A STUDY ON THE NATURE OF LAYERS FORMED DURING LIQUID NITRIDING IN UREA-SODA BATHS.

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. A.S.W. Kurny, Associate Professor, Department of Metallurgical Engineering, BUET, Dhaka, and it has not been submitted elsewhere for the award of any other degree or diploma.

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Supervisor

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ABSTRACT

Liquid nitriding of mild steels have been performed in the temperature range of 525°C-575°C and for times of upto 5 hrs of treatment. The nature of layers formed have been investigated by optical metallography, microhardness measurements and X-ray diffraction techniques. Relative wear rates were determined on a pin-on-disc type apparatus. Effects of addition of sulfur to these baths has also been studied.

The thickness of the compound layers have been found to increase with treatment time at a particular nitriding temperature and with temperature at a particular treatment time. Higher hardness values were obtained on samples treated at lower temperatures. Addition of sulfur has been found to increase the surface hardness values and decrease the depth of nitrogen penetration. The wear resistance of mild steel samples nitrided in urea-soda baths increased with treatment time at any particular temperature whereas decreased with an increase in treatment temperature at a constant nitriding time. Addition of sulfur was found to increase the wear resistance.

X-ray diffraction techniques showed that the nitrided layer consists of Fe_3N and Fe_4N nitrides. An unidentified phase have also been detected in the nitrided layers. The compound layer was found to consist predominantly of Fe_3N nitride. Addition of sulfur in the baths have been found to lead to the formation of FeS_2 in the compound layers of mild steel samples.

CONTENTS

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Chapter - I

INTRODUCTION

1.1 Introduction

A hard wear resistant surface with a tough ductile core are essential properties for the satisfactory performance of many engineering components. Generally it is not possible to impart such a combination of properties only by thermal and/or mechanical treatments. This is because hardness is generally associated with brittleness and so a component treated for maximum hardness becomes too brittle whereas the same component treated for maximum toughness will not be hard enough. Consequently, several processes known as carburising, cyaniding, nitriding, etc. have been developed by which this highly desirable combination of properties can be attained commercially.

In carburising, the high temperature modification, γ -iron is impregnated with carbon in the temperature range of its stability i.e. above the upper critical temperatures and the saturation takes place below the solubility limit of carbon in γ -iron. The carbon impregnated layer is subsequently quenched resulting in the formation of a metalstable phase, martensite, which is directly responsible for the high hardness. In nitriding, low temperature modification, α -iron is impregnated with nitrogen and the impregnation with nitrogen occures above the solubility limit of this element in α -iron. The surface hardness of nitrogen impregnated steel is caused by the highly dispersed nitride precipitates whose quantity and dispersion influence the attainable hardness. Thus the surface hardness obtained by the processes carburising and.

cyaniding processes depend upon the heat treatment after the composition of the surface has been altered. In the case of nitriding, the composition of the case is altered in such a way that the compounds formed are inherently hard and for this reason no further heat treatment is necessary.

The process of nitriding, if handled properly, gives very high surface hardness and wear resistance, not attainable by any other case hardening technique. Moreover, nitriding of steels is performed at much lower temperatures and so the properties of the core are not altered.

The nitrided parts are free of internal stresses and therefore free from aging effects, making them especially suitable for gears, cranshafts, gauges etc. Nitrided layers can retain hardness at high temperatures making them specially suitable for certain applications.

Wear-resistance is greatly increased by nitriding and tool marks and surface scratches seem to have little effect in the fatigue properties of nitrided steel. The formation of the high nitrogen phase in the nitrided case increases the corrosion resistance of steel in atmospheric air, fresh water, superheated steam and gasoline media etc. increases the fatigue limit under corrosive condition.

During nitriding of steels at temperatures below the eutectoid temperature (591°C). The α-phase starts getting saturated with

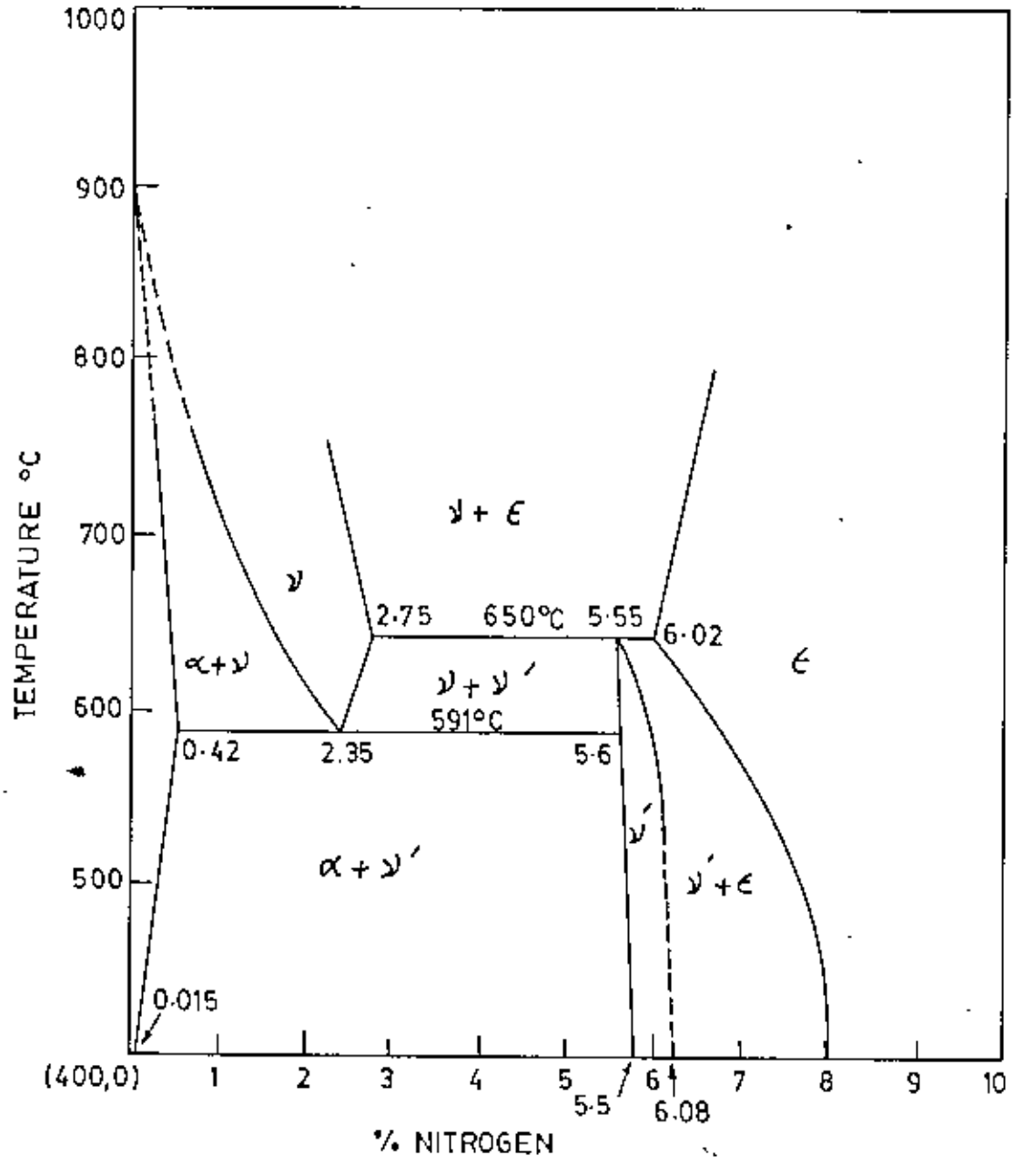


FIG. THE Fe-N EQUILIBRIUM DIAGRAM.

nitrogen. When the limit of solubility of nitrogen in α-phase for the given temperature is reached, the next phase (γ') begins to form. Upon further saturation with nitrogen, the ε-phase will be formed. As a result the ε-phase richest in nitrogen, will be at the surface of the component being nitrided. It will be succeeded by the γ'-phase and finally, the α-phase which goes over to the core:

$$\varepsilon \dashrightarrow \gamma' \dashrightarrow \alpha \dashrightarrow \text{core}$$

when the temperature is lowered, the ε and α-phase decompose and the excess γ'-phase is precipitated as shown by the equilibrium diagram (Fig. 1.1). Therefore, at room temperature we obtain a case in which the phases are arranged in the following order (from the surface to the core):

$$\varepsilon + \gamma' \text{ (excess)} \dashrightarrow \gamma' \dashrightarrow \alpha + \gamma' \text{ (excess)} \dashrightarrow \text{core}$$

1.2 Types of Nitriding

Nitriding is more expensive, more complex and more time consuming than any other surface hardening technique. However, the process of nitriding has received considerable attention from the industrial as well as scientific community. As a result nitriding can now be performed in various saturating media, solid, liquid or gaseous. Numerous modifications of the techniques have been evolved to suit specific requirements in service. Nitriding processes are classified on the basis of the medium from which nitrogen is generated

in atomic form and are used to saturate the steel surface. The more common processes include:

1.2.1 Gas Nitriding:

Gas nitriding is usually accomplished in muffle furnaces. Ammonia gas is introduced into a gas tight furnace chamber heated upto a temperature of 500°C - 600°C and decomposes according to the following equations:

$$2NH_3 = 3H + N \text{ (atomic)}$$

$$2N = N_2$$

$$2H = H_2$$

It is important to note that ammonia gas decompose giving the nitrogen in nascent or mono-atomic form, which is the only form capable of entering the steel and diffusing into it. If the ammonia gas is decomposed outside the gas tight retort of the furnace and then the dissociated ammonia is admitted into the retort, no nitriding of the steel will occur, because the molecular nitrogen contained in the decompose ammonia is not capable of diffusing into the steel. The possibility of iron reacting with nitrogen was known as early as in 1906 but the present commercial viability of the process is due to the thorough study of the problem in 1919 by Dr. Adolph Fry[1] of the Krupp works in Essen, Germany and its further development by subsequent investigators throughout the world.

1.2.2 Ion-Nitriding:

The most recent development in the field of nitriding is the glow discharge or ion-nitriding. This uses the plasma state of matter and is also called plasma nitriding. The process with its high degree of variability and adaptibility, appears to have a broader range of application than any of the other nitriding techniques.

The concept and the principle of ion-nitriding were first established in Germany By Bernerd Berghaus[2] in the early 1930's. In this technique, a low pressure nitrogen gas introduced into a vacuum chamber (1-10 torr) is ionised under the influence of a high d.c. voltage (400-1000V) and becomes electrically conductive. Positive nitrogen ions are attracted by the cathodic workpiece where, on heating its surface. They cause the nitriding action. The energy transfered to the workpieces by the ion-bombardment is utilised to heat the workpiece to the necessary treatment temperature (400-600^{o}C). The temperature of the workpiece is measured and controlled by means of thermocouples which are inserted in the charge. Thus no external heating is required.

1.2.3 LIQUID NITRIDING

In liquid nitriding the work is heated in molten salt baths containing cyanides. The sodium cyanide in the bath reacts with the oxygen in the air and is oxidised according to the reaction:

1. $NaCN + O_2 \longrightarrow NaCNO$

2. $NaCNO + O_2 \longrightarrow Na_2CO_3 + CO + 2N_{at}$

3. $CO \longrightarrow CO_2 + C_{at}$

Thus both nitrogen and carbon is picked up by the steel during heating in cyanides. This simultaneous saturation of the steel with carbon and nitrogen results in superior properties of this layer.

When performed in the temperature range of 540-575°C, this process adds more nitrogen and less carbon and is therefore classified as nitriding. Heating of steels in cyanide baths in the temperature range of 820-870°C, adds up more carbon and less nitrogen and according the operation is called cyaniding.

The liquid nitriding technique has several modifications and is applied to a wide variety of carbon, low alloy and tool steels. In order to accelerate the chemical activity of the bath, enlarge the number and types of steels that can be processed and to improve the properties, several special liquid nitriding processes have been developed.[3-5] In one such process, called liquid pressure nitriding[3], anhydrous ammonia is introduced into a cyanide bath. The bath is sealed and maintained at a pressure of 1 to 30 atmospheres. Because the molten cyanides are diffused with anhydrous ammonia, a newly prepared bath does not require aging and may be put into immediate operation. In yet another process, aerated bath nitriding[3], measured amounts of air are pumped through the

molten bath. The introduction of air provides agitation and stimulates chemical activity.

