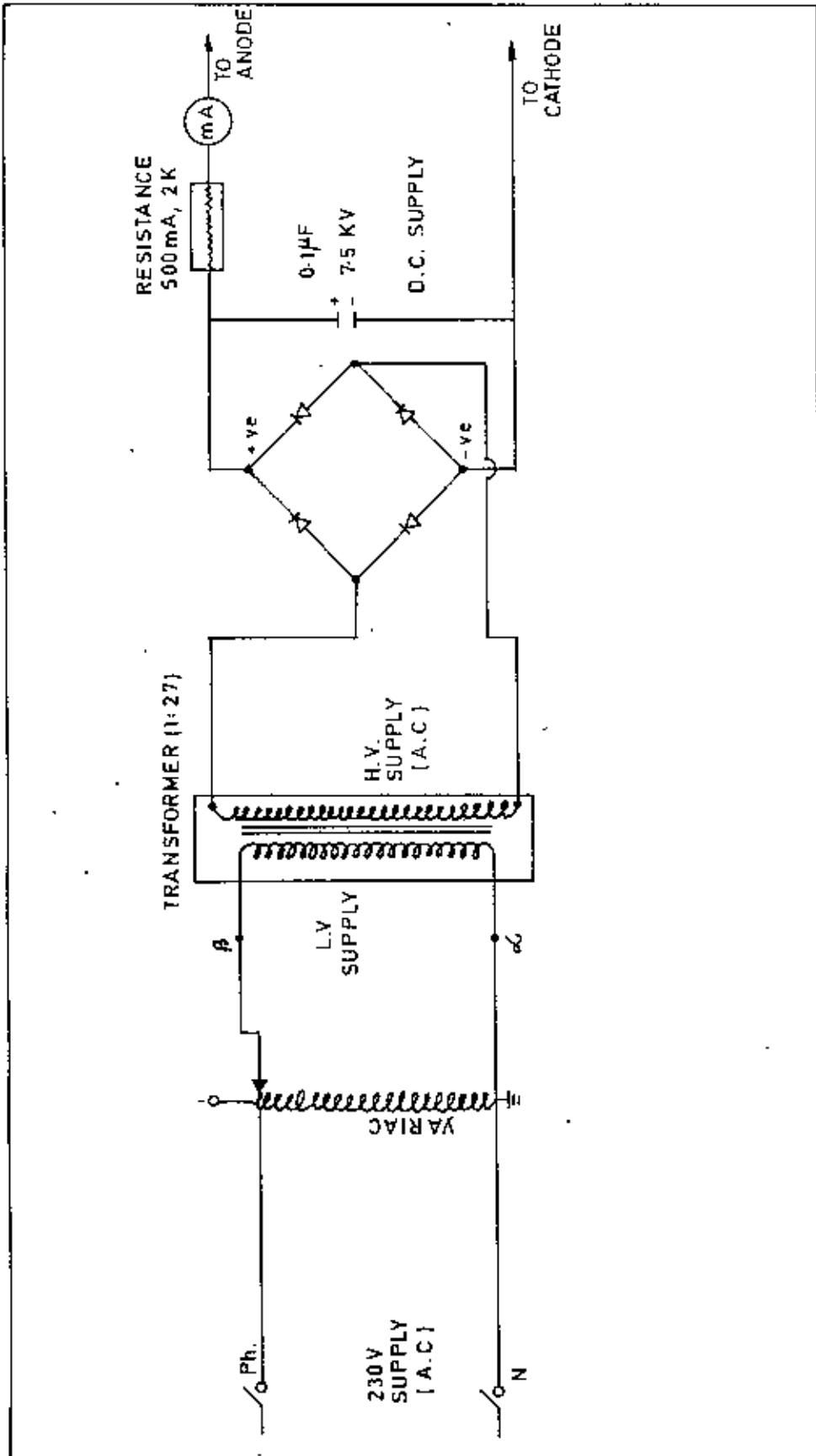


FIG. 3 4 CIRCUIT DIAGRAM OF POWER SUPPLY UNIT

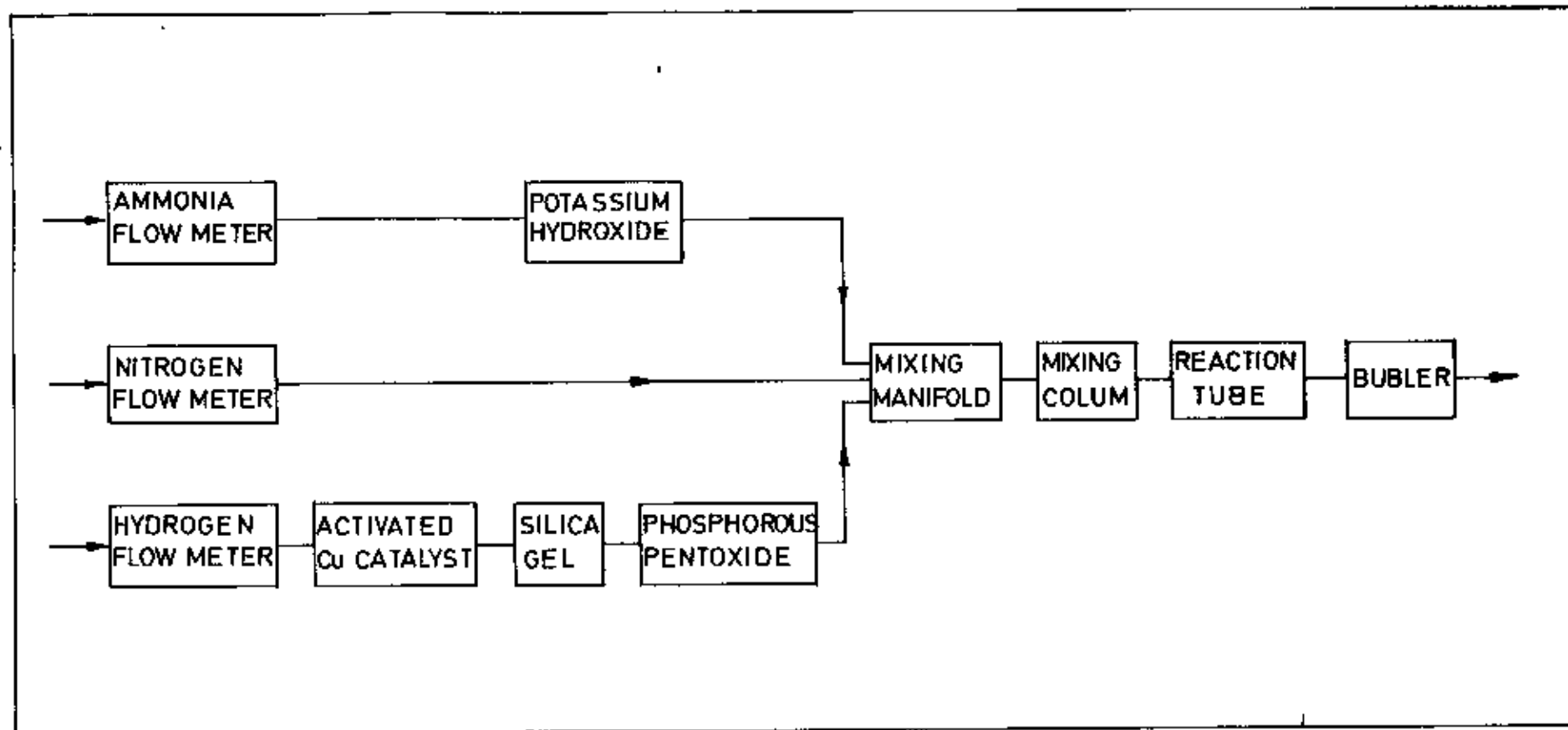


FIG. 3-5 LINE DIAGRAM OF THE NITRIDING APPARATUS

The supply unit supplies the gases to the chamber where nitriding was carried out in 100% NH_3 . Ammonia gas coming out of the cylinder through a regulator was made to enter a constant gas pressure head capillary flow meter (Fig. 3.6). From the flow meter the ammonia gas entered 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 entered into the nitriding chamber. The flow rates of the gases were controlled by the capillary flowmeters (Fig. 3.6); control of flow rates was obtained by altering the head of vacuum pump oil in the blender tubes. Vacuum pump oil was used in the manometer and bubblers because of its low vapour pressure and comparative inertness to these gases.

The nitriding chamber consisted of a horizontal ammonia reaction tube at the middle of which was wound a nichrome wire heating element (Fig. 3.7). The coiled heating wire was covered with fire clay. The wound furnace tube was surrounded by a mild steel shell and the space between the shell and the tube was covered with refractory gorgs. The nichrome wire when connected to power supply provided a constant temperature hot zone of about 20 cm long.

A chromel alumel thermocouple was inserted in to the refractory lining to reach the middle position of the wound tube. The thermocouple was connected to an automatic temperature controller