The presence of sulphur in liquid nitriding baths is known[4-6] to result in improved properties particularly in the scuffing resistance. In presence of sodium sulphide, additional reactions occur within the melt:

$$Na_2SO_3 + 3NaCN \longrightarrow Na_2S + 3NaCNO.$$

Hence the sulphur content accelerates the formation of cyanate radical and the nitriding effect is greatly increased. The degree to which sulphur becomes a part of the compound zone has not yet been completely understood; nonetheless, practical application is now well established; and in addition to increasing the wear resistance, the fatigue resistance of treated materials is increased by as much as 100%.

A typical commercial bath for liquid-nitriding is composed of a mixture of sodium and potasium salts. The sodium salts which comprise 60-70% (by wt.) of the total mixture consists of 96.5% NaCN, 2.5% Na_2CO_2 and 0.5% NaCNO. The potasium salts 30-40% (by wt.) of the mixture, consist of 96% KCN, 0.6% K_2CO_3, 3% KCNO, 0.5% KCl. The operating temperature of this salt bath is about 565^{O}C. This bath is widely used for nitriding tool steels, including high speed steels and a variety of low alloys steels including nitralloys.

Uses of liquid nitriding are similar and at times identical to gas nitriding. However, in some cases liquid nitriding has proved to be superior to other case hardening methods. Moreover nitriding in the liquid baths has all the advantages of heating in a liquid bath.

1.2.3.1 Liquid-Nitriding in Urea-Soda Baths:

Inspite of all these advantages liquid nitriding suffers from a major disadvantages, in that the salt is deadly poisonous and requires very special care during storage, handling and operation. Effect to overcome this difficulties has resulted in a number of modifications[3,6] of liquid nitriding technique. These include cyanate-cyanide baths, carbamide baths and nitride-soda baths. In addition to these a new technique[7] of nitriding in Urea and Soda has been developed in the department of Metallurgical Engineering, BUET, Dhaka. Results obtained[7-13] so far has been very encouraging.

During melting intimate mixtures of equal volumes of urea and sodium carbonate react to form sodium cyanide, ammonia, carbon dioxide and water vapour. Of these products ammonia, carbon dioxide and water vapour leave the pot leaving only sodium cyanide in the bath. The sodium cyanide then reacts with oxygen according to the following reactions produce active nitrogen and carbon.

$$CO(NH_2)_2 + Na_2CO_3 = NaCN + NH_3 + CO_2 + H_2O$$

$$2NaCN + O_2 = NaCNO.$$

$$2NaCNO + O_2 = Na_2CO_3 + 2N_{at} + CO$$

$$2\,CO = CO_2 + C_{at}$$

It is thus apparent that urea and soda may be used as the starting material of a bath for liquid nitriding of steels. Although the final composition of this bath is similar to that based on cyanides, it is advantageous in that toxic cyanide salts need not be stored.

1.3 Aim and Scope of Present Work

Liquid nitriding in urea-soda is a process developed at the Department of Metallurgical Engineering at the Bangladesh University of Engineering and Technology, Dhaka. Recent review papers[14-15] on liquid nitriding also confirm that such baths for nitriding are not in use. Results of nitriding in this inherently less toxic bath has been very satisfactory. The technique is very simple and the raw materials urea and soda are readily available all over Bangladesh. Utilisation of this technique may greatly help the production of machine spares and components of good quality in Bangladesh. These studies' were concerned mainly with the process parameter like the time and temperature of treatment and their effects on hardness, depth of penetration etc. in the nitrided sample.[7-9] Attempts[13] have been made to study the mechanical properties of steels liquid nitrided in these baths. The behaviour of this bath has also been studied[11-12] and the optimum bath

composition for satisfactory nitriding has been identified. No efforts have so far been made to relate the properties of the nitrided specimens to the structures of the nitrided layers.

This study aims to determine the nature of the layers formed during nitriding in urea-soda baths by using optical metallography and X-ray diffraction techniques, and also to relate the hardness and wear properties of the nitrided samples to the structures of the nitrided layers.

It is known that the addition of sulphur compounds to a molten bath improves the wear properties of steels nitrided in conventional cyanide-based baths. Effects of addition of sulphur on the nature and properties of the steels nitrided in urea-soda baths have also been investigated in an exploratory manner.

Chapter – 2

LIQUID NITRIDING IN UREA-SODA BATHS – A SURVEY

2.1 Introduction:

Liquid nitriding in urea-soda baths is a process developed in the department of Metallurgical Engineering at Bangladesh University of Engineering and Technology, Dhaka. No work on baths based entirely on urea-soda has been reported even in recent review papers.[14-15] Investigations[15] on the addition of 0.5 pct. urea to conventional liquid nitriding baths have, however, been performed and was found to improve wear resistance. 5 pct. urea has been used to regenerate cyanide-cyanate melts. It has been claimed that the utilisation of this new technique will help to improve the quality of machine spares and components in Bangladesh. In this chapter a description of the process and a brief review of the work done so far has been attempted.

2.2 Preparation of the bath:

Equal volumes of urea and soda are thoroughly mixed and then melted in a pot by very slow-heating. During melting intimate mixture of urea and sodium carbonate react to form sodium cyanide, ammonia, carbon dioxide and water vapour. Of these production ammonia, carbon dioxide and water vapour leave the pot and thus only sodium cyanide is left in the bath. This sodium cyanide then reacts with oxygen to produce active nitrogen and carbon.

2.3 Aging:

A minimum cyanate content was found to be essential for satisfactory nitriding and it was recommended that the molten salt should

be aged for about 12 hrs at 560-580°C before any work is placed in the bath.[9] During aging the cyanide content decreased while the cyanate content increased due to oxidation. Experiments 11,13 in this bath have shown that 25-35% cyanate in the bath gives good result. Because of continued oxidation the ratio of cyanate to cyanide changes with time during nitriding. Careful control is therefore necessary for satisfactory operation and proper additions must be made to maintain the bath composition. It has already been pointed out that no experiments to determine the exact nature and amount of additions has so far been performed.

2.4 Maintenance:

To protect the bath from contamination and to obtain satisfactory nitriding., all worked placed in the bath should be thoroughly cleaned and free of oxides. Over heating (above 590°C) causes breaking down of the salt to carbonate and should be avoided.[13] Carbonate content in excess of about 25% should be removed by decreasing the bath temperature. At low temperatures the carbonate solidifies and settles at the bottom and may then be removed by a spoon.

2.5 Behaviour of the Bath:

It has been observed that like the conventional liquid nitriding baths based on cyanides this bath also had a limited life and after the expiry of this useful life satisfactory nitriding could

not be obtained.[11,13] This has been attributed to the high carbonate build up in the bath. For example, the bath based on urea-soda on isothermal aging became viscous after about 60 hrs at 500°C and 46 hrs at 540°C. No nitriding could then be performed and the salts in the bath had to be discarded. At still high temperatures 575°C for example, the rate of evaporation of the salts was found to be very high.

Urea and Soda react with oxygen in air and hence gets oxidised to cyanate. This cyanate on further oxidation forms atomic nitrogen and carbon and also sodium carbonate. It can also be noted that a higher amount of carbonate forms at a higher temperature i.e. the rate of reaction is faster at higher temperatures. This gradual increase in the amount of carbonate is not unexpected because on melting cyanide is formed in the bath. This gets oxidised to cyanate and then to carbonate. This carbonate does not take part in further reaction while more carbonate forms due to further oxidation of cyanite. Thus the carbonate content in the bath increases continuously. The salt mixture was melted by heating at the specified temperatures. It took 2 to 3 hrs before a completely molten salt bath could be obtained. Reactions during this stage is perhaps responsible for the high carbonate content in the bath. Moreover, equal amounts of Urea and Soda was melted and thus the amount of soda in excess of the amount required for the reaction was also present in the bath, resulting in a high carbonate content at the early stages of operation. Experi-

ments has not however been performed with stoichiometric amount of carnonate in the preparation of the bath. Moreover, although it has been indicated[11] that the useful life of the bath could be increased by

a. Periodic addition of only urea or a mixture of greater amount of urea together with a smaller amount of carbonate to replenish the spent salt.
b. Removing the excess carbonate by lowering the bath temperature and thus allowing the carbonate to settle at the bottom. The carbonate could then be removed easily by a perforated spoon.
c. Using sodium carbonate in amounts exactly required for the balanced equation of the reaction with urea. No experiments have so far been performed.

2.6 Effect of Process Variables:

As in other techniques of nitriding, the maximum hardness of the specimens nitrided in this bath has been obtained[8-9] after shorter treatment times at higher temperatures, while at lower treatment temperatures, the maximum hardness is obtained by nitriding for a longer period. Results of nitriding in inherently less toxic bath has shown that the case depth produced is higher[8] than that obtained in conventional baths. Exploratory experiments[12] on the effects of nitriding on the mechanical properties like fatigue, wear resistance and tensile properties have shown that these

properties can be significantly altered by nitriding in this bath in much the same way as by nitriding in the conventional cyanide based baths. Optimum treatment conditions capable of giving best results were, however, not identified.

2.7 Safety Precautions:

Operating personnel must be carefully instructed in handling the poisonous cyanide containing salts. All chemical containers must be clearly marked to indicate contents. Personnel should be provided with facilities for washing their hands thoroughly to prevent contamination by the cyanide salts. Sheild, gloves, aprons and eye protection should be worn by operating personnel. Parts should be preheated to drive off any moisture that may be present before they are immersed in the molten salt bath. Proper venting of furnace and rinse tanks to the outdoors is recommended to provide safety against fumes and spattering and to minimise corrosion in the work area. Nitrate - nitrite salts must not come in contact with nitriding salts in the molten salts; contact will result in an explosion.

2.8 Economic Considerations:

The raw-materials urea and soda are readily available all over Bangladesh. The cost of nitriding is also greatly reduced by the use of this bath. For example 1 kg of salt for a conventional cyanide bath costs nearly Taka 1000/- (One thousand) while production of 1 kg of salt in urea-soda baths involves a cost of less than Taka 30/- (thirty) only.

Chapter - 3

MATERIALS AND METHODS

MATERIALS AND METHODS

3.1 Introduction:

Liquid nitriding of mild steel specimens in baths based on Urea-Soda were performed and the nature of the layers formed were determined. Effects of sulfur on the nature and properties of the nitrided layers has also been explored. In this chapter, the preparation and heat treatment of the specimens used in the present investigations are described. The different experimental techniques used to follow the effects of nitriding are also described.

3.2 Specimen Preparation:

A one-inch dia mild steel rod was hot forged into a 1"/16 thick flat bar and specimens measuring 20 mm X 20 mm were prepared for optical metallography hardness measurements and structure determination. 10 mm long mild steel pins for wear studies were prepared by machining mild steel rods.

3.3 Heat Treatment:

The high hardness of the nitrided layers has to be supported by a strong core. It is thus a usual practice to nitride specimens at temperatures 30-50^{o}C below tempering temperatures.

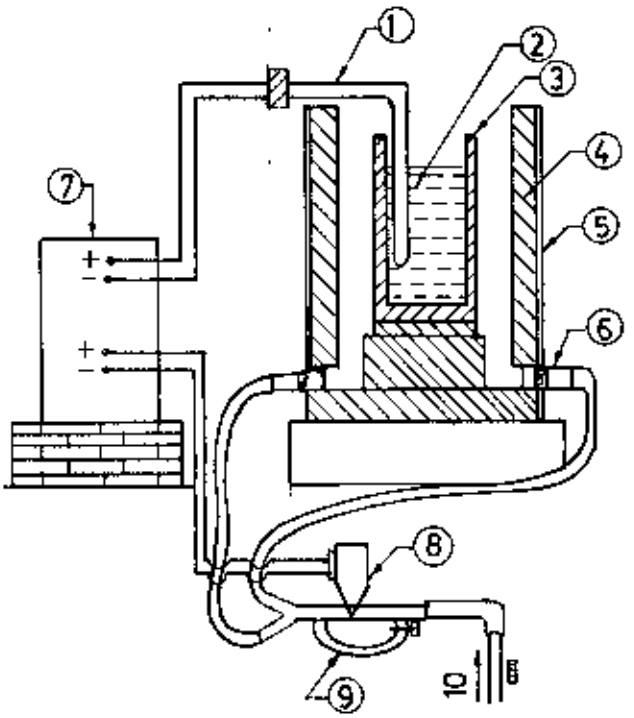
Since it was expected that quenching will not cause appreciable hardening in mild steels, the specimens were not heat-treated.

However, in order to obtain uniform specimens, all the samples were normalised by heating to 910°C and cooling in still air. These were then polished and stored in a desicator prior to nitriding.

3.4 Nitriding:

A cast iron pot heated in a gas fired pit furnace has been used as a bath in these experiments (Fig. 3.1). A chromel-alumel thermocouple placed inside a stainless steel tube closed at one end and immersed within the liquid was used to measure the temperature. A solenoid control valve designed and fabricated in the dept. of metallurgical engineering was used to control the bath temperature to ± 5°C. In an effort to study the effects of addition of sulfur on the structure and properties of nitrided layers, sulfur in the form of sodium sulfide (Na_2S) was added to the molten bath, in such quantities that sulfur in the bath amounted to 2.00 per cent. The specimens were suspended within the molten salts by nichrome wires. After nitriding for a specified time at the desired temperature, the specimens were taken out. These were then taken, washed throughly in running water, neutralised in alkaline calcium hypochlorite solution, dried and stored in a desicator.

Nitriding has been carried out for the following time and temperatures:



1. Thermocouple to pot (salt bath)
2. Salt bath
3. Cast iron pot
4. Refractory lining
5. Steel Plate
6. Burner
7. Controlling pyrometer
8. Solenoid valve
9. Bypass line with valve
10. Gas supply to the furnace

FIG. 3.1 SCHEMATIC DIAGRAM OF GAS FIRED LIQUID (UREA-SODA BATH) NITRIDING FURNACE WITH AUTOMATIC CONTROL SYSTEM.

Materials: Mild steel, Bath: Urea-Soda without sulphur addition and sulfur addition.

Bath	Temperature ^{o}C	Time of treatment (hrs)
Urea-Soda (no sulphur)	525	½, 1, 2, 3, 5
	550	½, 1, 2, 3, 5
	575	½, 1, 2, 3, 5
Urea-Soda with sulphur	575	½, 1, 2, 3, 5

3.5 Optical Metallography

Small pieces from the nitrided samples were cut off using a silicon carbide wheel for optical metallography work. Specimens were carefully cut at 90 degrees to nitrided surface and mounted such that only the transverse section is revealed. Standard methods were used in specimen preparation for observation. 5 percent solution of nitric acid in alcohol was used as an etchant to reveal the structure of the nitrided specimens. The microstructure were then observed and photographed in a microscope.

3.6 Hardness Measurements

A Shimadzu microhardness tester has been used to carry out the hardness measurements and a load of 100 gm. was applied for 5 sec. to cause the indentation. No further treatment of the

nitrided samples were done for these microhardness measurements. Hardness and penetration distance profiles were also determined on all samples, for which specimens prepared for optical metallography were used. These measurements were made with 100 gm. load applied for 5 seconds and the distance between two successive indentations were kept constant as far as possible.

3.7 Wear Studies

Nitriding by any of the available techniques improves wear properties. One of the main reasons of choosing nitriding treatment for machine components and tools is the improvement in the wear resistance and dry-running properties of the material. It is generally considered that the wear-resistance improves with increasing hardness of the case. But hardness is not always a significant factor in determining wear resistance; the highest wear resistance does not always coincide with maximum hardness.

Wear of solid surfaces is a complex phenomenon, the nature of which may be affected by a slight change in operating conditions. For this reason, practical tests in laboratory seldom give reproducible or conclusive results. However, these tests if performed carefully, give useful information regarding wear loss of materials in actual service conditions.

The wear loss measurements have been done on a simple wear machine consisting of a pin made of the nitrided specimen, rubbing the

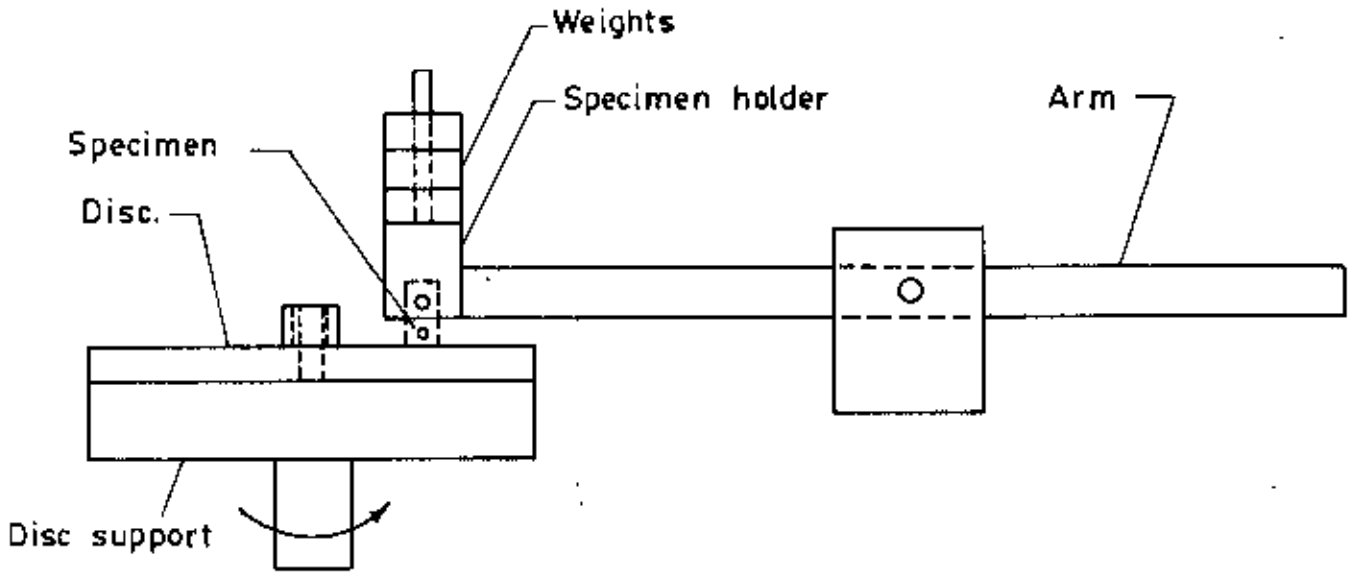


FIG. 3.2 THE WEAR APPARATUS.

Chapter-4

RESULTS AND DISCUSSIONS

flat face on a smooth hardened die-steel disc. A schematic diagram of the wear apparatus is shown in Fig. 3.2. The specimen could be positioned at four different values of disc radius by moving the arm horizontally.

10 mm diameter pins, 10 mm long were nitrided in the bath. To simulate the actual working conditions under which nitriding is reputed to considerably improve the wear resistance of a material these of tests were performed under normally dry conditions.

The load on the pin was kept constant throughout the series at 1.485 kg. which implies a bearing pressure of 0.0058 kg/mm^2. The tests were conducted for a constant contact distance of 198.85 meters to note the effect of nitriding time and temperature on the wear properties of the material and also to find out whether addition of sulphur in the bath helps to improve wear properties.

3.8 X-Ray Diffraction Studies

The aim of the X-ray diffraction studies was to determine the structure of the nitrided layer formed on the surface during nitriding in the bath. Nitrided sheet specimens, without any further treatment were studied for X-ray work. X-ray diffraction patterns were recorded using Fe radiation in a Jeol X-ray diffractometer. A scanning speed of 1 degree per minute with a chart speed of 1 cm per minute were used to record the patterns and were used to identify the phases present and to index the diffraction lines.

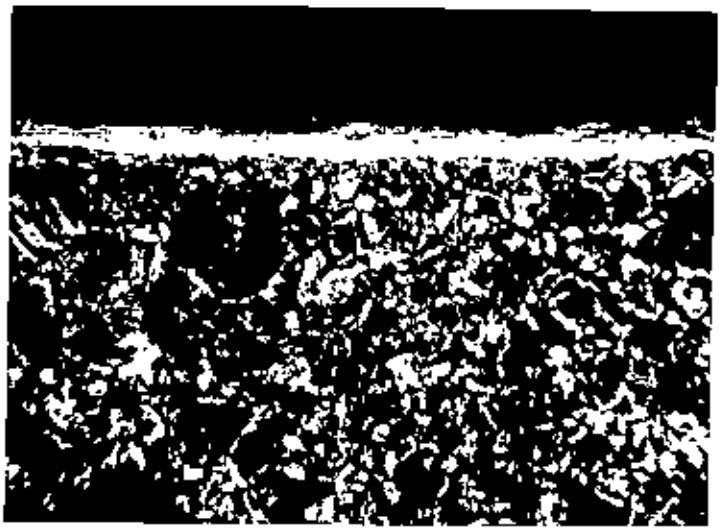
4.1 INTRODUCTION:

Mild steel specimens have been liquid nitrided in urea-soda baths in the temperature range of 525 - 575^{o}C and for times of upto 5 hours of treatment. The effects of nitriding in this bath have been followed by optical metallography, microhardness measurements and x-ray diffraction techniques. Relative wear measurements have also been performed on a pin-on-disc' type apparatus designed and fabricated in the department of metallurgical engineering at the Bangladesh University of Engineering and Technology, Dhaka. Effects of addition of 2 per cent sulfur to this bath have also been investigated. The results of these investigations have been presented and discussed in this chapter

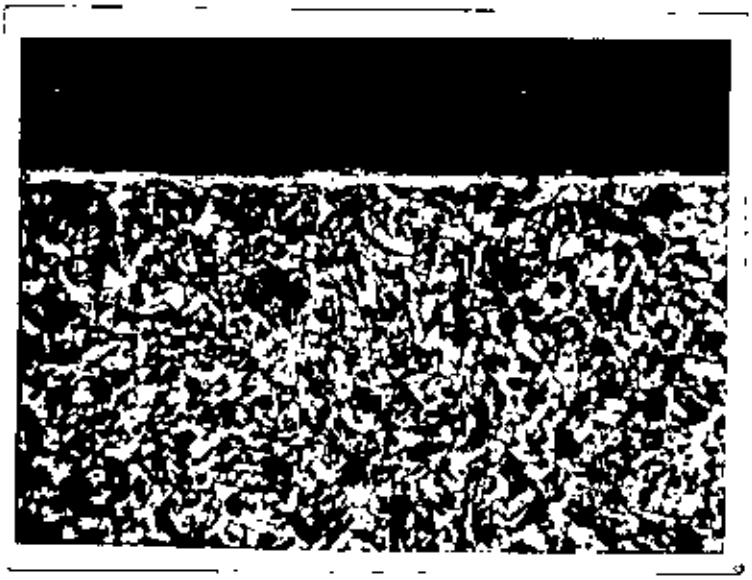
4.2 OPTICAL METALLOGRAPHY

4.2.1 Introduction:

The microstructural changes occuring in the steels during liquid nitriding were followed by optical microscopy. Transverse sections of nitrided specimens were mounted in thermo-setting resin and were prepared by using standard techniques. The nitrided specimens were etched with 5% nital and the structures were observed at x200 magnification and photographed on an optical metallograph. The microstructures of the specimens are presented in Fig. 4.1 to 4.3. The study of the microstructures show that the compound layers formed during nitriding in this bath is compact and the addition of sulfur to the molten salts leads to the formation of a thinner compound layer.



(a) x200 5 pct. Nital.

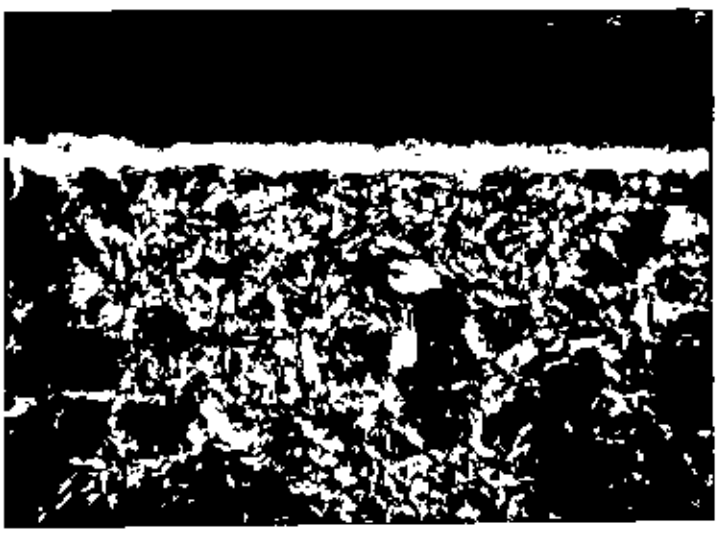


(b) x200 5 pct. Nital.