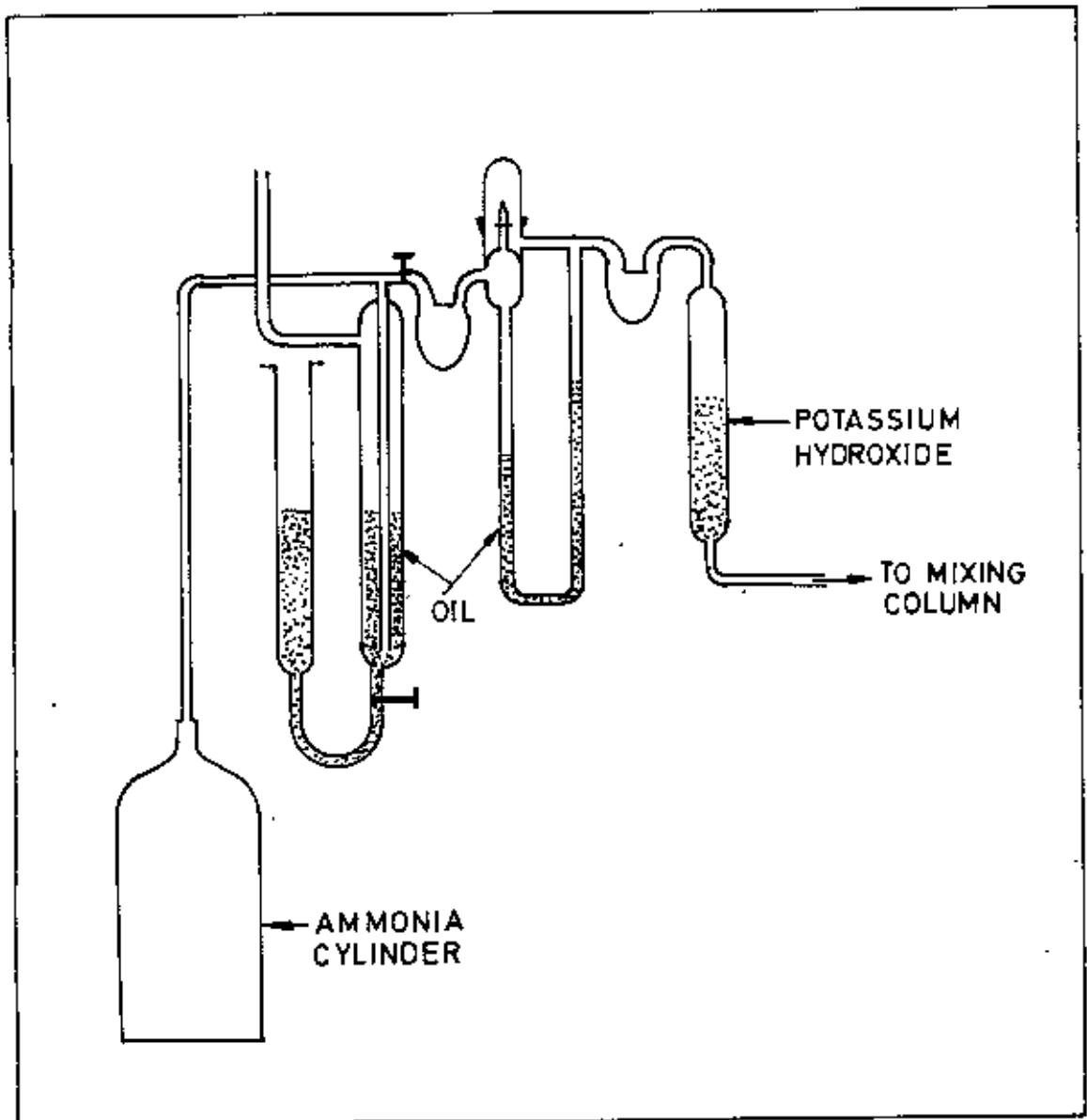


FIG. 3-6 AMMONIA FLOWMETER WITH PURIFICATION TRAINS

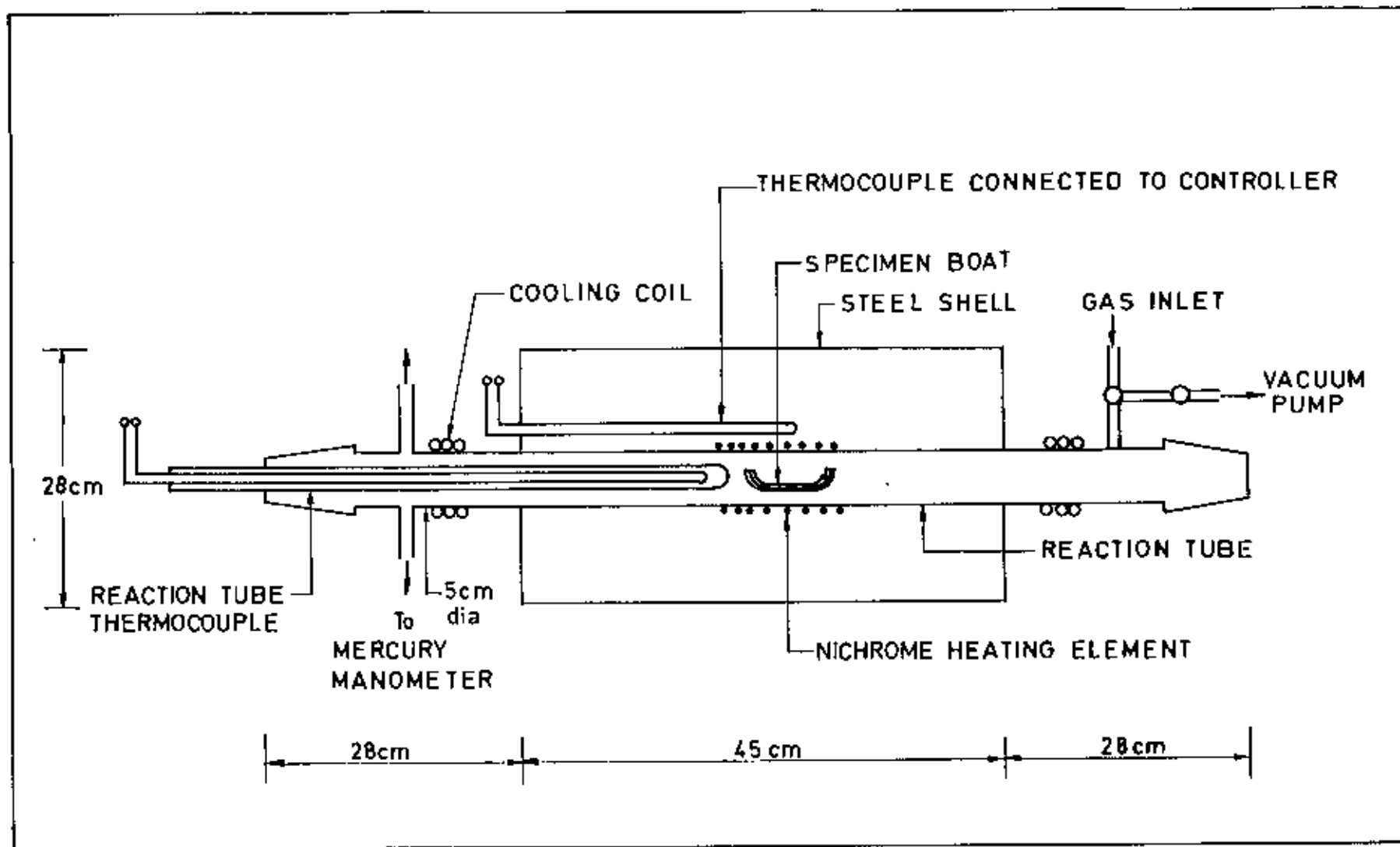


FIG. 3.7 NITRIDING FURNACE

which controlled the temperature of the hot zone to about $\pm 5^{\circ}\text{C}$. Another chromel alumel thermocouple in quartz glass tube was inserted into the hot zone through one end of the reaction tube. This thermocouple was also connected to the display terminals of the above controller which showed the hot zone temperature on a digital display. The other end of the reaction tube was used for introducing the nitriding specimens to the hot zone. A port near this end of the tube was connected to the gas supply unit (Fig. 3.7). The same port was also connected to a vacuum pump of the rotary type so that the reaction tube could be evacuated prior to the nitriding run. Near the thermocouple end of the reaction tube a port for the exit of the exhaust gases was provided. This end was also connected to a mercury manometer.

Copper cooling coils were provided near both ends of the furnace tube adjacent to the joints of the grounded glass connections with the alumina tube to protect the sealing gum (araldite) against heat while in operation.

3.4 Nitriding Operation

3.4.1 Ion Nitriding

After preparations the samples were placed on the cathode. The vacuum chamber was then sealed and evacuated to about 1×10^{-2} torr. During this evacuation the limbs of oil manometer, which was used to measure the system pressure during nitriding, were also evacuated by properly operating stop cork. After the desired vacuum had been reached the diffusion pump and one limb of manometer were isolated and a mixture of 25%N₂ and 75%H₂ was introduced through the needle valve. The pressure inside the chamber, measured with the manometer was maintained at 6 torr, balanced against the mechanical pump. The roughing valve was partially closed at this stage to minimise the consumption of the gas.

The power supply was switched on and the voltage was gradually increased to strike a glow. Since the presence of a tenacious chromium oxide layer on the surface of stainless steel would inhibit nitriding, a sputtering treatment (sputtering gas mixture of nitrogen and hydrogen (1:3), gas pressure 6 torr, d.c. voltage of 900V, current 200 ma, time 10sec) was given to remove the oxide and to expose the fresh surface of the sample for nitrogen ion bombardment. The voltage and the current was adjusted to maintain

a constant nitriding temperature. The temperature was read off on a temperature indicator. At the end of predetermined time period at the desired temperature the power supply was switched off and the specimen was allowed to cool to room temperature in the reaction chamber. Treatment gas (25%N₂ and 75%H₂) was allowed to flow through the reaction tube during the cooling period to prevent oxidation due to leakage of air. After cooling the workpiece was taken out and stored in a desicator.

3.4.2 Gas Nitriding

After preparation 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 specimen was allowed to cool to room temperature in the reaction tube. Ammonia gas was allowed to flow into the reaction tube during the cooling period to prevent oxidation due to leakage of air. After cooling, the reaction tube was evacuated and then purged with nitrogen. The samples were then taken out and stored in a desicator.

The treatment conditions for ferritic and austenitic stainless steels are presented in Tables 3.2 and 3.3.

3.5 Methods of Investigation

3.5.1 Optical Microscopy

The nitrided specimens were cutoff into small pieces at right angles to the nitrided surface by using a silicon carbide disc cutter with copious flow of water. These were then mounted in thermosetting resin in such a way that only the transverse section is revealed. The specimen were then prepared for optical metallography by using standard techniques. Vilellas reagent and picral-HCl were used as etchant to reveal the structure of steels. The microstructures were observed and photographed by using optical microscopy and micrography.

List of etching reagents are shown in Table.3.4.

3.5.2 X-ray Metallography

The phase composition of the nitrided layer was determined by means of x-ray diffraction, using a diffractometer with CuK_α radiation. The operating condition of x-ray diffractometer is shown in Table 3.5.

Table 3.2: Ion nitriding conditions of the steels investigated.

Material	Temperature °C	Time of treatment(Hr.)
Ferritic stainless steel	450	0.5, 1.0, 2.0
	475	0.5, 1.0, 2.0
	500	0.5, 1.0, 2.0
Austenitic stainless steel	450	0.5, 1.0, 2.0
	475	0.5, 1.0, 2.0
	500	0.5, 1.0, 2.0

45

Table 3.3: Gas nitriding conditions of the steels investigated.

Material	Temperature, °C	Time of treatment(Hr.)
Ferritic stainless steel	450	8.0
	500	8.0
	550	8.0
Austenitic stainless steel	450	8.0
	500	8.0
	550	8.0

Table.3.4. List of Etching Reagents.

Reagent	Composition
Nital	HNO ₃ - 2 ml Ethyl alcohol - 98 ml
Picral-HCl	Picric acid - 4 gm Ethyl alcohol -100 ml HCl - 4 ml
Villelas reagent	Picric acid - 1 gm HCl - 5 ml Ethyl alcohol -100 ml
Marble's reagent	Copper sulphate-10 gm HCl -50 ml Distilled water-50 ml

Table 3.5: Operating Condition of X-ray Diffractometer.

Radiation	: CuK_α
Voltage & current	: 30 kv, 15ma
Scan rate	: $2^\circ/\text{min}$
Chart speed	: 20 mm/min
Scale factor	: 800 cps

3.5.3 Hardness Measurement

Microhardness values were determined by using a Shimadzu Microhardness Tester. Microhardness measurements were carried out by using 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.

Hardness versus penetration distance profiles were also determined on all samples for which specimens prepared for optical metallography were used. These profiles give valuable information regarding the depth of nitrogen penetration and is therefore used extensively in studies of nitriding.

Chapter IV

RESULTS

4.1 Introduction

In the present investigation ion-nitriding of austenitic and ferritic stainless steels has been carried out in a mixture of 25N₂:75H₂ in the temperature range of 450 to 500^oC for times of up to 2 hours. Nitriding in 100% ammonia gas atmosphere has also been done in the temperature range of 450-550^oC for times of upto 8 hours. The results of these experiments have been analyzed in terms of the depths of the nitrided layer, the nature of the phases formed at the surface of the nitrided specimens, the surface hardness and the hardness versus penetration distance profiles of the nitrided specimens.

4.2 Nitrided Layer

The nitrided layer corresponds to the high hardness region of the nitrided steel and this layer is regarded as one in which alloy nitrides are formed. Commercially it is this layer which needs to be as thick as possible for a given nitriding period.

Effective case depth is usually defined as the perpendicular distance from the surface of a hardened component to the furthest point at which a specified level of hardness is obtained. Case depths are usually determined by microhardness measurement on an unetched cross-section of the component, using either the diamond pyramid or Knoop indenter. Measurement consists of making a hardness survey from near the nitrided case to the base metal or to a depth at which the predetermined minimum hardness is obtained. Etching experiments²² have shown that effective case depths can also be revealed and subsequently be measured by etching in picral-HCl⁵ and in Villela's^{17,23} reagents. Hardness measurements on sample etched in picral were performed to compare the effectiveness of these two methods. Both the methods showed the same effective case depth (Fig. 4.1). In this study the depths of nitrided layers were measured by the etching technique. Picral-HCl reagent was used for ferritic stainless steel and Villela's reagent for austenitic stainless steel.

4.2.1 Development of Nitrided Layer During Ion Nitriding

a. Ferritic Stainless Steel:

Metallographic sections of the specimen of ferritic stainless steels ion nitrided at various temperatures are shown in Fig. 4.2. The figure shows that the nitrided layer appears dark when etched

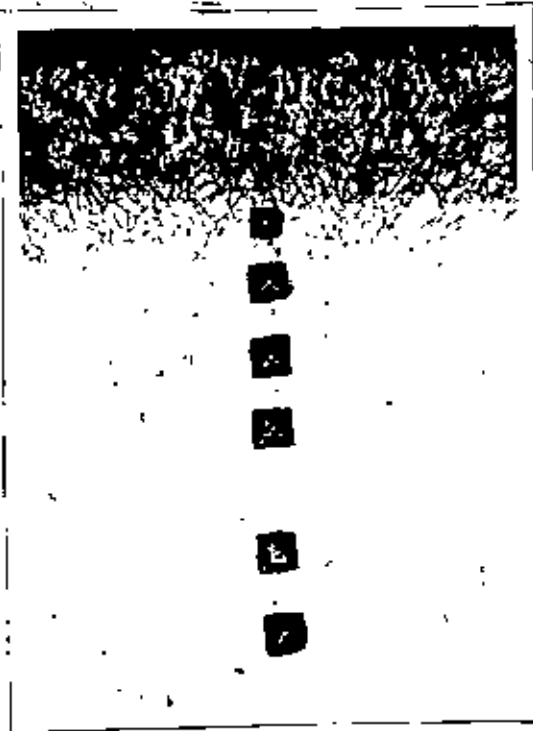


Fig.4.1 Optical micrographs showing the boundary between the nitrided case and core of Ferritic stainless steel ion nitrided at 475°C for two hours (hardness indentation marks on the lightly etched specimen, etchant: picral-HCl).

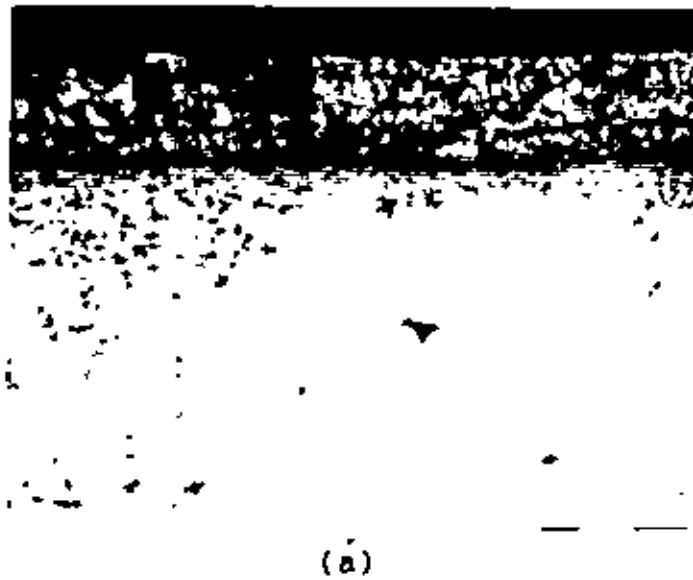


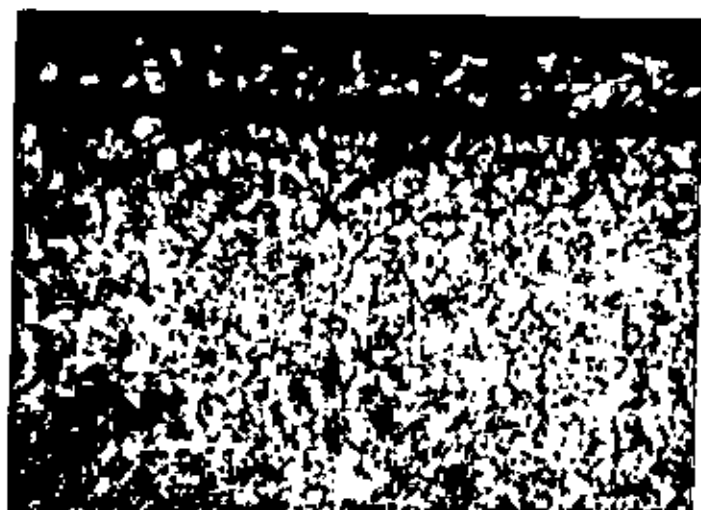
Fig.4.2 Optical micrographs showing the variation of thickness of the nitrided layer formed on ferritic stainless steel at different ion nitriding times and temperatures (etchant: Picral-HCl)

(a). nitrided at 450⁰C for 2 hours.

(b). nitrided at 500⁰C for 2 hours.

with picral-HCl. The core of the steels remained unaltered during nitriding. The nitrided layers are found to be compact and free from pores. The effect of various etching reagent on the nitrided layer is shown in Fig. 4.3. In all cases nitrided layer appears dark. It is also noted that thickness of the nitrided layer is smallest when nitriding is performed at 450⁰C for half an hour. Raising the nitriding temperature to 500⁰C led to an increase in the layer thickness to 95 μm. The thickest layer resulted from nitriding for two hours at 500⁰C. When etched with 2% nital, ion nitrided ferritic stainless steel samples showed a sublayer (Fig.4.4).

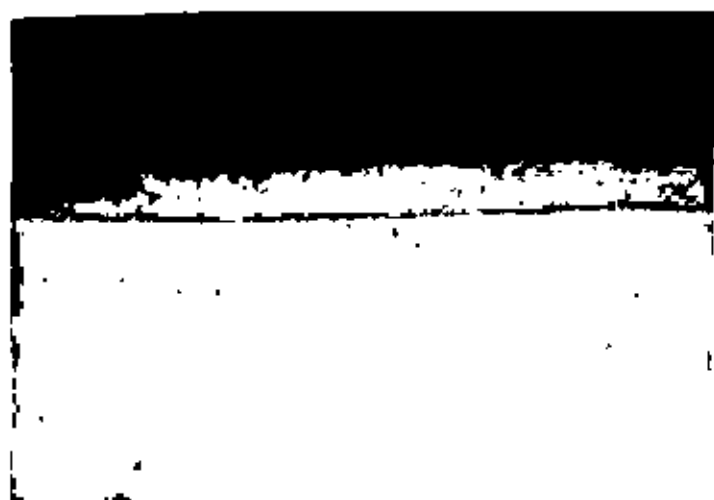
The dependence of case depth on treatment time is shown in Fig.4.5. The case depth is seen to increase linearly with the square root of time at each ion nitriding temperature. This is in good agreement with other results²⁴. Therefore the rate limiting step is volume diffusion of nitrogen. The case depth was also found to increase with increasing temperature for a fixed treatment time. This may be attributed to the increased nitrogen diffusivity at higher temperatures. Ferritic stainless steel showed a growth rate of 7.87×10^{-4} cm²/sec at 450⁰C and of 1.23×10^{-3} cm²/sec at 500⁰C (Fig.4.6). This shows that the growth rate increases with increasing temperature.



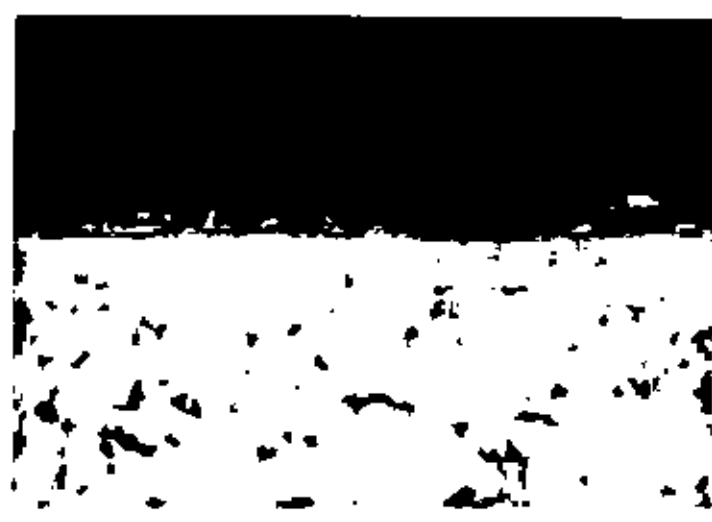
(a)



(b)



(c)



(d)

Fig.4.3 Microstructures revealed by different etching reagents on the same specimen of ferritic stainless steel ion nitrided at 450°C for 1 hour.

a. Picral-HCl b. Nital

c. Marble's reagent d. Villelas reagent

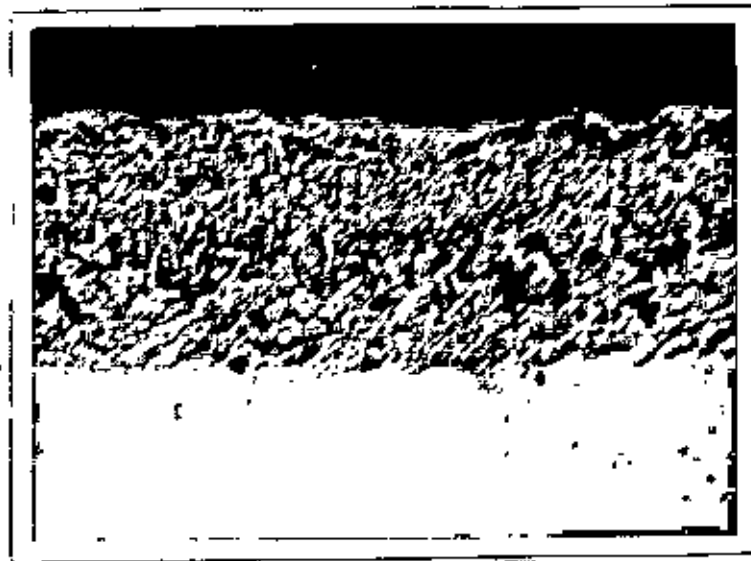


Fig.4.4 Optical micrographs showing the sublayer formed on ferritic stainless steel ion nitrided for two hours at 500°C (etched in 2% nital).

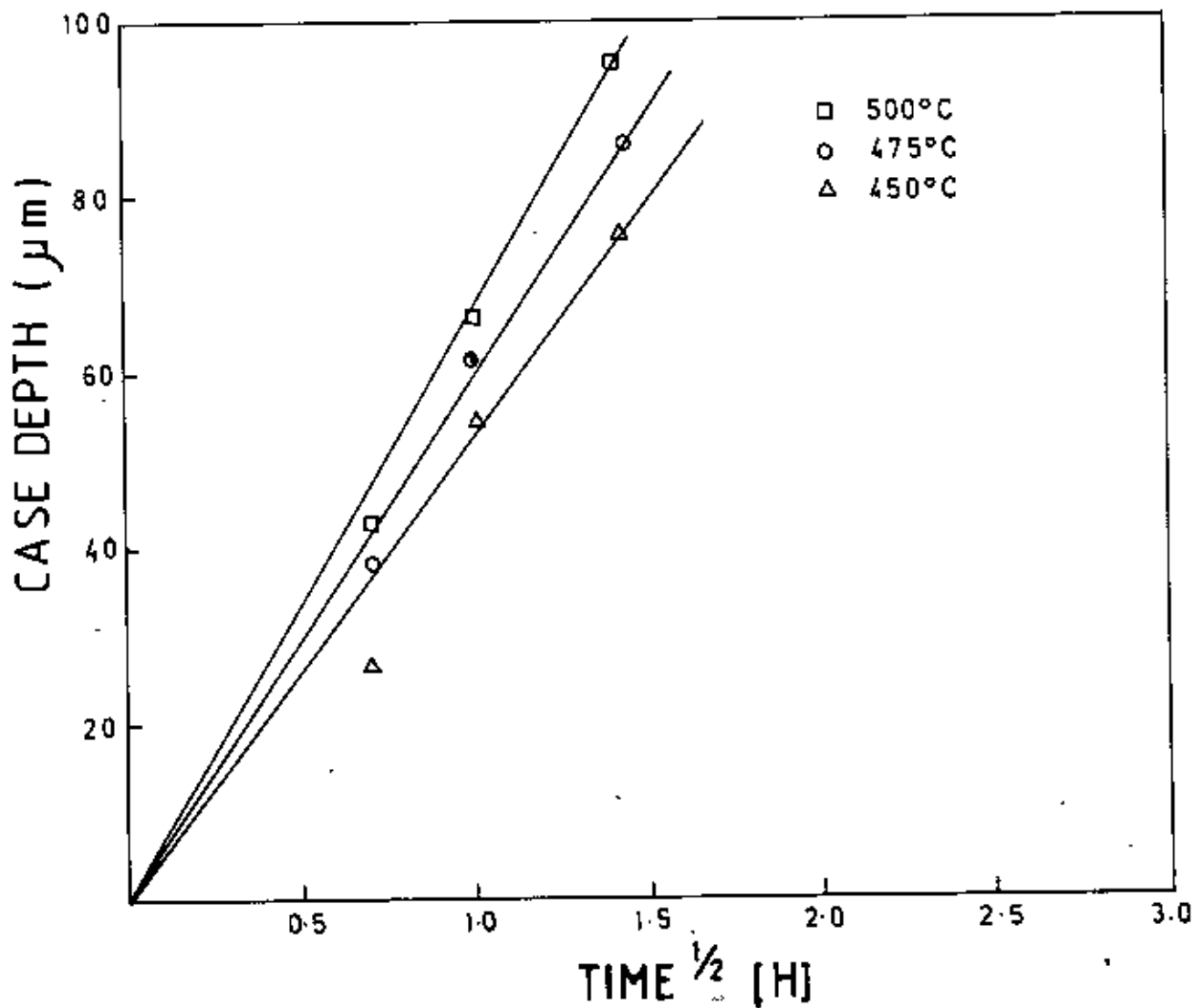


Fig. 4.5 Relationship between case depth and square root of the nitriding time for ferritic stainless steel [ion nitrided at different temperatures].

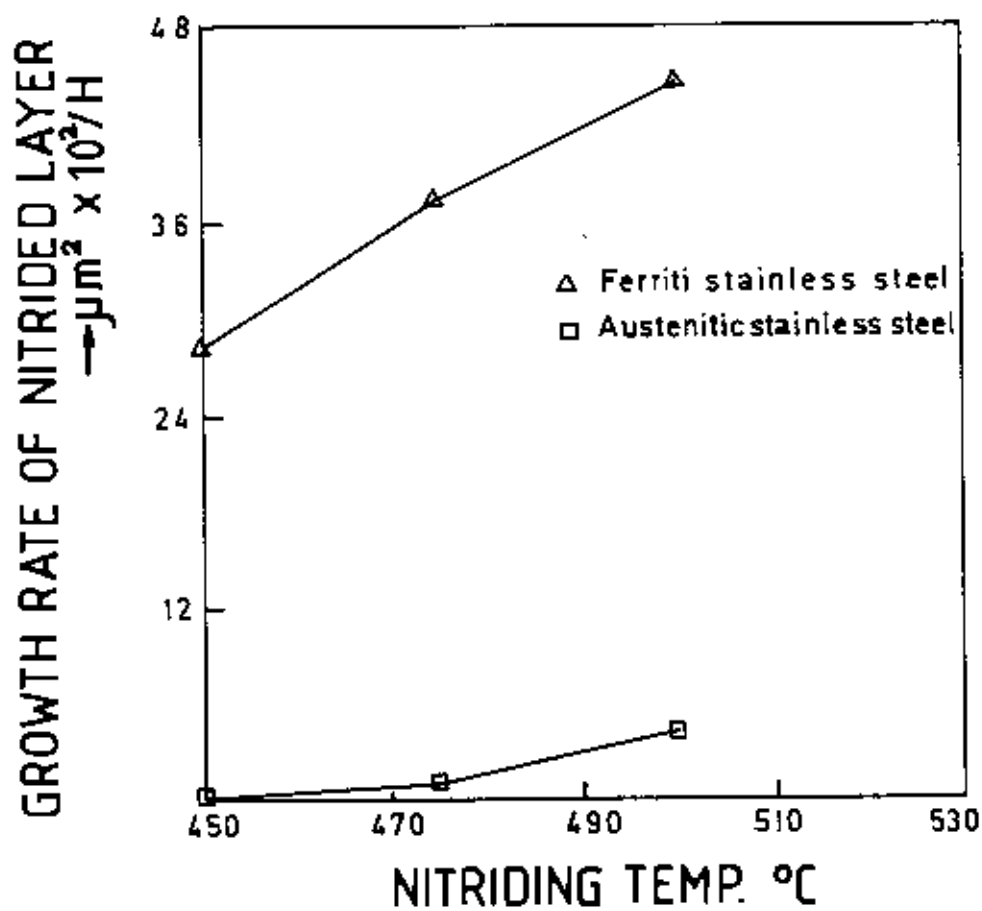
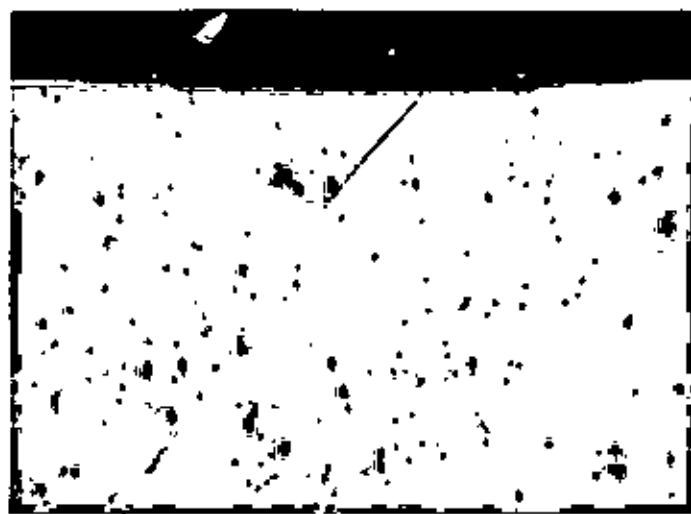


Fig. 4.6 The growth rates of the nitrided layers of ferritic and austenitic stainless steels [ion nitrided at different nitriding temperatures].

b. Austenitic Stainless Steel:

Fig. 4.7 shows the microstructures of the samples nitrided at different temperatures for a fixed treatment time. These show that on etching with Vilella's reagent the nitrided case appears dark. No white layer was found to have formed on the case. Nitrided layer was free from crack and porosity, and the core structure remained unchanged. The thickness of the nitrided layer increased from 10 μm on samples ion nitrided for 2 hours at 450⁰C to 30 μm on samples ion nitrided for 2 hours at 500⁰C. Nitriding for a period 0.5 hour at 450⁰C showed only a very thin nitrided case. The dependence of case depth on time is shown in Fig. 4.8. The case depth is seen to increase linearly with square root of time at each ion nitriding temperature. From the slope of the nitrided case depth versus temperature, it can be seen that the case depth increases with increasing temperature for a fixed treatment time which may be attributed to the increased nitrogen diffusivity. Fig.4.6 shows that the growth rate of nitrided case was slower upto 475⁰C, beyond which the growth rate increased appreciably; a growth rate of 8.749×10^{-11} cm^2/sec , at 450⁰C increasing to 1.094×10^{-9} cm^2/sec at 500⁰C.