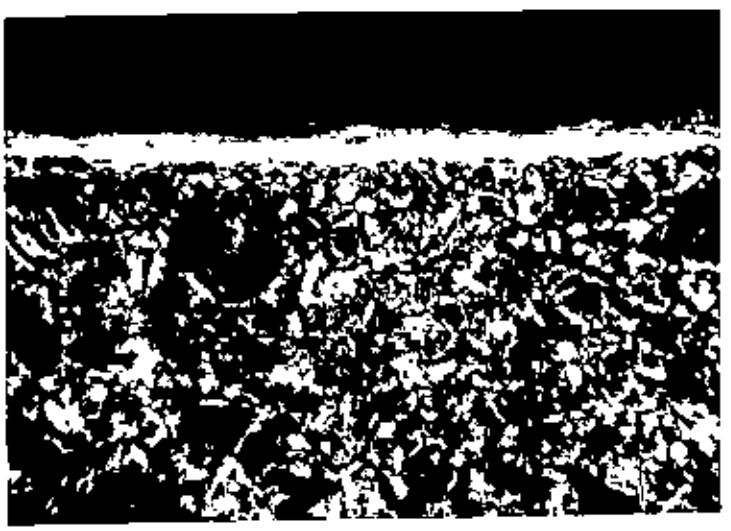
Fig. 4.1: Optical micrograph of mild steels liquid nitrided in ...

a) Urea-Soda Baths for 3 hrs at 575^{o}C.

b) Urea-Soda Baths for 3 hrs at 550^{o}C.

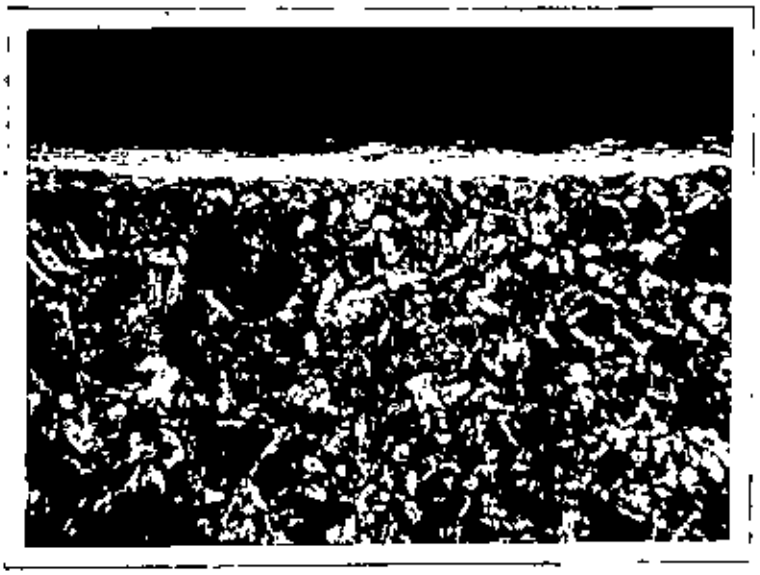


(a) x200 5 pct. Nital.



(b) x200 5 pct. Nital.

Fig. 4.2: Optical micrograph of mild steels liquid nitrided in
a) Urea-Soda Baths for 5 hrs at 575°C.
b) Urea-Soda Baths for 3 hrs at 575°C.



(a) x200 5 pct. Nital.

(b) x200 5 pct. Nital.

Fig. 4.3: Optical micrograph of mild steels liquid nitrided in

a) Urea-Soda Baths for 3 hrs at 575^{O}C

b) Urea-Soda Baths containing 2 pct. sulfur for 3 hrs at 575^{O}C.

4.2.2 Effect of Time and Temperature:

Fig. 4.4 shows the variation in thickness of the compound layer formed on the mild steel samples treated in urea-soda baths. It can be seen that the thickness of the compound layer increases with time at temperature. A comparatively thin compound layer is formed on the steels treated at lower temperatures (550°C, 525°C), while the compound layer thickness is more on samples nitrided at higher temperatures (575°C). The nature of the curves shows that the growth of the layer is diffusion controlled and such results are therefore to be expected.

4.2.3 Effect of sulphur on the thickness of the compound layer

Fig. 4.5 shows that at 575°C, a comparatively thin compound layer is formed on mild steel specimens nitrided in urea-soda baths containing 2 % sulphur as compared to a thicker layer formed on mild steel specimens treated at the same temperature in baths containing no sulphur. It is to be mentioned that a black adherent layer formed on the samples treated in baths containing sulfur. Formation of such layers limits the pick up of nitrogen and carbon by the steel, thereby causing a decreases in the nitriding potential and leading to the formation of a thinner compound layer. It will be seen in a later section that in good agreement with this observation a lower case depth has been found to have formed on the mild steel specimens liquid nitrided in urea-soda baths containing sulfur. Mitchell and Dawes[16] also noted that with higher contents of sulfur in nitriding baths a heavy adherent black deposit is formed on the surface of the nitrided steel.

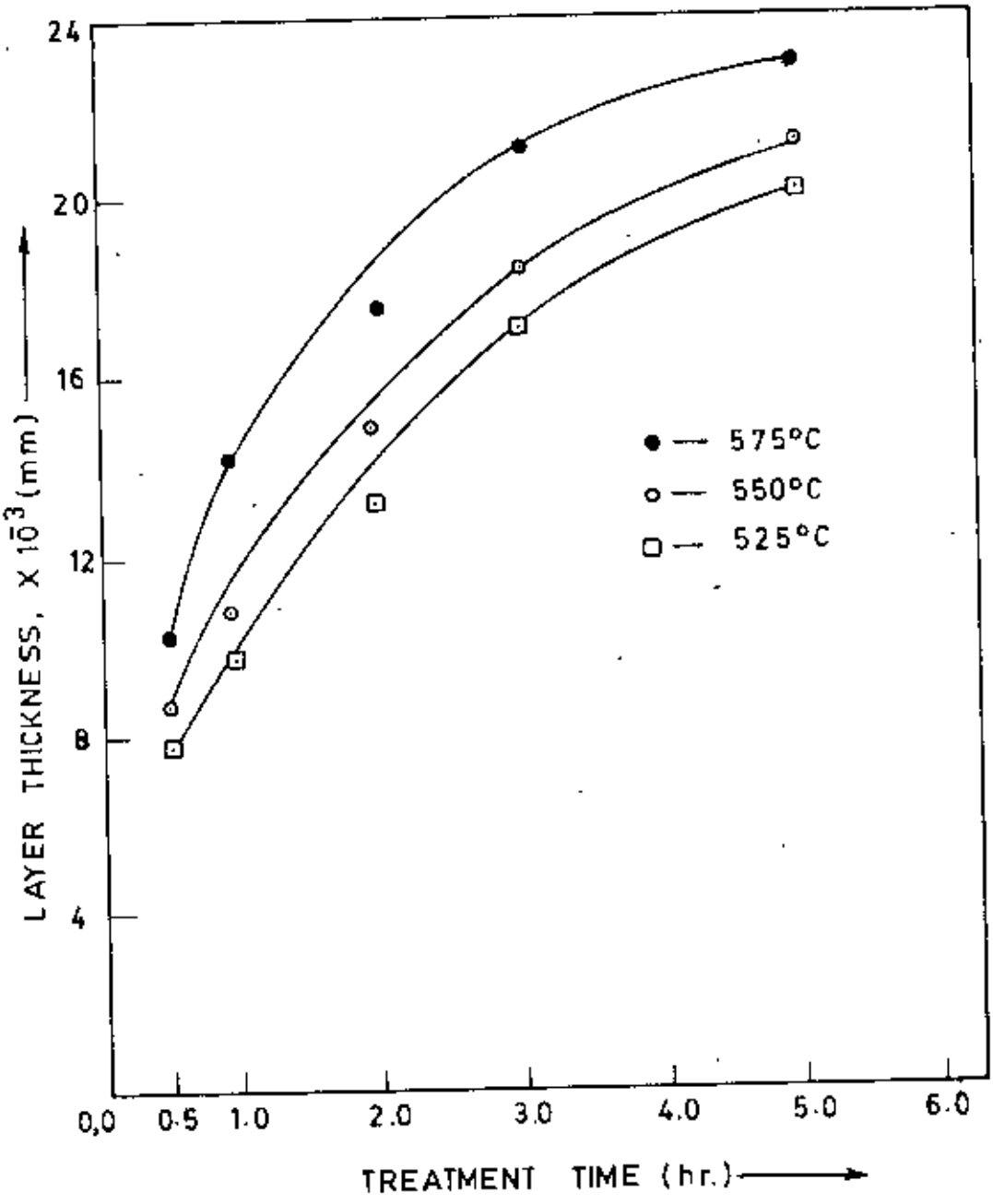


FIG. 4.4 VARIATION IN THE COMPOUND LAYER THICKNESS WITH TREATMENT TIME AT DIFFERENT TEMPERATURES OF THE MILD STEEL SPECIMENS LIQUID NITRIDED IN UREA-SODA BATHS.

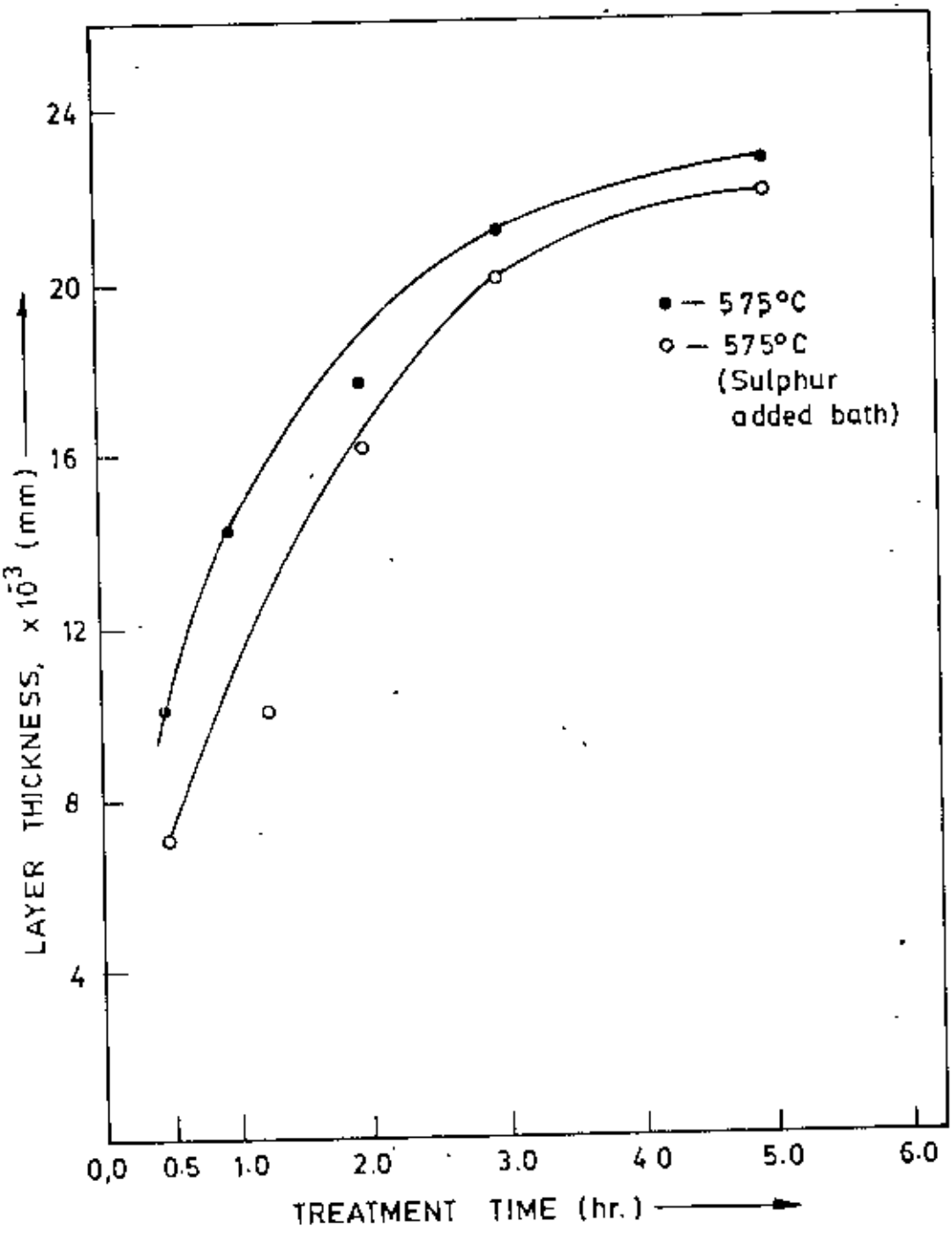


FIG.4.5 EFFECT OF ADDITION OF SULPHUR ON THE THICKNESS OF THE COMPOUND LAYERS FORMED ON MILD STEELS DURING LIQUID NITRIDING IN UREA-SODA BATHS.