(a)



(b)

Fig.4.7 Microstructure showing the variations of thickness of the nitrided layer formed on austenitic stainless steel ion nitrided for 1 hour at different temperatures (etchant: Vilella's reagent)

(a) nitrided at 450°C (b) nitrided at 500°C

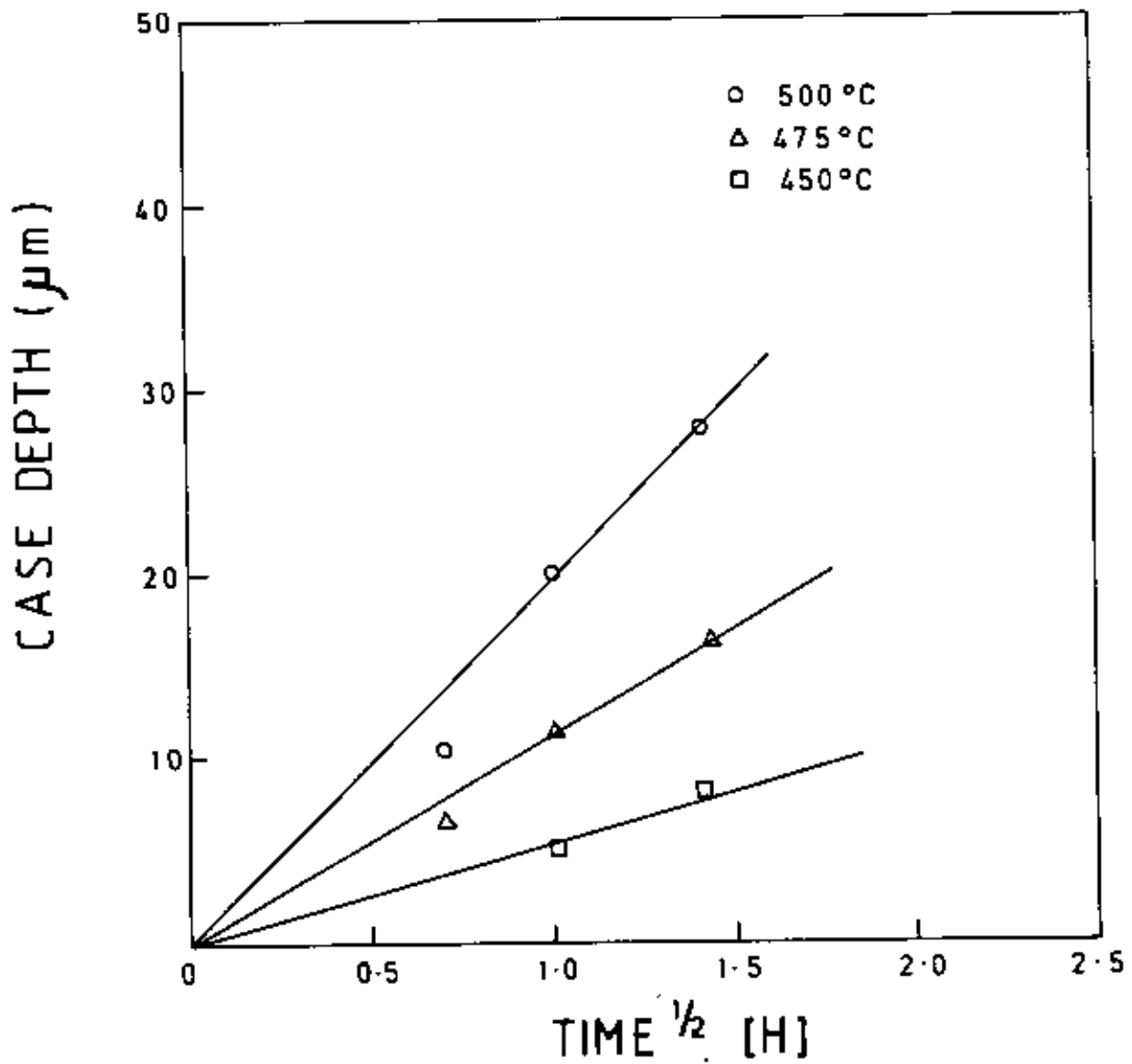


Fig. 4.8 Case depth at different ion nitriding temperatures as a function of nitriding time for austenitic stainless steel.

4.2.2 Development of Nitrided Layer During Gas Nitriding

Ferritic Stainless Steel: Microstructure of the specimen gas nitrided at 450°C for 8 hours is shown in Fig. 4.9. These layers are not compact and pores appear to be present, whereas core structure is unchanged. The thickness of the nitrided layer increased from $60\ \mu\text{m}$ for 8 hours of treatment at 450°C to $130\ \mu\text{m}$ for 8 hours of treatment at 550°C . For a specified treatment time the case depth increases with increasing temperature because of the increased nitrogen diffusivity. It may be noted that similar results were obtained during ion nitriding of ferritic stainless steels.

Austenitic Stainless Steel: The gas nitrided case on austenitic stainless steel was clearly revealed by etching in Villela's reagent. After etching with Villela's reagent the nitrided case appears dark. White layer was not found to have formed on the sample. Nitriding at 450°C showed a very thin layer. With increasing temperature the growth rate of the nitrided layer increased (Fig. 4.10). It has already been mentioned that these nitrided layers were not compact and pores were present in the layer (Fig. 4.11). Core structure remained unchanged.

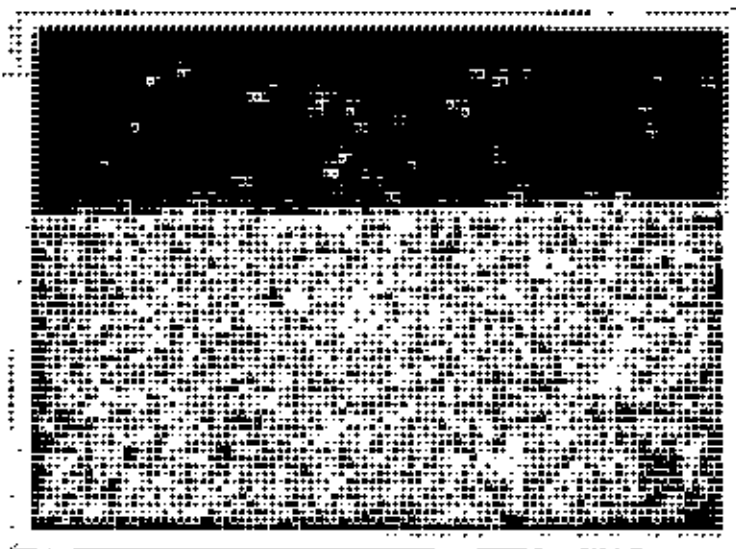


Fig.4.9 Microstructure of gas nitrided ferritic stainless steel showing a well defined nitrided case [nitrided at 450⁰C for 8 hours, etchant: picral-HCl].

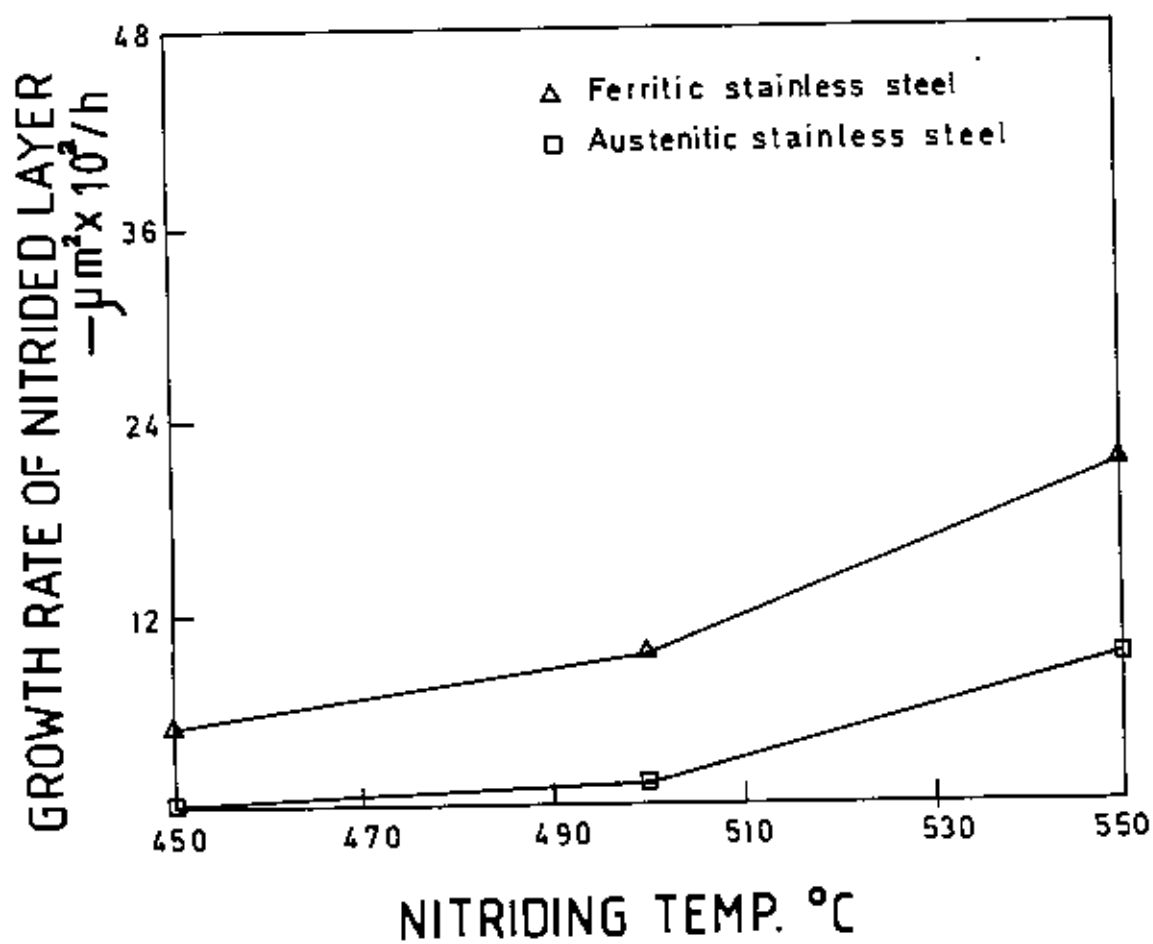


Fig. 4.10 The growth rates of the nitrided layers of ferritic and austenitic stainless steels gas nitrided at different nitriding temperatures.

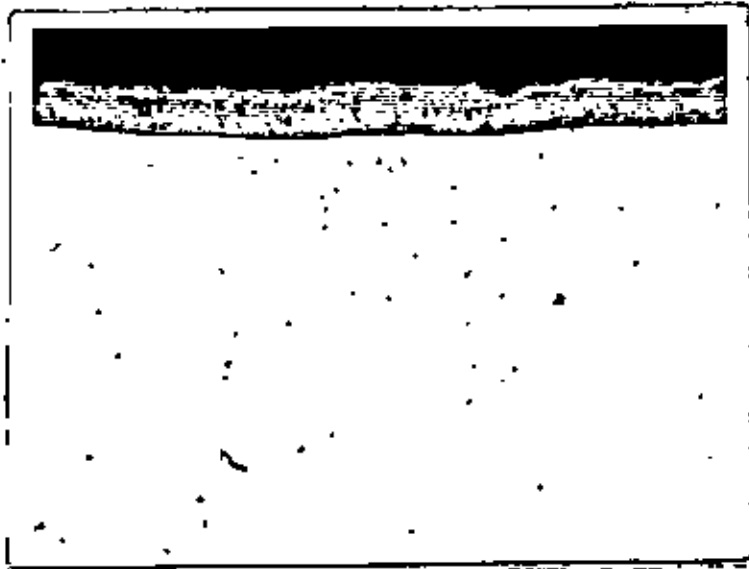


Fig.4.11 Micrograph showing the porousness of the nitrided layer formed on austenitic stainless steel gas nitrided for 8 hours at 500°C (etchant: 2% nital).

4.2.3 Comparison Between Ferritic and Austenitic Stainless Steels

It can be seen from Fig. 4.6 that the growth rate of nitrified case of ferritic stainless steel was higher than that of austenitic stainless steel at all temperatures investigated. The difference in growth rate between the ferritic and the austenitic stainless steel is higher at high temperature (500°C) than at low temperature (450°C). In the case of austenitic stainless steel growth rate increased appreciably above 475°C . In the case of gas nitriding ferritic stainless steel also shows (Fig. 4.10) higher growth rate than austenitic stainless steel. In both cases growth rate increases appreciably after 500°C .

The case depth versus temperature curves (Fig. 4.12 a & b) has shown that with increasing temperature the case depth increases in both ion and gas nitriding. Ion nitriding at 500°C for a period of 2 hours produced a thicker case than that produced by gas nitriding for 8 hours at 500°C i.e. the depth of case increases at a faster rate in ion nitriding than in gas nitriding. The penetration rates of nitrogen have been universally found to be faster in ion nitriding than in gas nitriding²⁵⁻²⁸. Ion nitriding produced pore-free compact nitrified layer whereas gas nitriding produced a porous nitrified layer. The results obtained are in good agreement with the results obtained by other investigators^{1, 5}.

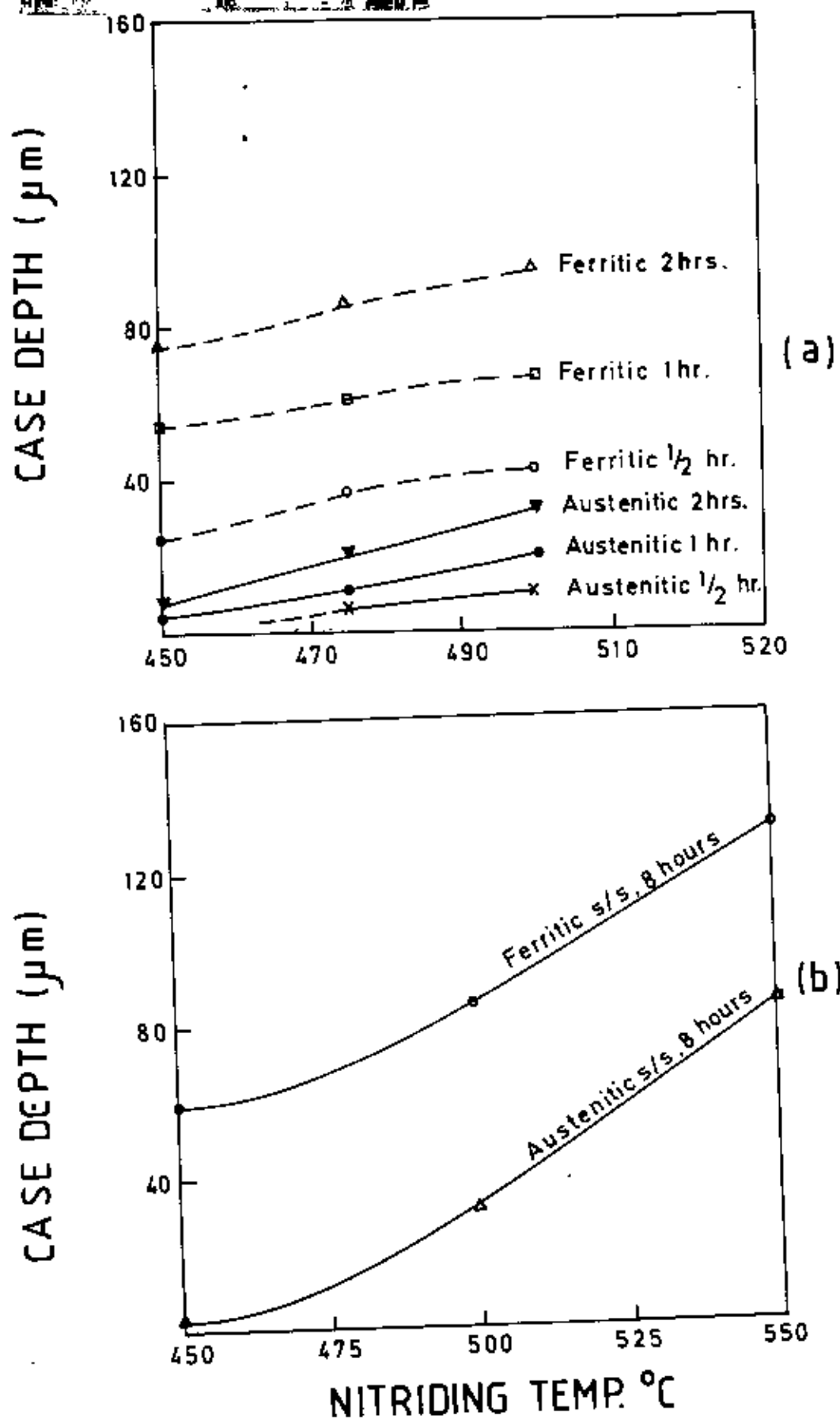


Fig. 4.12 Comparison of the thickness of the nitrided layer formed on ferritic and austenitic stainless steels
 (a) ion nitrided
 (b) gas nitrided

4.3 Phase Identification by X-ray Diffractometry

Before nitriding the samples were analyzed by x-ray diffraction and it was confirmed that the samples used were austenitic and ferritic stainless steels. Three prominent diffraction peaks, corresponding to the (110), (200), and (211) planes were detected on ferritic stainless steels. This gives an average lattice constant $a_f=0.287$ nm which agrees well with the value 0.286 nm quoted for pure iron¹¹. Diffraction lines corresponding to the (111), (200), and (220) planes were detected on austenitic stainless steels. Austenitic iron gives an average lattice constant $a_\gamma=0.359$ nm, which also agrees well with the value 0.356 nm quoted for pure γ iron¹¹. No other diffraction line was observed on the patterns recorded.