4.3 HARDNESS MEASUREMENTS:

4.3.1 Introduction:

Microhardness measurements both on the surface and as a function of distance from the surface have been made on all samples. Hardness versus penetration-distance profiles give useful information regarding the depth of penetration of nitrogen and the variation of hardness from the surface to the core and are used extensively. The results of hardness measurements obtained in these studies are discussed below.

4.3.2 Surface hardness

Surface hardness measurements were carried out on all liquid-nitrided samples by using a Simudzu microhardness tester. A 100gm load was used for 5 sec to cause the identations.

Fig. 4.6 shows that the surface hardness of all nitrided samples falls gradually with treatment time at all temperatures investigated. Moreover, it has been observed that the hardness values (VHN) obtained on samples treated at lower temperatures ($525^{o}C$) are always higher than the surface hardness obtained on samples treated at higher temperatures ($550^{o}C$ and $575^{o}C$). The rate of decrease in surface hardness is greater at higher temperatures.

Hardness in nitriding is caused by finely dispersed nitride particles within the matrix and is dependent on the size of

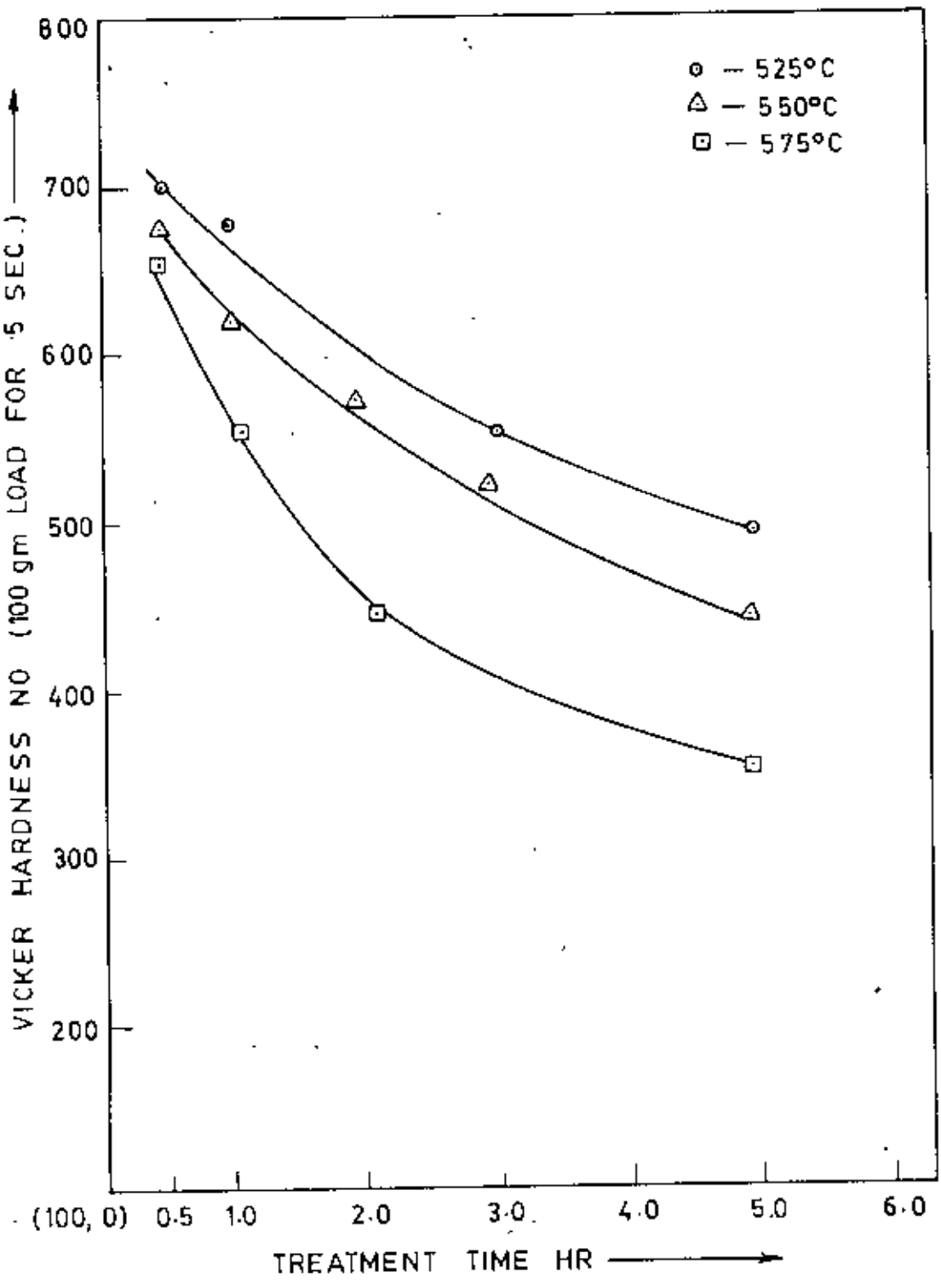


FIG.4.6 VARIATION IN SURFACE HARDNESS WITH TREATMENT TIME OF MILD STEEL SPECIMENS LIQUID NITRIDED IN UREA-SODA BATHS.

the nitride particles. Philips and Seybolt[17] studied precipitation of alloy-nitrides using electron microscopy and noted that coarse nitrides caused only small to moderate hardening. They identified tiny particles, which were hard to resolve, to be the principle source of hardening.

The growth of the nitride particles is depended on time and temperature and therefore the rate of growth is likely to be higher at higher temperatures, thus causing a faster decrease in hardness at higher temperatures.

4.3.2.1 Effect of sulfur on surface hardness:

Fig. 4.7 shows that the addition of sulphur in liquid nitriding baths causes an increase in surface hardness as compared to the surface hardness of the mild steel samples nitrided at the same temperature in baths without sulphur. It is seen therefore, that additions of sulphur increases the surface hardness.

4.3.3 Hardness versus penetration distance profiles

Section orthogonal to the treated surfaces were mounted and were used for microhardness measurements as a function of distance from the edge. The zero point for the distance scale corresponds to the extreme outer edge of the sample including the compound layer. The hardness measurements started at the point of closest approach to the edge and were spaced equally

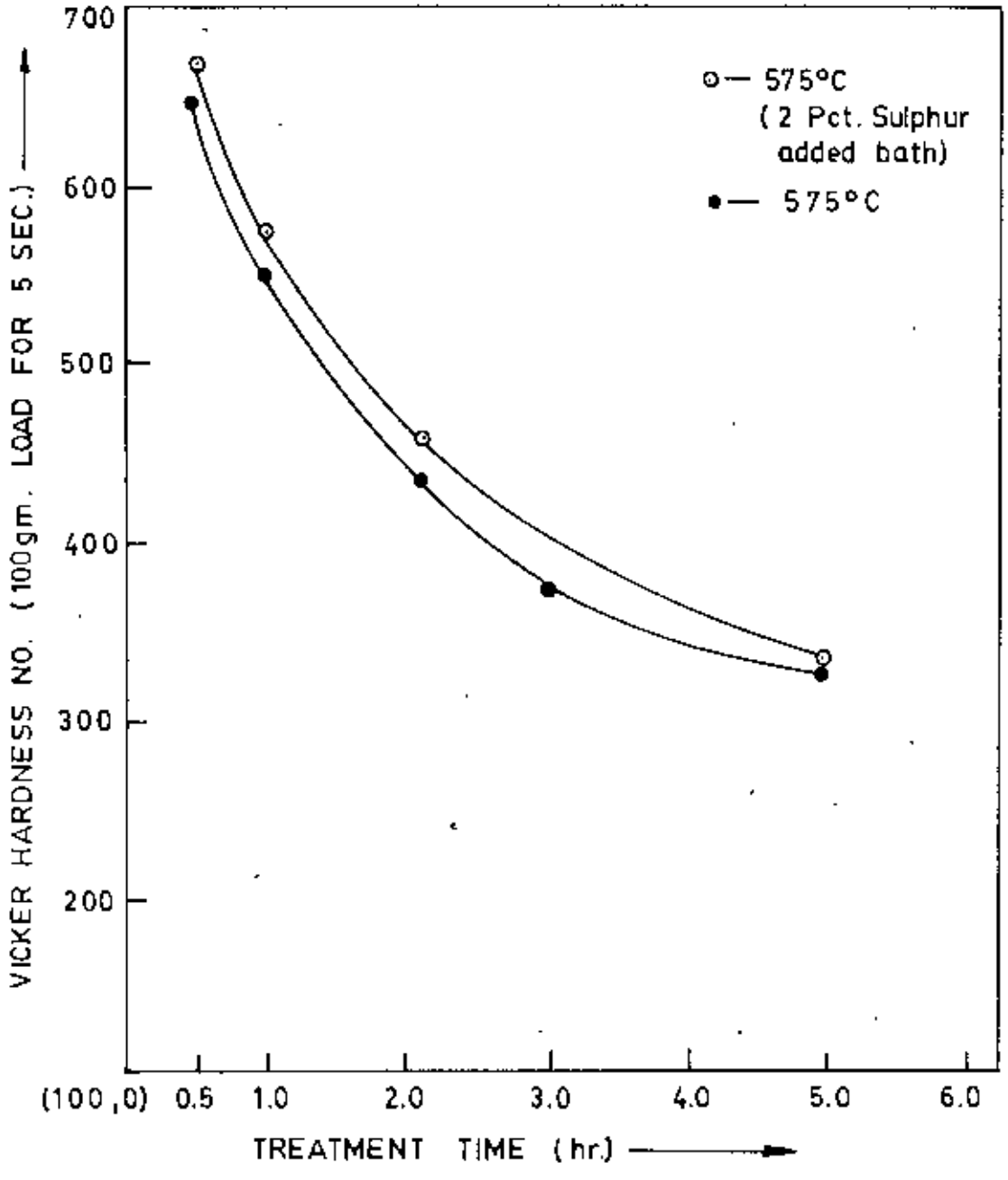


FIG.4.7 EFFECT OF SULPHUR ADDITION ON SURFACE HARDNESS OF STEELS LIQUID NITRIDED IN UREA–SODA BATHS.

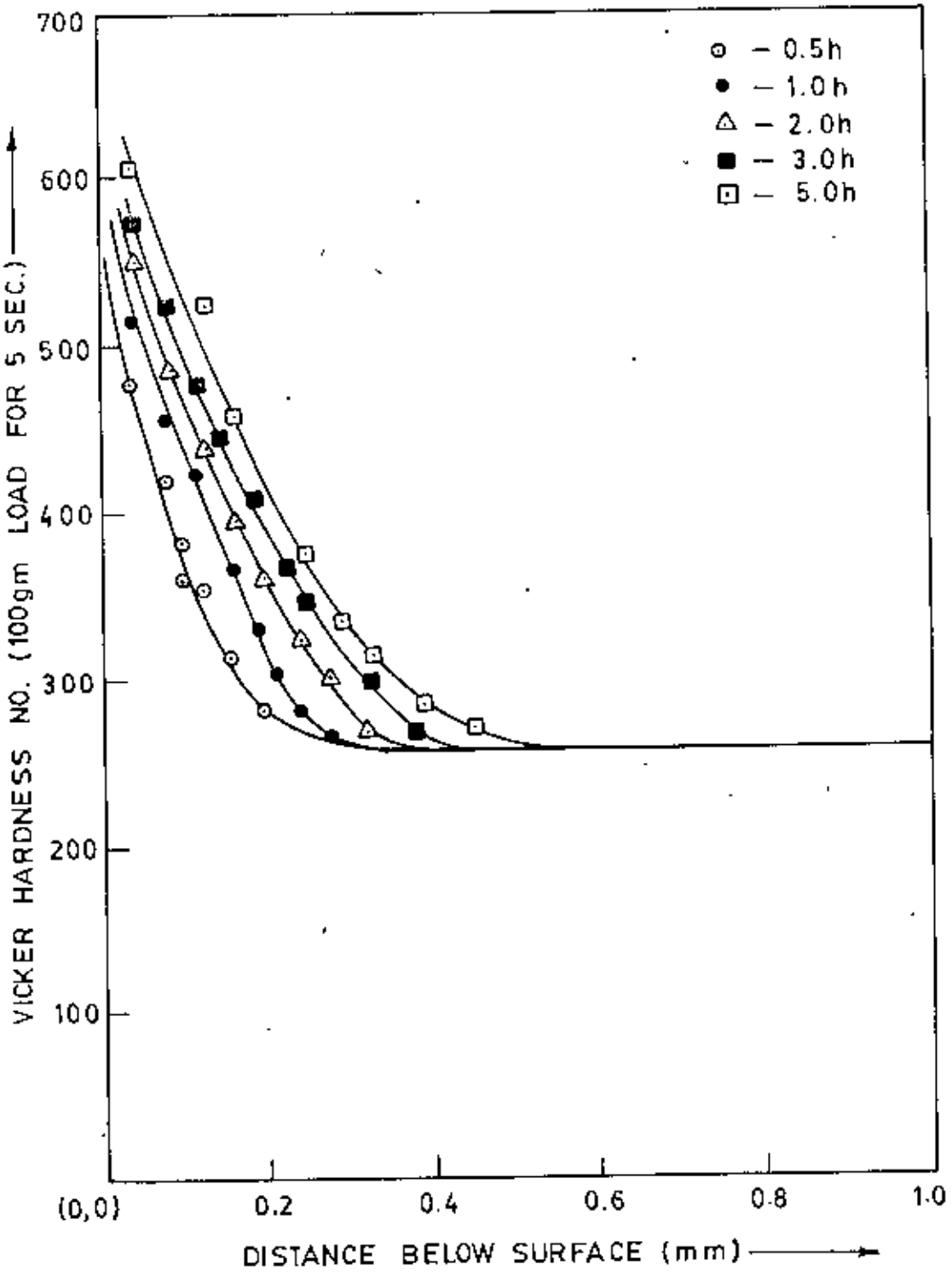


FIG.4.8 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME OF MILD STEEL SPECIMENS LIQUID NITRIDED AT 525°C IN UREA-SODA BATHS.