The structure of the surface layers of the samples ion nitrided at 500°C for 0.5 hour and 2 hours were analyzed by x-ray diffractometry. Specimen of ferritic stainless steel nitrided for 0.5 hour at 500°C shows α and CrN phase (Fig. 4.13a), on the other hand specimens nitrided for 2 hours at 500°C shows α , CrN and γ' phases (Fig. 4.13.b), (111), (200), and (220) peaks are identified for γ' and CrN phases. The α lines have an average lattice constant $a_f=0.289$, which is 0.65% larger than the corresponding value prior to nitriding. Austenitic stainless steel also shows γ and CrN phase after 0.5 hour of ion nitriding. After 2 hours of nitriding peaks corresponding to γ , γ' , and CrN, can be observed. γ' and CrN phases

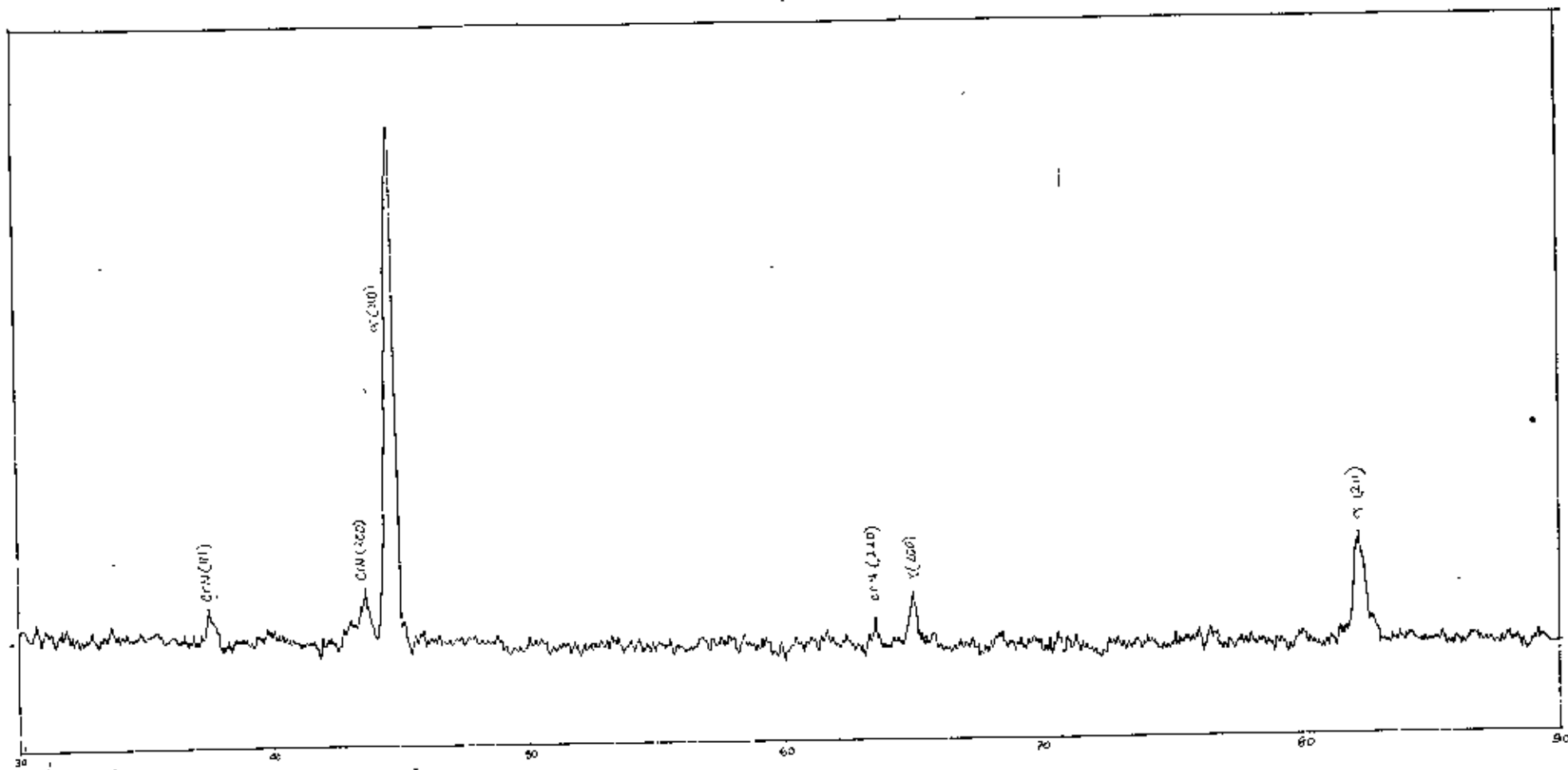


Fig. 4.13a X-ray diffraction pattern of the ion nitrided ferritic stainless steel specimen nitrided for half an hour at 500°C

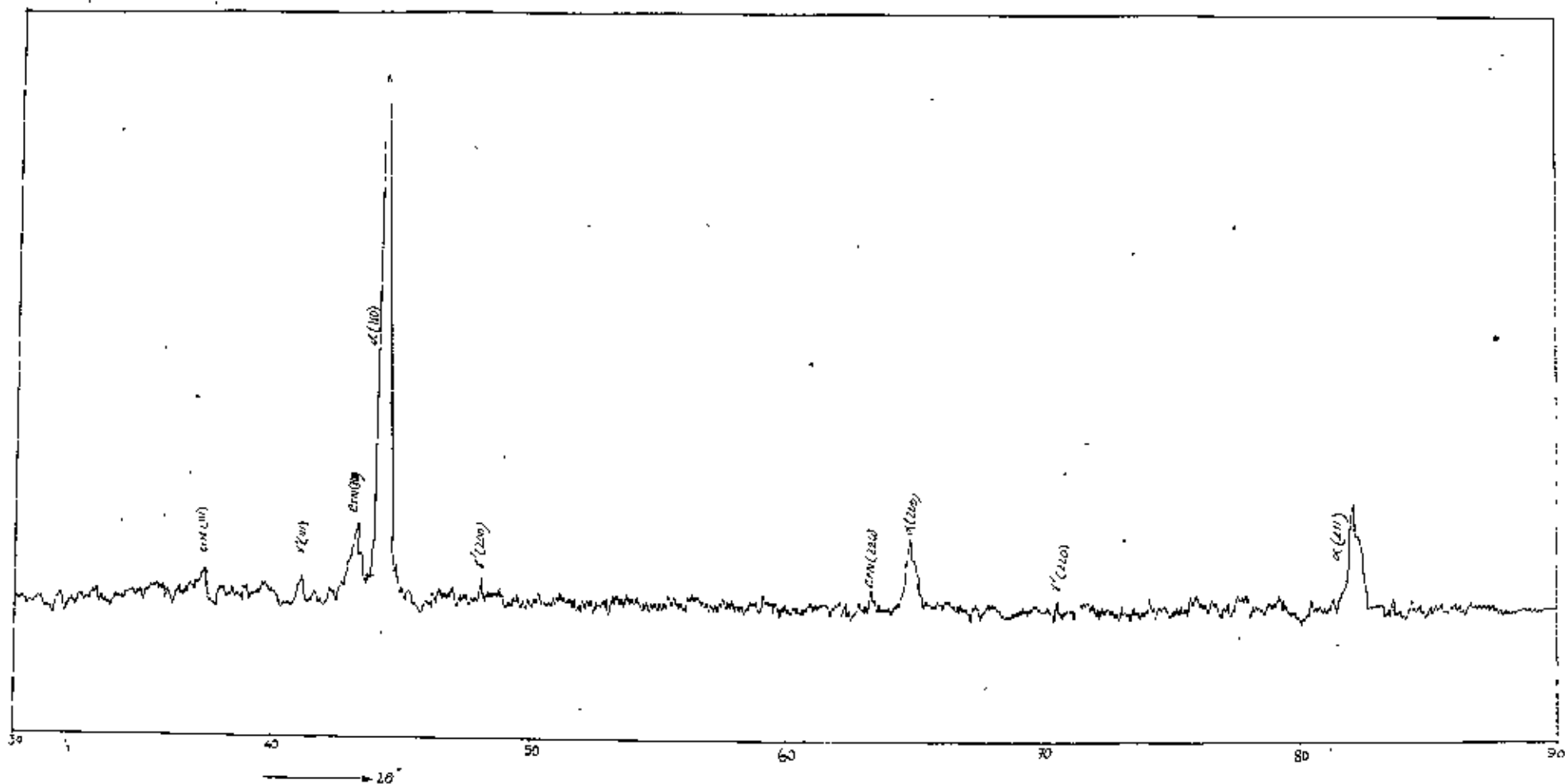


Fig. 4.13b X-ray diffraction pattern of the ion nitrided ferritic stainless steel specimen nitrided for 2.0 hours at 500°C

has shown peaks corresponding to the planes (111), (200) and (220) peaks. The γ phase has an average lattice constant of $a_{\gamma}=0.3609$ nm which is 0.2% larger than the corresponding value prior to nitriding.

4.4 Hardness Measurement

Hardness measurements on the surface of the nitrided samples and also as a function of distance on sections orthogonal to the nitrided surface were carried out on all ion nitrided and gas nitrided specimens, using a Shimadzu microhardness tester and a 100 g load. Small variations in hardness values were noted on the samples. The surface hardness values reported here, are the average of 5 random hardness values and are intended to serve as a measure of hardening achieved.

4.4.1 Surface Hardness

4.4.1a Surface Hardness of Ferritic Stainless Steel After Ion Nitriding

Surface hardness depends upon both time and temperature of nitriding (Fig. 4.14). At a temperature of 450°C the surface hardness increased with increasing time. Maximum hardness at the

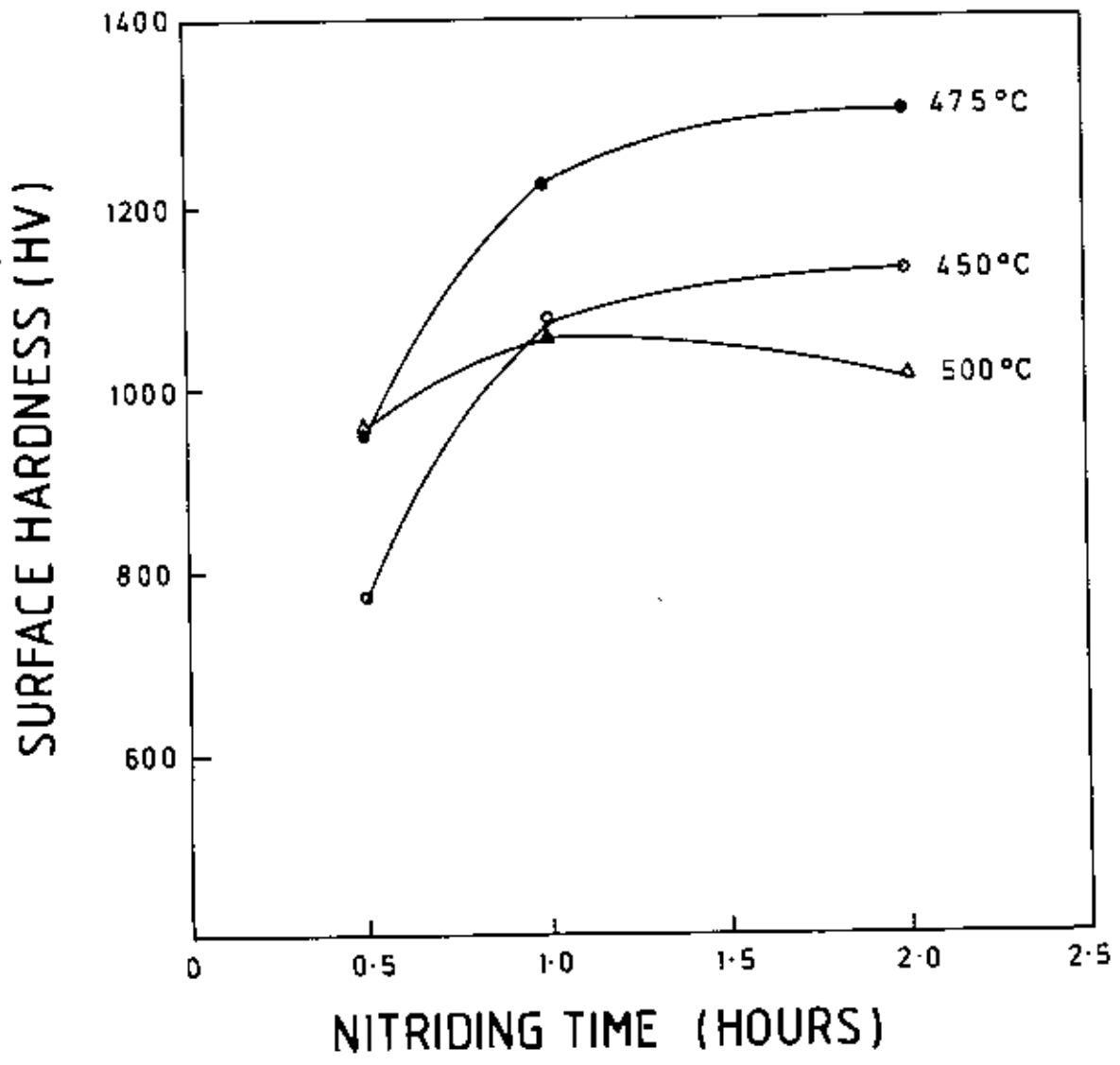


Fig. 4.14 The dependence of the surface hardness on the ion nitriding time for ferritic stainless steel.

surface was obtained after nitriding for 2 hours at 475⁰C and then the hardness values showed a decreasing trend (Fig. 4.15). When nitrided at a temperature of 500⁰C the hardness decreased continuously with increasing treatment time. The decrease in hardness is related to the coarsening of nitride particles²⁹.

Coarsening of nitrides is functions of both temperature and time of treatment. At lower temperature longer time is required whereas at higher temperatures particles grow at a faster rate.

4.4.1b Surface Hardness of Austenitic Stainless Steel After Ion Nitriding

Fig.4.16 shows the surface hardness of the ion nitrided austenitic stainless steels as a function of treatment time at different temperatures. The hardness at the surface increased with increasing treatment time and temperature in the temperature range of 450⁰ to 500⁰C. Lowest hardness was obtained at 450⁰C and highest at 500⁰C. Lower hardness at low temperatures has been attributed⁵ to the very low diffusion rates at 450⁰C which results in the formation of a small percentage of nitride for which hardness increment was not high. It has been shown³⁰ that samples ion nitrided at low temperatures form clusters of mostly spherical particles distributed in a non-uniform manner. The inter-particle distances are not uniform, resulting in a very low increase in surface

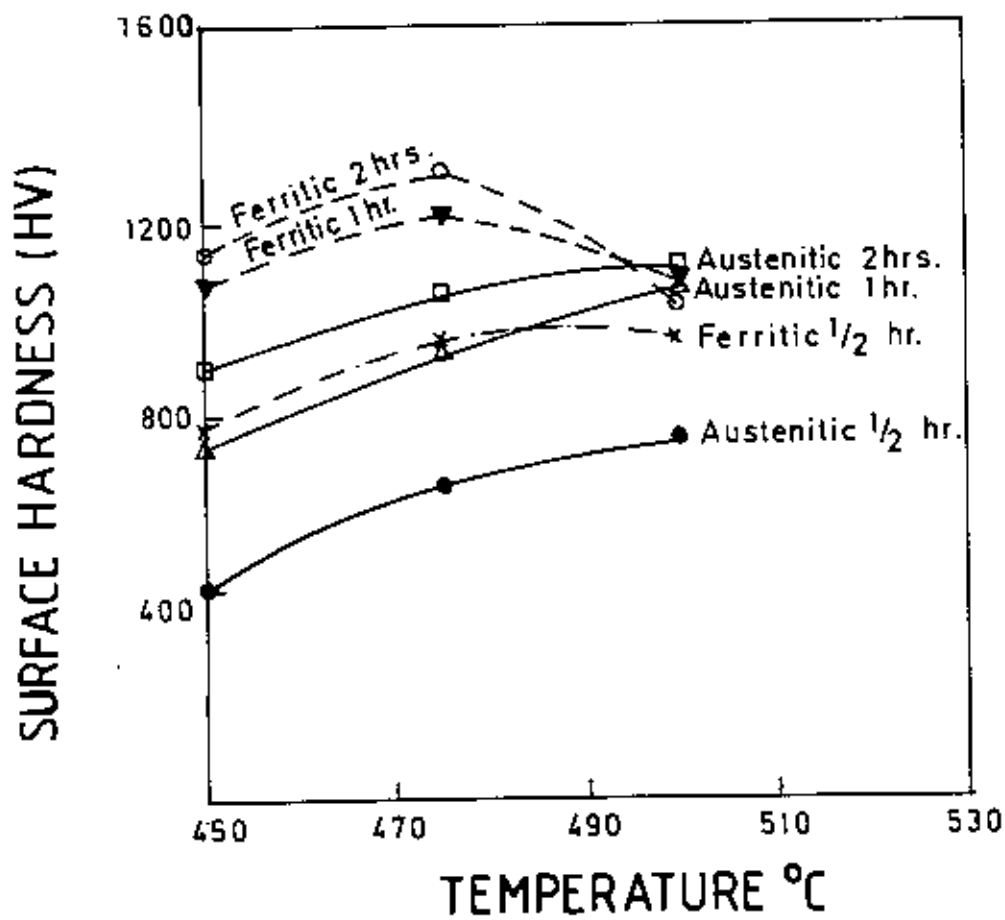


Fig. 4.15 The dependence of the surface hardness on the ion nitriding temperature for austenitic and ferritic stainless steels.

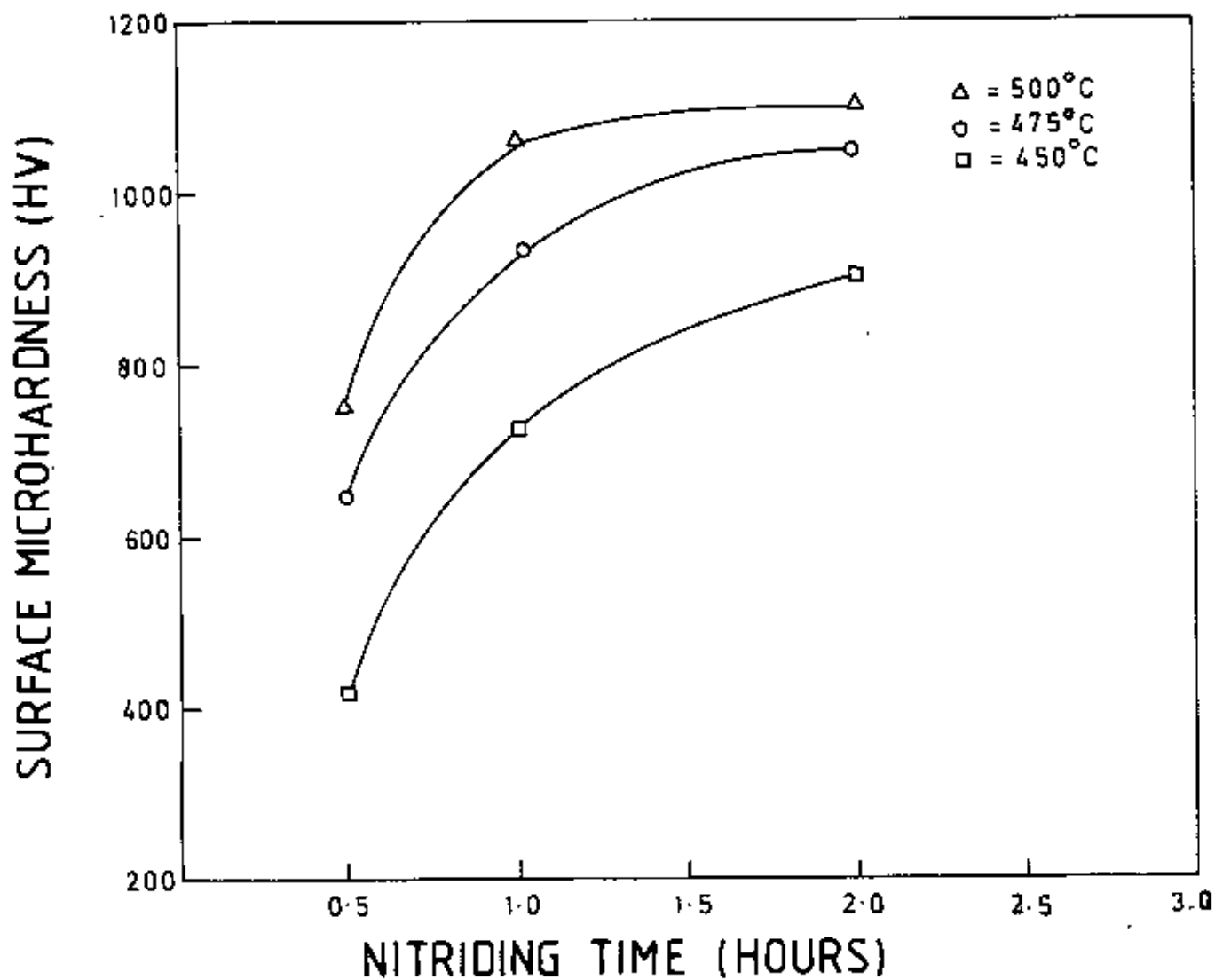


Fig. 4.16 The dependence of surface hardness on the ion nitriding time for austenitic stainless steel.

hardness.

4.4.1c Surface Hardness of Austenitic and Ferritic Stainless Steels After Gas Nitriding

Ferritic Stainless Steel: The hardness obtained on samples nitrided at 450^o, 500^o, 550^oC for 8 hours of treatment time is shown in Fig. 4.17. It can be seen that with increasing treatment temperature surface hardness is increased. Highest surface hardness was obtained at a temperature of 550^oC. This has been attributed to the formation of a uniform nitride layer which results in increase in surface hardness²⁹.

Austenitic Stainless Steel: Fig. 4.17 shows that with increase in treatment temperature the surface hardness increases, lowest hardness being obtained at 450^oC and highest at 550^oC. At low temperatures diffusion rate is slower, resulting in lower hardness.

4.4.2 Hardness Versus Distance Profile

4.4.2a Hardness Profile of Ion Nitrided Ferritic Stainless Steel

Fig. 4.18 shows the variation in the hardness versus penetration distance profiles with the treatment time and temperature for ferritic stainless steel. From the figure it can be observed that the case depth i.e. the distance at which the slope of the hardness

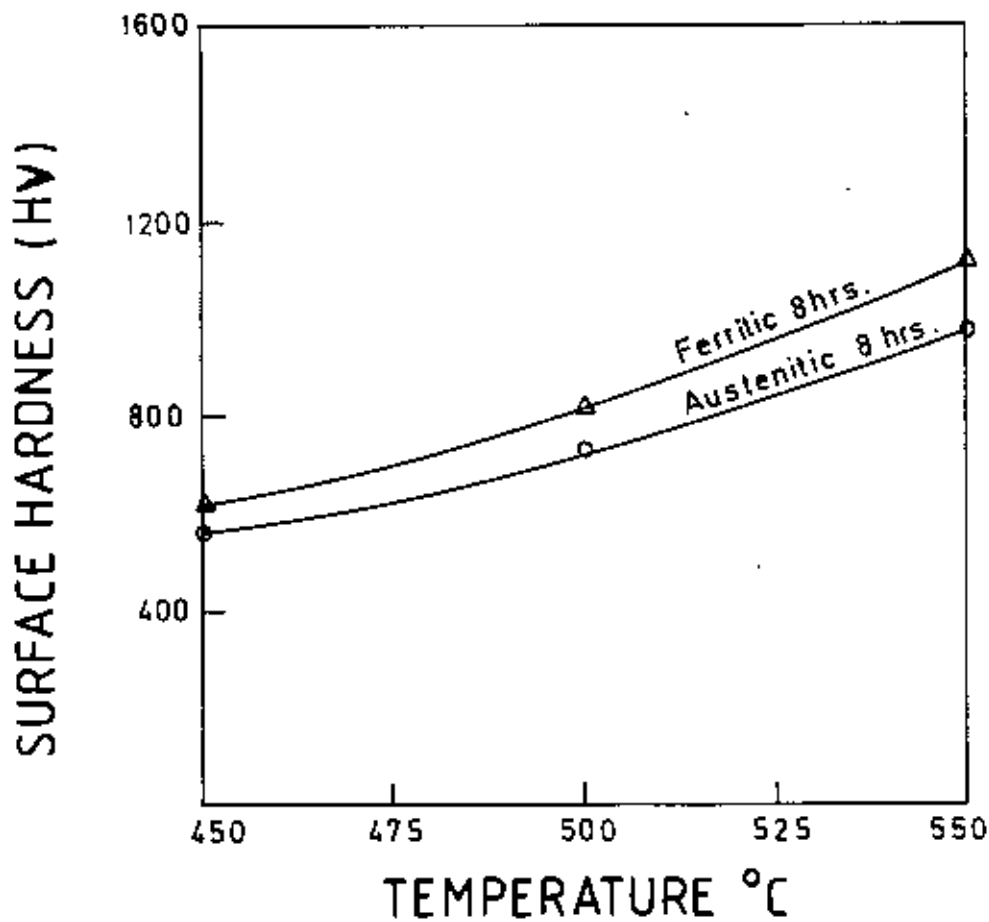


Fig.4.17 The dependence of the surface hardness on the gas nitriding temperature for ferritic and austenitic stainless steels.

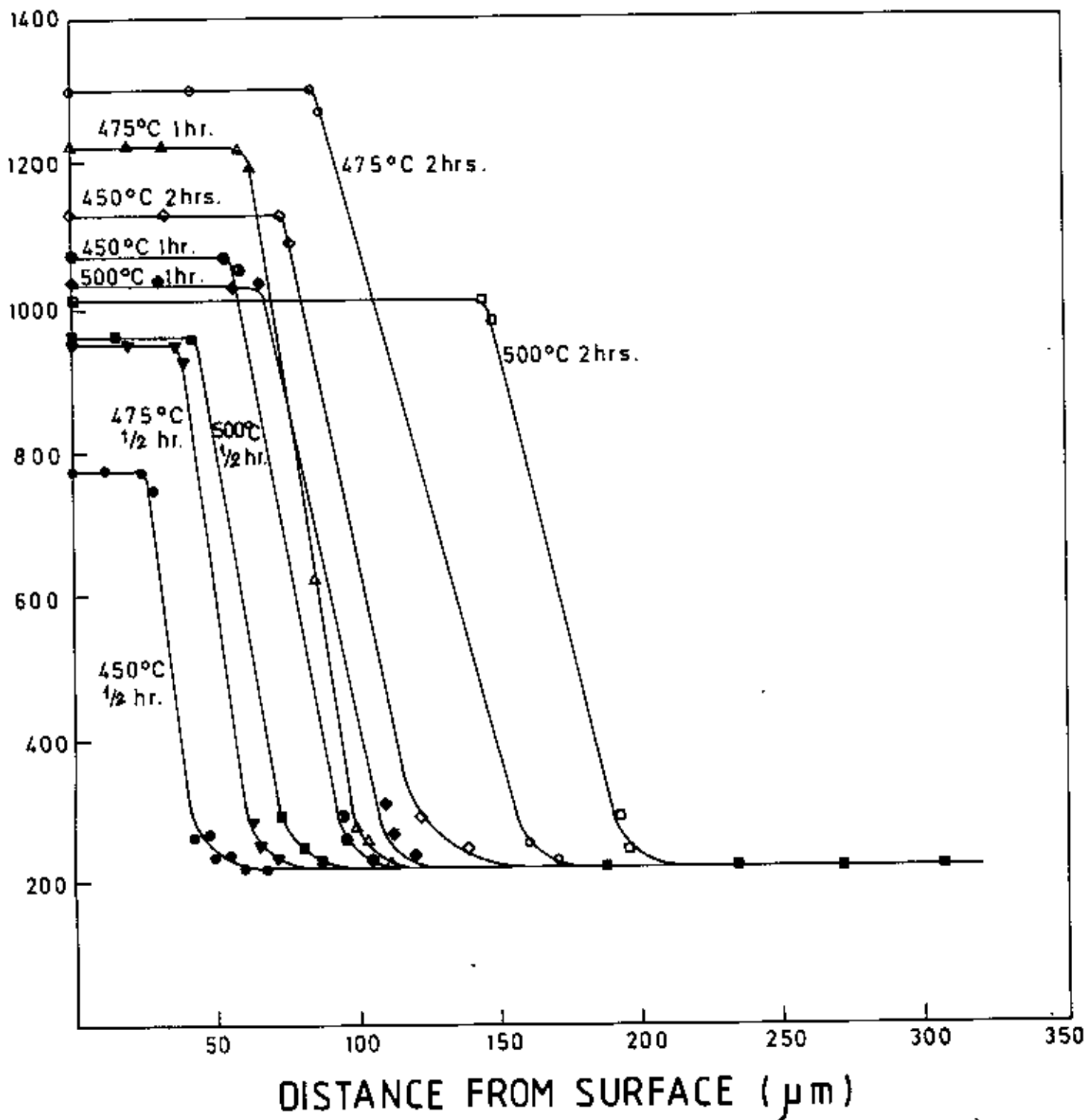


Fig. 4.18 Hardness versus depth profiles for ferritic stainless steel ion nitrided at temperatures and times indicated.

versus penetration distance profiles becomes minimum, increases with increasing treatment time at a particular temperature and also with temperature at constant nitriding time. The hardness in the nitrided layer (HV) attains a high value and remains constant throughout the layer, the HV value markedly drops to minimum in the base metal. It has already been shown that (Fig. 4.1) the location at which such a drastic change in HV (microhardness) occurs, corresponds well with the nitriding front determined by optical microscopic observation. However, in hardness determination, the indentation near the nitriding front crosses both the internal nitriding layer and the unnitrided region, so that HV is an average of the hardness in both regions. In case of ion nitriding maximum hardness obtained from nitriding at 475°C for 2 hours. The hardness decreased with increase in temperature of treatment.