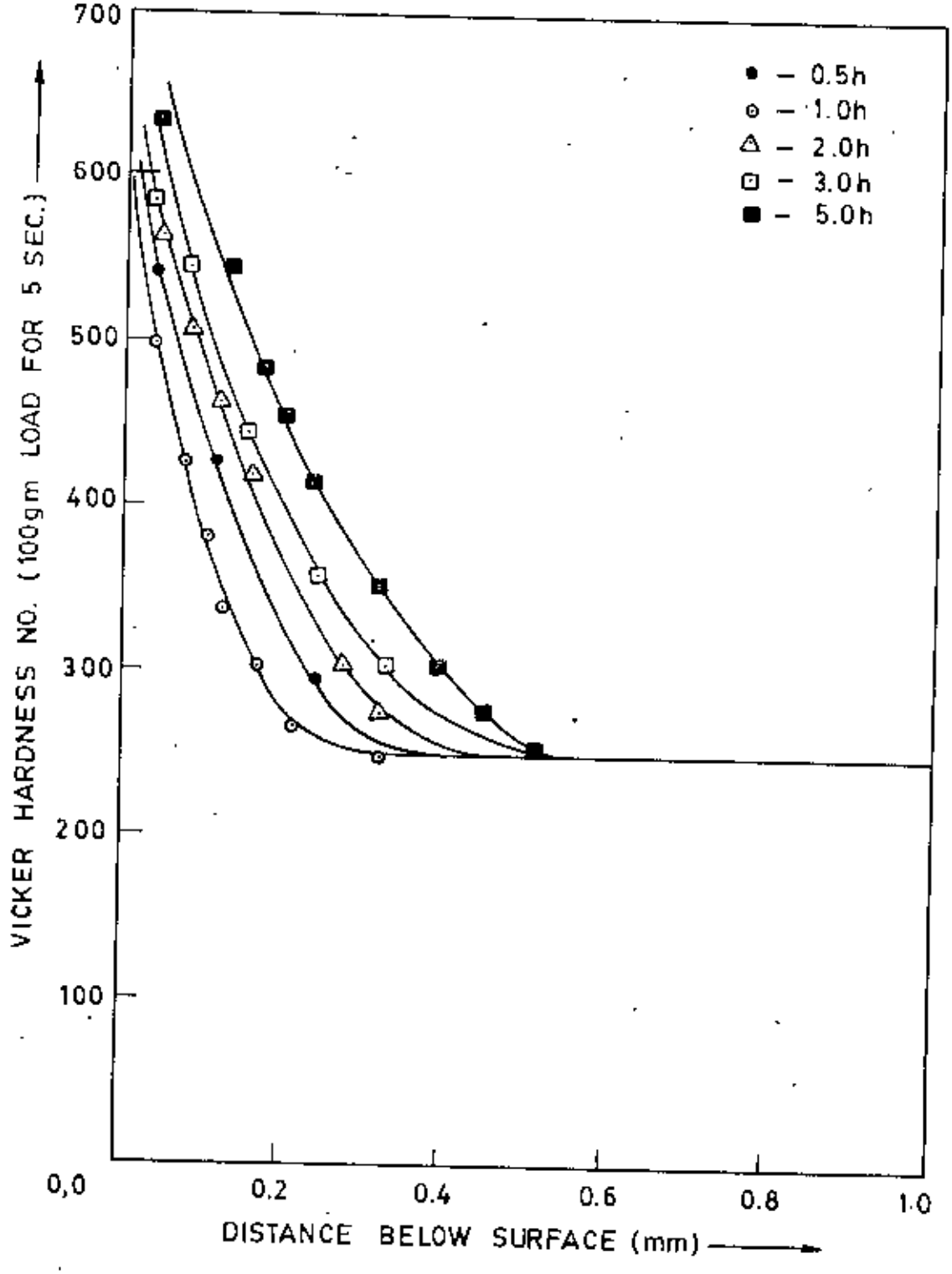


FIG.4.9 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME OF MILD STEEL SPECIMENS LIQUID NITRIDED AT 550°C IN UREA-SODA BATHS.

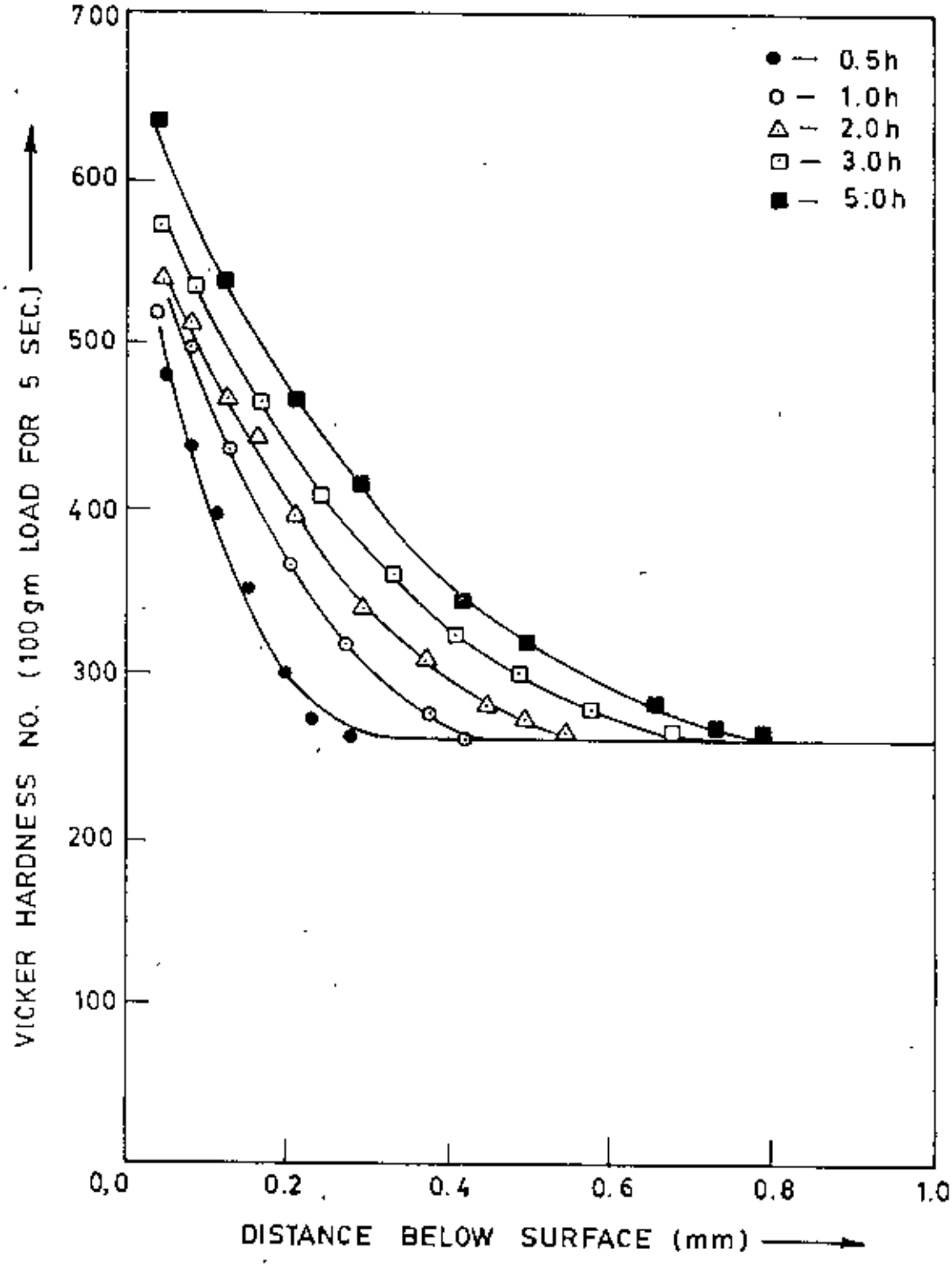


FIG. 4.10 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME OF MILD STEEL SPECIMENS LIQUID NITRIDED AT 575°C IN UREA-SODA BATHS.

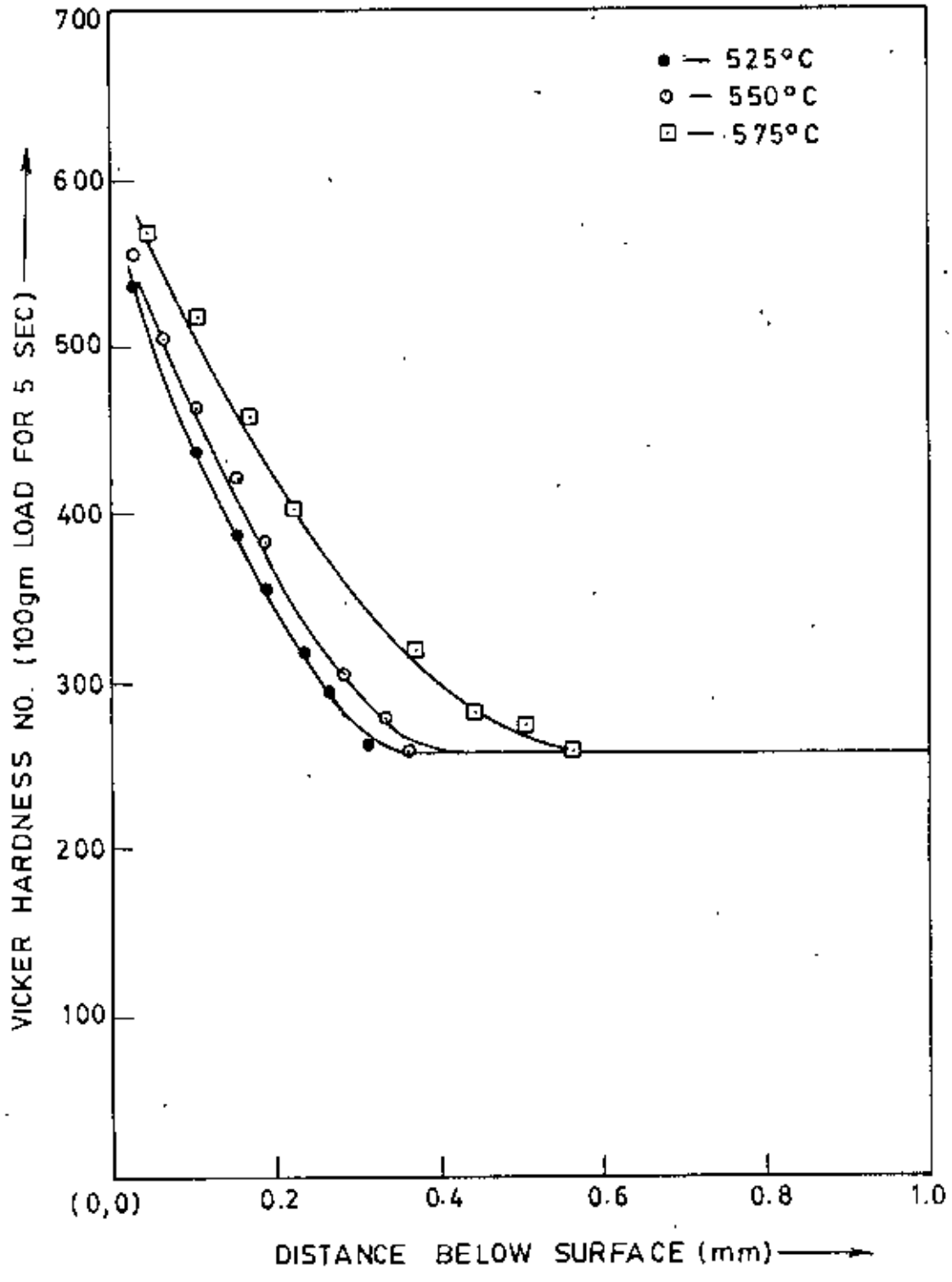


FIG. 4.11 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURES OF MILD STEEL SPECIMENS LIQUID NITRIDED FOR 2 HOURS IN UREA-SODA BATHS.

as far as possible. Fig. 4.8 to Fig. 4.11 show the variation in hardness versus penetration distance profiles with treatment time at constant temperatures and with temperature for a fixed treatment time for mild steel samples nitrided in urea-soda baths.

From these figures it can be observed that case depth, i.e. the distance at which the slope of the hardness versus penetration distance profiles becomes minimum, increases with increasing treatment time at a particular temperature and also with temperature at constant treatment time. This is to be expected. It can also be noted that with increasing treatment time at a particular temperature the hardness curves has a more gradual slope from surface to the core. This is because of the decrease in concentration gradient of nitrogen with increasing nitriding time. A comparison[9] of case-depths produced by nitriding in conventional baths and in baths based on urea-soda, has shown that nitriding in urea-soda baths produces a greater depth. The deeper penetration of nitrogen during nitriding in urea-soda baths resulting in the higher case depths has been attributed to the formation of ammonia gas in the bath.

Fig. 4.12 shows the variation in case depth with treatment time for the mild steel specimens. It can be observed that case-depth increases with increasing time at constant temperatures and also with increasing temperatures at constant time. The

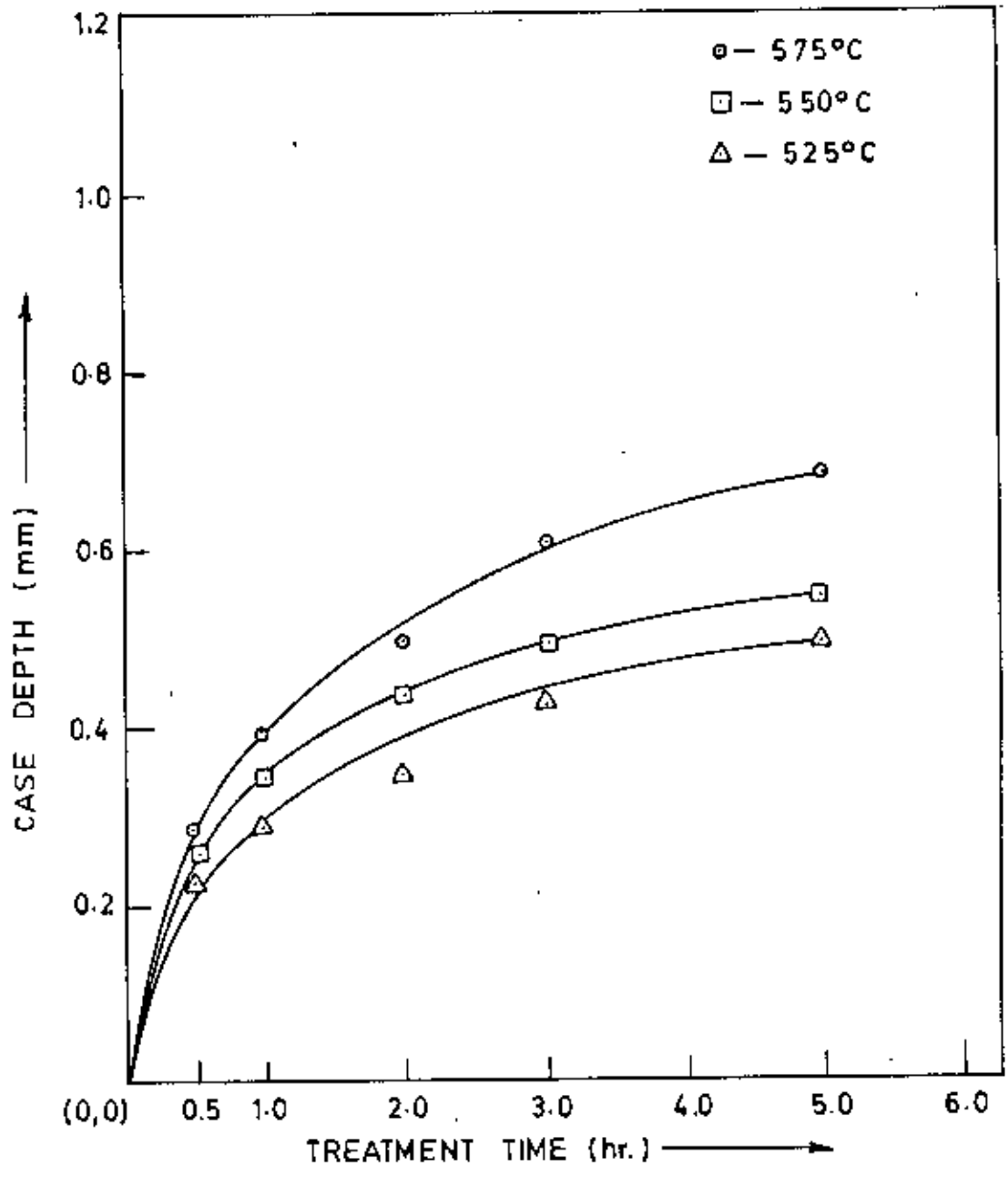


FIG.4.12 VARIATION IN CASE DEPTH WITH TREATMENT TIME AT DIFFERENT TEMPERATURE OF MILD STEEL SPECIMENS LIQUID NITRIDED IN UREA-SODA BATHS.

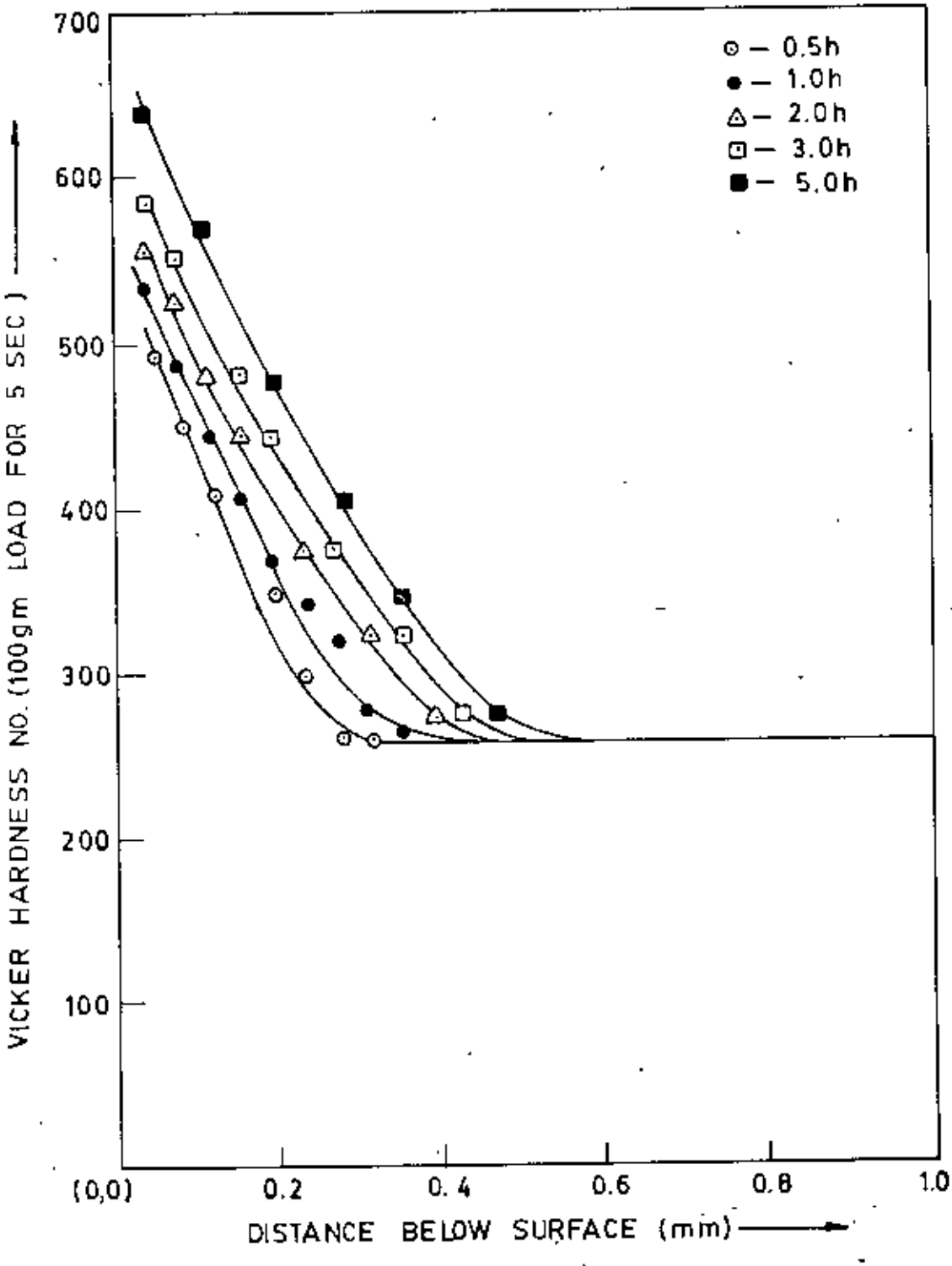


FIG.4.13 VARIATION IN HARDNESS VERSUS PENETRATION-DISTANCE PROFILES WITH TREATMENT TIME OF MILD STEEL LIQUID NITRIDED AT 575°C IN UREA-SODA BATH WITH THE ADDITION OF 2 Pct. SULPHUR.