4.4.2b Hardness Profile of Ion Nitrided Austenitic Stainless Steel

The hardness build up in this steel is shown in Fig. 4.19. The hardness profile was found to be very steep. The case depth increases with increasing treatment time and also with temperature for a constant nitriding period. Ion nitriding shows a sharp boundary between the case and the core of austenitic stainless steel. This has been attributed to the high percentage of alloying elements (18% Cr)³¹. Hardness profile also shows that the hardness of the core remains unaltered i.e. the structure of the core does

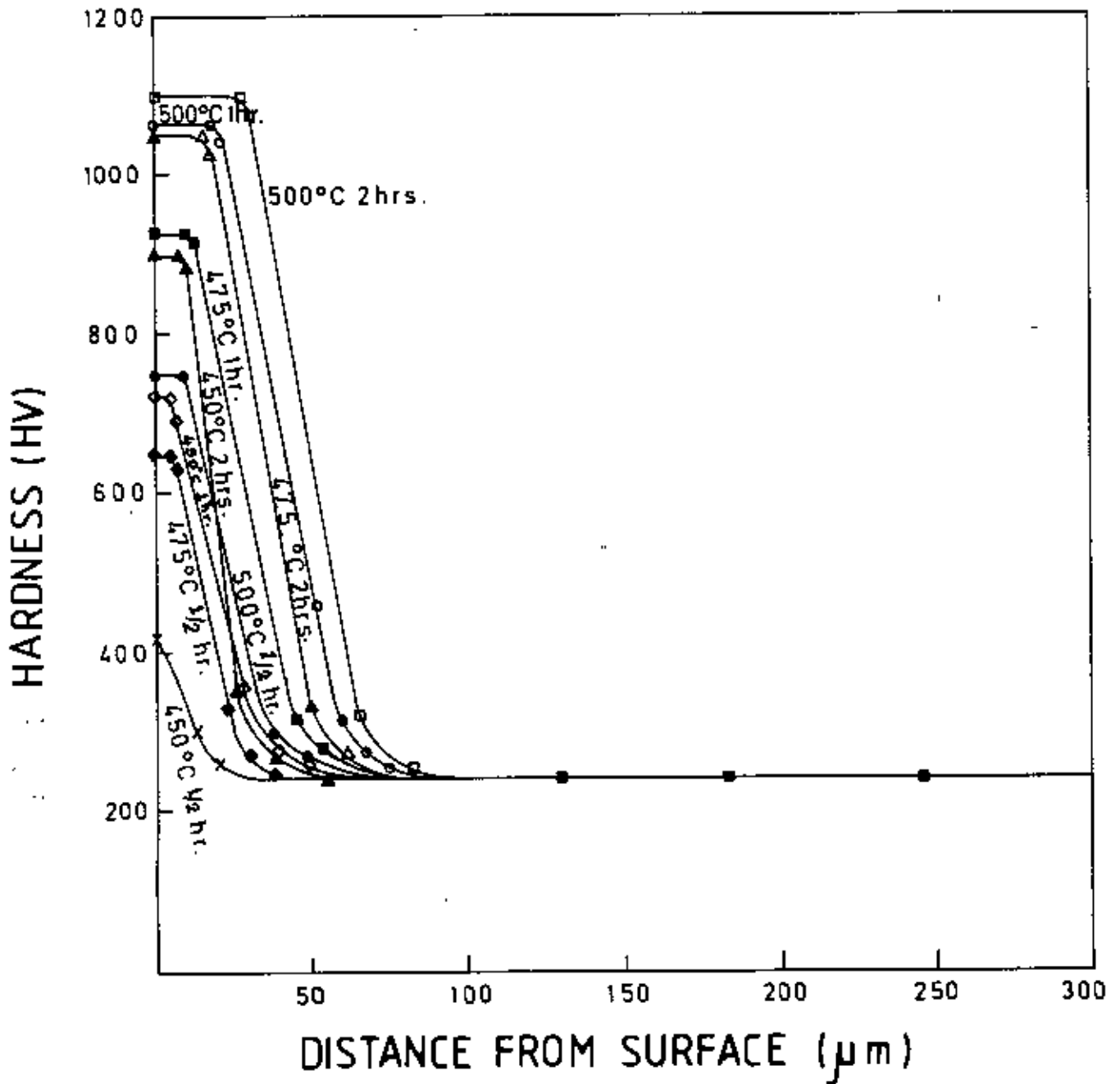


Fig. 4.19 Hardness versus depth profiles for austenitic stainless steel ion nitrided at temperatures and times indicated.

not change.

4.4.2c Hardness Profile of Gas Nitrided Ferritic and Austenitic Stainless Steels

Ferritic Stainless Steel: Fig.4.20 shows the variation in hardness versus penetration distance profile with the treatment time for gas nitriding of ferritic and austenitic stainless steels. Case depth of ferritic stainless steel increases with increasing nitriding temperature. The slopes of the hardness profile is less steep in gas nitriding than in ion nitriding.

Austenitic Stainless Steel: Gas nitriding produced a lower case depth at 450⁰C, but increased case depth was found at 550⁰C (Fig.4.20). From the hardness profiles it is clear that like ferritic steels the case depth of austenitic stainless steel increases with increasing nitriding temperature. The figure also shows that the hardness profile is less steep in gas nitriding than in ion nitriding.

4.4.3 Comparison Between Hardness Developed on Ferritic and Austenitic Stainless Steels

Ferritic stainless steel specimens shows(Fig. 4.15) an increase in surface hardness up to a temperature of 475⁰c for a 2 hours of ion nitriding treatment and then decrease with increase in both treatment temperature and time. In the case of austenitic stainless

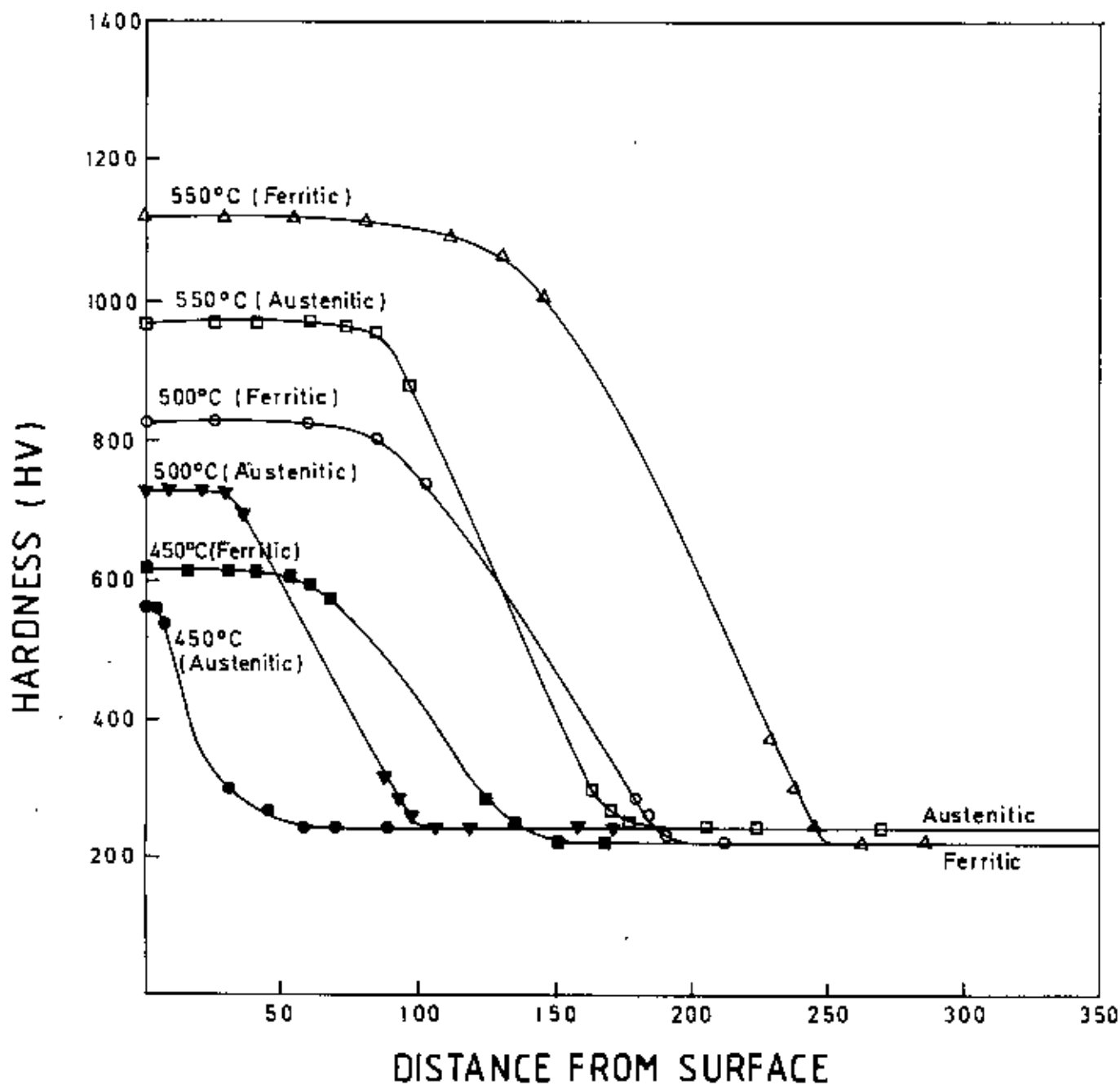


Fig. 4.20 Hardness versus depth profiles for ferritic and austenitic stainless steels gas nitrided for 8 hours at temperatures indicated.

steel hardness increased continuously with increasing treatment temperature.

Gas nitriding produced greater hardness at a temperature of 550°C for 8 hours of treatment for both the types of steels. 2 hours of ion nitriding of ferritic and austenitic stainless steels produced greater hardness than 8 hours of gas nitriding (Fig. 4.15 and 4.17). It can be seen that hardness of the nitrided case depends on the nitriding temperature as well as time. At lower nitriding temperature maximum hardness is obtained after a longer time period of nitriding while at higher temperature it is obtained after a shorter nitriding period.

Hardness profiles were found to be steeper in ion nitriding than in gas nitriding for both types of steels (Fig. 4.18 to 4.20).

Chapter V

DISCUSSION

5.1 Development of Microstructure

Both ion and gas nitriding treatments led to essential changes in the structure of the surface layer. On etching the nitrided zone was clearly revealed. The nitrided case appeared dark and the core structure remained unchanged (Fig. 4.2). No white layer could be found on both ferritic and austenitic stainless steel after ion nitriding. The presence of alloying elements particularly, the nitride formers hinders the formation of the compound zone. In both ferritic and austenitic stainless steel the amount of chromium, a well known nitride forming element is quite high; ferritic stainless steel containing 11.5% Cr and the austenitic steels containing 18% Cr. Hence in these steel formation of white layer is more difficult.

Moreover nitriding of steels 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 in to the steel³². Such result were also observed by other scientists⁵. Ozabaysal et al³² studied the structure and properties of the iron nitrided layers on tool steels. Their study showed that the iron-chromium carbides were converted to chromium nitrides in regions close to the surface, and within the nitride case, whereas conversion was not complete at greater depths. This was attributed to the lower nitrogen activity at greater depths from the nitrided surface.

The growth of the nitrided case was found to be parabolic with time. This is in agreement with the well-accepted nitriding model suggested by Light Foot and Jack³³. A comparison of the slopes of the curves of case depth versus square root of time curves (Fig. 4.5 and 4.8), shows that nitriding reaction is faster in the ferritic stainless steel and slower in the austenitic stainless steel. The difference in the observed diffusion behavior of nitrogen arises from the structure dependency of nitrogen diffusion²⁴. Activation energy for nitrogen diffusion is known to be higher in f.c.c austenite (47.3 kcal/mole), than it is in b.c.c ferrite (18.3 kcal/mole)^{15, 24}. Therefore, in austenitic stainless steel lower case depths are produced because the diffusivity of nitrogen is lower in this steel than in the ferritic grade. Jack and his associates^{34, 35} undertook extensive experimental studies on the nitriding of irons

and steels containing various concentrations of chromium, titanium, tungsten, molybdenum, vanadium and aluminum. They have shown that case depth d can be expressed as

$$d = (2NDt/RX)^{1/2} \dots \dots 5.1$$

Where N = surface nitrogen concentration
 X = Original alloy element concentration
 R = the ratio of nitrogen to alloy element, in the
 nitride phase
 D = diffusion coefficient of nitrogen in ferrite, and
 t = time nitriding

Curves of Fig.4.6 and 4.10 also agree well with the general trend of the equation 5.1 proposed by Jack and his associates^{34, 35}. This means that as the alloy element concentration in the steel increases, the rate of growth of case depth decreases. Austenitic stainless steel contains greater percentage of alloying elements than ferritic stainless steel. So the rate of nitriding is lower in austenitic stainless steel than in ferritic stainless steel.

Growth rate of nitrided layer was found to be faster in ion nitriding than in gas nitriding. This can be explained as follows. The nitriding process involves the transfer of nitrogen from a nitriding atmosphere to the subsurface layer of an iron alloy. Since nitrogen will only diffuse through iron in the atomic form, it is necessary to provide a source of atomic nitrogen in proximity

to the metal surface. This atomic nitrogen must be transferred from the adsorbed state into the metal lattice. This may be explained⁵ in terms of Q_i and Q_0 . Here Q_i represents an activation energy for infusion which may include one or all of the following: (i) The generation of atomic nitrogen at the surface, (ii) adsorption on the surface and (iii) diffusion of nitrogen through a passivating layer. Q_0 represents the activation energy for interstitial diffusion of nitrogen through the metal lattice. Rates for the infusion and diffusion of nitrogen in the iron may be expressed as follows:

$$R_i \propto N_i V_i e^{-Q_i/kT} \dots\dots\dots 5.2$$

$$R_D \propto N_D V_D e^{-Q_D/kT} \dots\dots\dots 5.3$$

Where N_i and N_D are the concentrations of nitrogen and V_i and V_D are the collision frequencies for the infusion and diffusion steps respectively. Since the values for N and V of the infusion and diffusion process should vary slowly with temperature, the rates may be compared on the basis of activation energies (i.e. the largest activation energy corresponds to the rate limiting steps)⁵.

In ammonia nitriding atomic nitrogen is generated at the metal surface via the reaction : $4 \text{ Fe} + \text{NH}_3 = \text{Fe}_4\text{N} + 3/2 \text{ H}_2$. This reaction

proceeds rapidly⁵ at conventional ammonia gas nitriding temperature (550°C). In ion nitriding, the active nitrogen is generated by electronic collisions in a N₂ and H₂ mixture, hence it is independent of activity and temperature of metal surface. The activation energies for diffusion in the nitride case are 47.1 kcal/mole and 143.5 kcal/mole for ion nitriding and ammonia nitriding respectively⁵. The much larger activation energy for ammonia nitriding (143.5 kcal/mole) may be related to the difficulty of infusion of nitrogen into the chromium oxide film present on austenitic stainless steel during ammonia nitriding³ⁱ at 500°C. Thus the rate advantage for ion nitriding as compared to ammonia nitriding of austenitic stainless steel may be explained on the basis of $Q_i > Q_0$ during ammonia nitriding and $Q_i \leq Q_0$ during ion nitriding. The reduction of Q_i in ion nitriding may be attributed to : (i) the increased ability of a H₂ and N₂ plasma for removing the chromium oxide film at nitriding temperature, and (ii) the removal of an activation energy for producing atomic nitrogen since sufficient nitrogen energy is available in the plasma to provide atomic nitrogen independently on the catalytic activity of the metal surface. The most frequently stated argument for a rate advantage associated with the ion nitriding is that the metal surface approaches saturation faster or to a great extent as a result of higher nitrogen activity. The proponents⁵ of this mechanism claims that this leads to an increase in nitrogen concentration gradient at the surface, hence a faster diffusion

rate. Ion nitriding may only accelerate the nitriding rate for systems which are infusion limited during ammonia nitriding. Tentatively it appears that alloys with higher chromium contents exhibit infusion rate limitations during ammonia nitriding³, thus ion nitriding appears to be more effective for these alloys.

5.2 Development of Phases

It is well-known that the lattice constants of α and γ increase with increasing nitrogen concentration in these phases, and each peak of α and γ phase shifts to lower diffraction angle¹². In the present study also a comparison has shown that after a longer period of nitriding the peaks of the α and γ phases are located at lower angle of diffraction than those of the shorter time.

Maximum solubility of nitrogen in ferrite at eutectoid temperature is 0.1 wt.%. The fcc nitrogen austenite is iso-structural with carbon austenite³⁷ but has a wider range of homogeneity and exists down to 590°C. γ' phase is stable between 5.29 and 5.71 wt% of nitrogen at the eutectoid temperature. ϵ -phase contains from 7.1 wt.% to 11 wt.% of nitrogen at the eutectoid temperature. The lattice constant for ferritic stainless steel a_f increased by 0.65% upon nitriding at 500°C for 2 hours. While in the case of austenitic stainless steel a_γ increased by 0.2% upon nitriding under identical conditions i.e. for 2 hours at 500°C. The increased

lattice constant a_α and a_γ upon nitriding indicates that both α and γ structures are influenced by the nitrogen, but ferritic structure is influenced more strongly. γ' phase $[M_4N=(Fe, Cr, Ni)_4N]$ also formed during nitriding. This drastic crystallographic transformation in the nitrided region may account for their different visual appearance from the bulk and is also responsible for the hardening of the nitrided region. No ϵ -phase was found to have formed on the case. Formation of ϵ -phase requires more than 7.1 wt% N_2 . It has already been mentioned that stainless steels contain higher percentage of chromium which is a strong nitride former. The high percentage of chromium present at the steel, hinders the formation of ϵ -phase.

5.3 Development of Hardness and Hardness Profile

Surface hardness of nitrided steels is a function of nitriding temperature and time. It can be seen that the highest hardness was obtained on the surfaces of ion nitrided ferritic steel after 2 hours of treatment at a temperature of 475°C but austenitic steel showed increase in hardness up to 500°C . There appear to be several complementary factors which could contribute to the hardening of these nitrided steels. At the lowest ion nitriding temperature the nitrogen uptake and the precipitation density are low and therefore the amount of hardening is also low³⁰. At higher temperatures and/or longer treatment times precipitate growth

becomes important. As has also been observed in many precipitation hardening alloys¹¹, in the present study a maximum surface hardness is achieved that corresponds to a particular ion nitriding time and temperature. This hardness in turn is related to both precipitate density and precipitate size. Therefore during nitriding of ferritic stainless steels for a period of 2 hours at a temperature of 475°C an optimum size and density of nitride precipitate is obtained. In this regard, the behavior of austenitic stainless steel is worth mentioning. Having a higher activation energy for nitrogen diffusion^{15, 24}, this steel has lower nitrogen diffusivity than the ferritic. Since precipitation phenomena in nitriding systems are diffusion controlled²⁴, it can be expected that this steel receives a lower surface hardness than the ferritic grade. Increase of surface hardness was observed in austenitic stainless steel up to a temperature of 500°C. Thus to give optimum hardness after a 2 hours treatment time the austenitic stainless steels required higher temperature of treatment than ferritic stainless steel.

In samples ion nitrided at lower temperatures clusters of mostly spherical particles distributed in a non-uniform manner are formed resulting a very low increase in hardness³⁰. As the temperature of nitriding is increased more and more of the typical regions described above are formed. This ultimately leads to a layered structure. The build up of the layers occurs to various degrees,

this contributing to the variation in the surface hardness³⁰.

In both types of stainless steel a steep hardness gradient developed under ion nitriding condition. This indicates the interface between the case and the core is very sharp. This sharp interface observed in the case of stainless steel confirms the earlier result of Mortimer et al³⁸. This is likely to happen because the amount of Cr in stainless steel is quite high, so there is a 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 hard uniform subscale and this subscale advances in to the material developing the steep hardness profile. The maximum hardness developed in the present investigation for ion nitriding is 1300 VHN for ferritic stainless steel and 1100 VHN for austenitic stainless steel(Fig.4.15). Gas nitriding produced maximum hardness 1115 VHN for ferritic stainless steel and 965 VHN for austenitic stainless steel(Fig.4.17).

Response of steel to nitriding depends upon composition of the steel. Steels containing more than 5 wt% Cr display sharp interfaces and a shallow nitrided depth which is inversely proportional to the Cr content of the steel³¹. Ferritic stainless steel shows less steepness than austenitic stainless steel because

the amount of chromium in ferritic stainless steel is about 60% of the chromium content of austenitic stainless steel.

In comparison to gas nitriding, ion nitriding produced maximum surface hardness within a shorter period of time at low temperature. This may be due to difference in diffusion rate. During ion nitriding the metal surface approaches saturation at a faster rate or to a greater extent as a result of higher nitrogen activity⁵ and thus results in a higher surface hardness in a shorter treatment time.

Hardness profiles were less steep in gas nitriding than ion nitriding. The slopes of hardness versus penetration distance curves depend upon composition of the alloy, temperature and time of treatment. In this investigation alloy composition and temperature of treatment were same. Time of treatment was different. Ion nitriding was performed for a period of upto 2 hours, whereas gas nitriding was performed for 8 hours. Gas nitriding shows gradual slope which may be due to the longer period of nitriding causing diffusion of nitrogen to greater depth and difference in concentration gradient of nitrogen in two processes.

Chapter VI

CONCLUSIONS

The following conclusions can be derived from the results of this study:-

1. Thickness of the nitrided layer was dependent upon the treatment temperature and time of treatment. Growth rate of the nitrided layer increased with increasing temperature and also with time at a specified temperature. Nitrided layer thickness was also found to depend upon the alloy content, the thickness of the nitrided layers decreased with increasing alloy content. No structural change could be observed in the core regions of ion nitrided ferritic and austenitic stainless steels.

2. The response of nitriding as measured by (i) case depth and (ii) surface hardness indicate that:

(i) The case depth obtained by ion nitriding was much higher in ferritic stainless steel than in austenitic stainless steel. Growth rate of nitrided layer was found to be faster in ion nitriding than in gas nitriding.

(ii) In case of ion nitriding the surface hardness was found to maximum at a treatment temperatures of 475°C for ferritic stainless steel and 500°C for austenitic stainless steel. Ion nitriding produced higher hardness at lower temperature and shorter period of treatment than gas nitriding.

3. Steep hardness profiles were observed in both the types of stainless steels. A lower steepness was obtained on gas nitrided stainless steels.

4. X-ray analysis showed that γ' and CrN phases formed during nitriding of stainless steels.

Chapter VII

SUGGESTION FOR FUTURE STUDY

- i). A comparative study of wear characteristics of ion nitrided and gas nitrided stainless steels should be made.
- ii). Corrosion characteristics of ion and gas nitrided stainless steels should be investigated.
- iii). A comparative study of creep and fatigue characteristics of ion nitrided stainless steels should be carried out.
- iv). Effect of higher nitriding temperature (above 500⁰C) on properties of stainless steels should be investigated.

LITERATURE CITED

1. P.C. Jindal: "Ion Nitriding of Steels", J.Vac. Sci. and Tech., March/April 1978, pp.313-317.
2. "Is Ion Nitriding Superior to Conventional Nitriding Process?", Midland Ross presentation on Heat Treating, Dec.1981, pp.40-43
3. W.D. Soccorscy & W.T. Ebinhara: "Technical Report, RE 70-156 (Science & Technology Laboratory)", Rock Island, Illinois, 1976.
4. A. Staines & T. Bell: "Heat treatment methods and media", Inst. of Metallurgist, London, 1979, pp.58-69.
5. R.M. Lerner: "Glow Discharge Nitriding of Nitralloy 135M and AISI 304 Stainless Steel", Journal of Iron & Steel Inst. London, 1972, p.631.
6. B. Edenhofer: "Physical & Metallurgical Aspects of Ion Nitriding", Heat Treatment of Metals 1974, pp.23-28.
7. V. A. Philips & A.U. Seybolt, TMS-AIME, 1968, p.2415.
8. C.K. Jones & S.W. Martin: "Ion Nitriding Heat Treatment", 1973.
9. T. S. Sudarshan: "Surface Modification Technologies", Marcel Dekker, Inc. New york, U.S.A , 1989.
10. Robert F. Hochman: "Effects of Nitrogen in Metals Surfeces", Proceedings of an international conference on ion nitriding, Ohio, U.S.A., 15-17 Sept. 1986.

11. Smithells Metal Reference Book, Butterworths 1983, chapter 6.
12. Kazuo Ichii, Kimio Fujimura & Takao Takase, "Structure of the Ion Nitrided Layer of 18/8 Stainless Steel", July 20, 1985, pp. 135-144.
13. Poranjpe, V.G., Cohen, Trans. AIME, 195, M & Bayer, M. B., p-261.
14. Fry, A.: Trans. American Soc. for Steel Treatment 1929, p.111.
15. "Metals Handbook", 1972, vol.7, 8th ed.
16. "Metals Handbook", ASM, Vol.2, pp.149-66.
17. D. Laundt: "Nitriding Furnaces", New York, Nitralloy Corp., 1943.
18. V.O. Homerberg & C.F. Floe, "Nitralloy and Nitriding", New York Nitralloy Corp., 1954.
19. Houvin J., Proceedings of the 18th Int. Conf. on Heat Treating of Materials, Detroit, Michigan, 1980, pp. 289-295.
20. Huddis, M. J.: Appl. phys., 1973, pp. 1489-96.
21. Jones C. K. & Martins S.W., Met. Prog. 1964, pp. 94-98.
22. "Metals Handbook", vol. 4, Heat Treating, 9th ed. 1981, p-191.
23. Shahjahan Mridha : Ph.D. Thesis, "Characterisation of Nitrided Alloy steels", Leeds Uni. 1980.
24. J.W. Christain: "Phase Transformation in Metals and Alloys", Pergamon Oxf. 1975, pp. 411-16.
25. F. Hombeck & B. Edenhofer: "Int. Conference of Physical Metallurgy Aspects of Surface Coatings", The Iron and Steel Inst. 1973, London.
26. C.K. Jones & S.W. Martin: "Met. Progress", 1964, p.94.

27. Yu.M. Lakhtin & Yu.N. Krymskii: "Protective coating on Metals", New York, London, 1970, pp.179-181.
28. W.D. Soccorsy & W.T.Ebinhara:" Tech. Report RE-70-156", US Army weapon command, Rock Island,Illinois, 1970.
29. Lightfoot, B.J.: Ph.D. Thesis, "Nitriding of Some Cr-Irons and Steels", Leeds Univ. 1973.
30. D. Sundararaman , P. Kuppusemi & V.S. Raghunathan, "Some Observations on the Ion Nitriding Behavior of a Type 316 Stainless Steel", Surface Tech., 1983, pp.341-347.
31. T. Spalvins: "Tribological and Microstructural Characteristics of Ion Nitrided Steels", Elsevier sequoia, printed in Netherlands, 1983, pp.157-163.
32. K. Ozabaysal, O.T. Inal & A.D. Roming, J.R. : "Ion Nitriding Behavior of Several Tool Steels", Materials Science & Engineering, 1986, pp. 179-189.
33. Light Foot, B.J. & Jack, D.H.: "Heat Treatment" London, The Metals Society, 1975, pp.56-65.
34. H. Jack et al, Scand. J. Metall., 1972, p.217.
35. J. Lightfoot & D.H. Jack: "Heat treatment,1973", (Metal Society London, 1975)
36. N.K. Kobel:" ASM. Tech. Report No. C.7-242", Nat. Met. Congress, Ohio, 1967.
37. Jack K.H.: Proc. Roy Soc., 1951, pp.200-215.
38. Mortimer et al, scand. J. Metall. 1972, p.203.