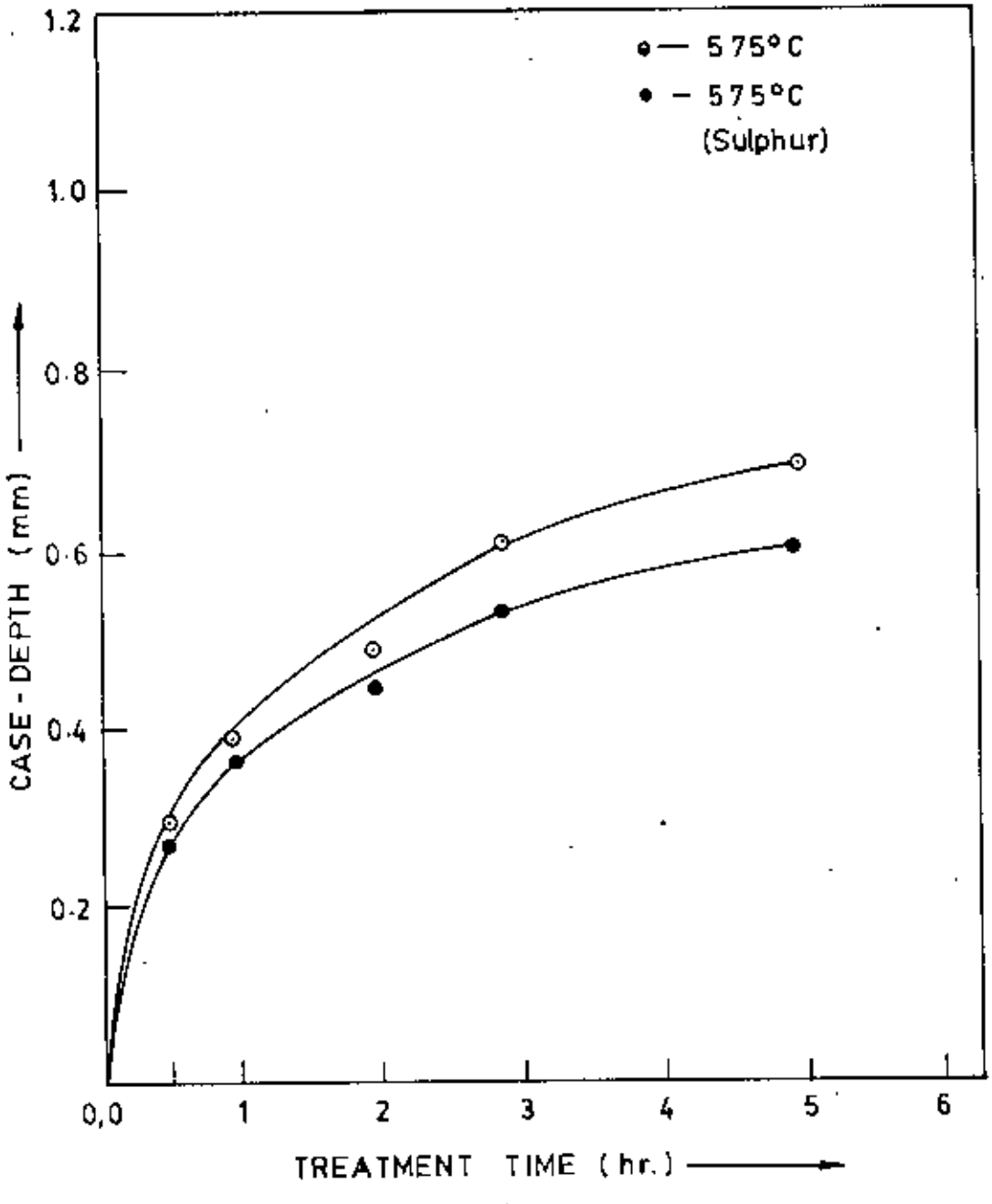


FIG.4.14 EFFECT OF ADDITION OF SULPHUR ON THE CASE-DEPTH OF MILD STEEL LIQUID NITRIDED IN UREA-SODA BATHS.

case-depths produced by nitriding for a specified treatment time at a particular temperature is smaller at lower temperatures but greater at higher temperatures. This is due to the increase in diffusivity of nitrogen and carbon at higher temperatures.

The causes of the differences between the surface hardness values obtained by direct measurements on the surfaces of the nitrided steels (Fig.4.6) and those obtained by extrapolation of hardness-penetration-distance profiles (e.g. 4.16) needs to be investigated. One could possibly try to relate this difference to the possible deterioration of the properties of the compound layers due to development of porosity during nitriding for longer periods of time.

4.3.3.1 Effect of Sulfur on Hardness-Penetration Distance Profiles

Fig. 4.13 shows the variation in hardness versus penetration distance profiles of mild steel specimens liquid nitrided in baths containing 2 per cent sulfur. Fig. 4.14 shows that a lower case depth is produced in the samples nitrided in baths containing sulfur than those nitrided at the same temperature in a bath containing no sulfur. It has already been pointed out that during nitriding in baths containing sulfur an adherent layer forms on the surface of steels thereby causing a decrease in the amount of nitrogen pick up and thus causing a lower case-depth.

4.4 X-RAY DIFFRACTION STUDIES

4.4.1 Introduction

X-ray diffraction was used to identify the phases formed during nitriding in urea-soda baths. The detailed methods of analysis and the assumptions involved therein are described by Cullity.[18] The detailed procedure used for the identification of phases formed, illustrated for chosen patterns, is presented is Appendix-A. Fe K_α radiation has been used in all these studies with a scanning speed of 1°/minute and a chart speed of 10mm/minute. The results of these studies are presented in this section.

4.4.2 Structure of Nitrided Layer

Fig. 4.15 to Fig. 4.19 show the x-ray diffractograms obtained on mild steel samples nitrided in urea-soda baths. Each of these figures corresponds to a particular treatment condition. An analysis of those patterns show that Fe_3N and Fe_4N nitrides form at all treatment temperatures and times investigated. Along with these nitrides diffraction lines belonging to an unknown phase were also observed at all temperatures and times studied. The unknown phase labeled as U was found to have a close-packed hexagonal structure. Since this phase could not be clearly identified, the reasons for its formation could not be investigated. It is assumed that, since simultaneous saturation with both carbon and nitrogen occurs during nitri-

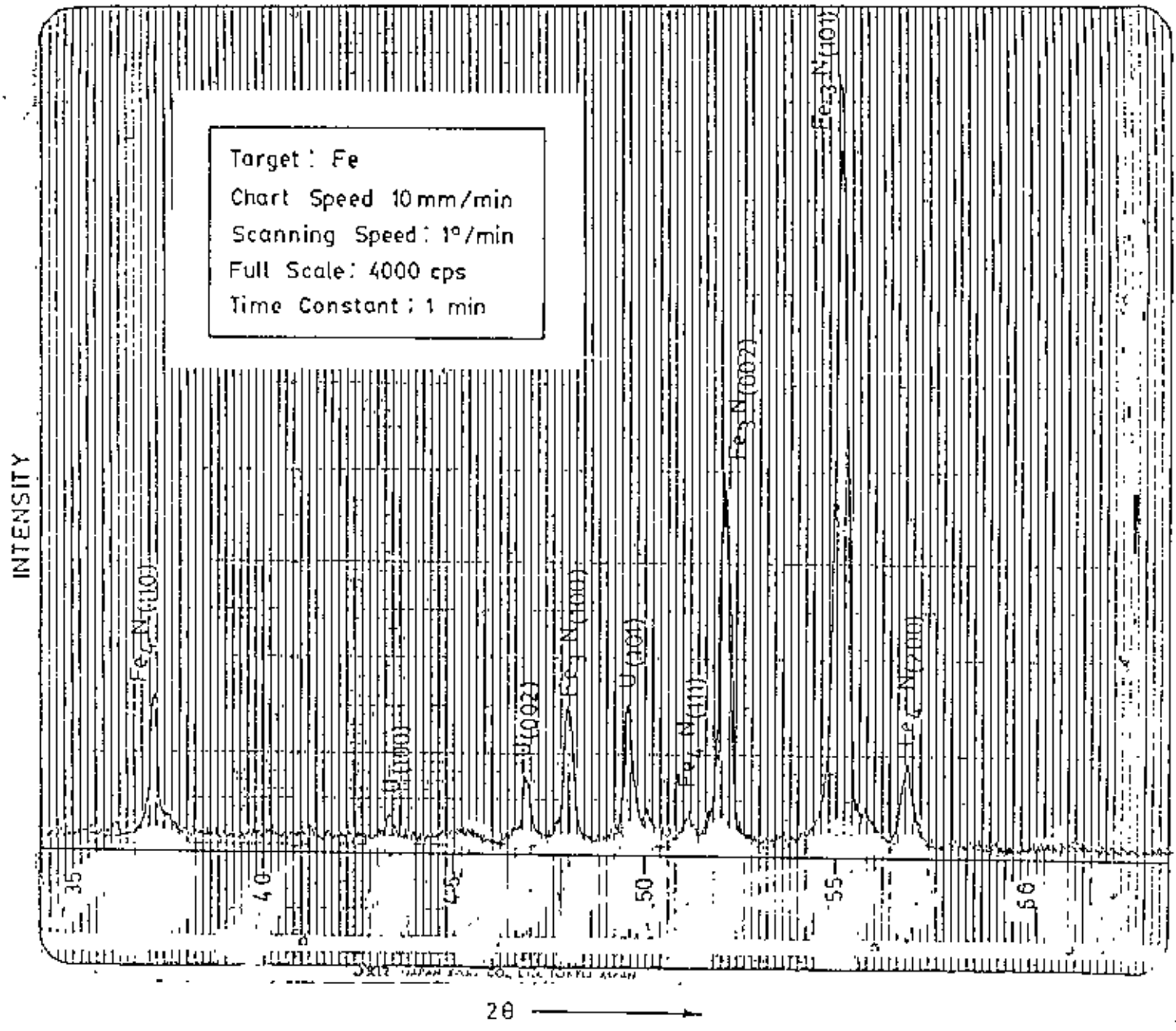


FIG. 4.15: X-RAY DIFFRACTION PATTERN OF A MILD STEEL SPECIMEN LIQUID NITRIDED FOR 3 HRS. AT 525°C IN UREA–SODA BATHS.

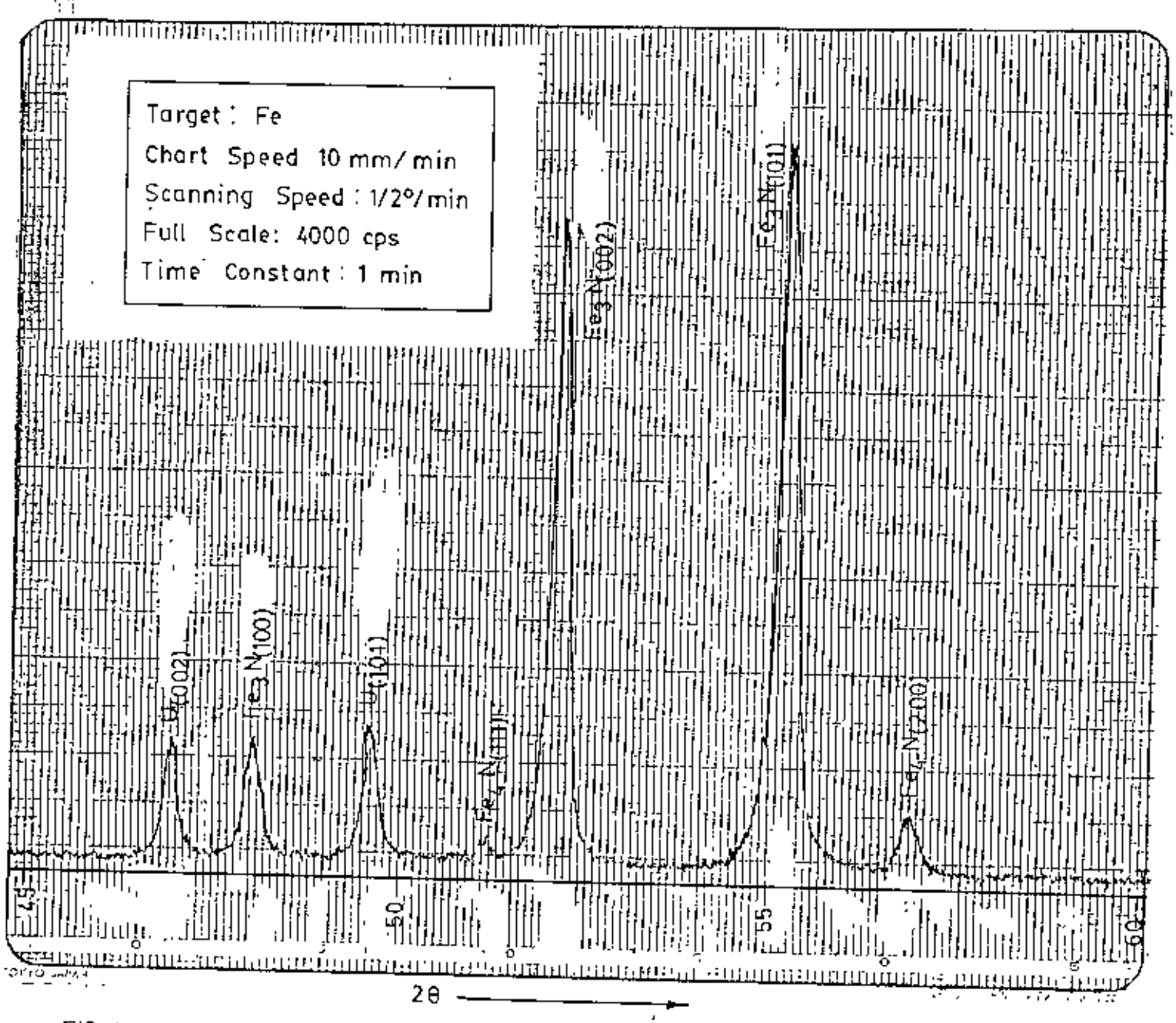


FIG. 4.16 : X-RAY DIFFRACTION PATTERN OF A MILD STEEL SPECIMEN LIQUID NITRIDED FOR 5 HRS. AT 525°C IN UREA-SODA BATHS.

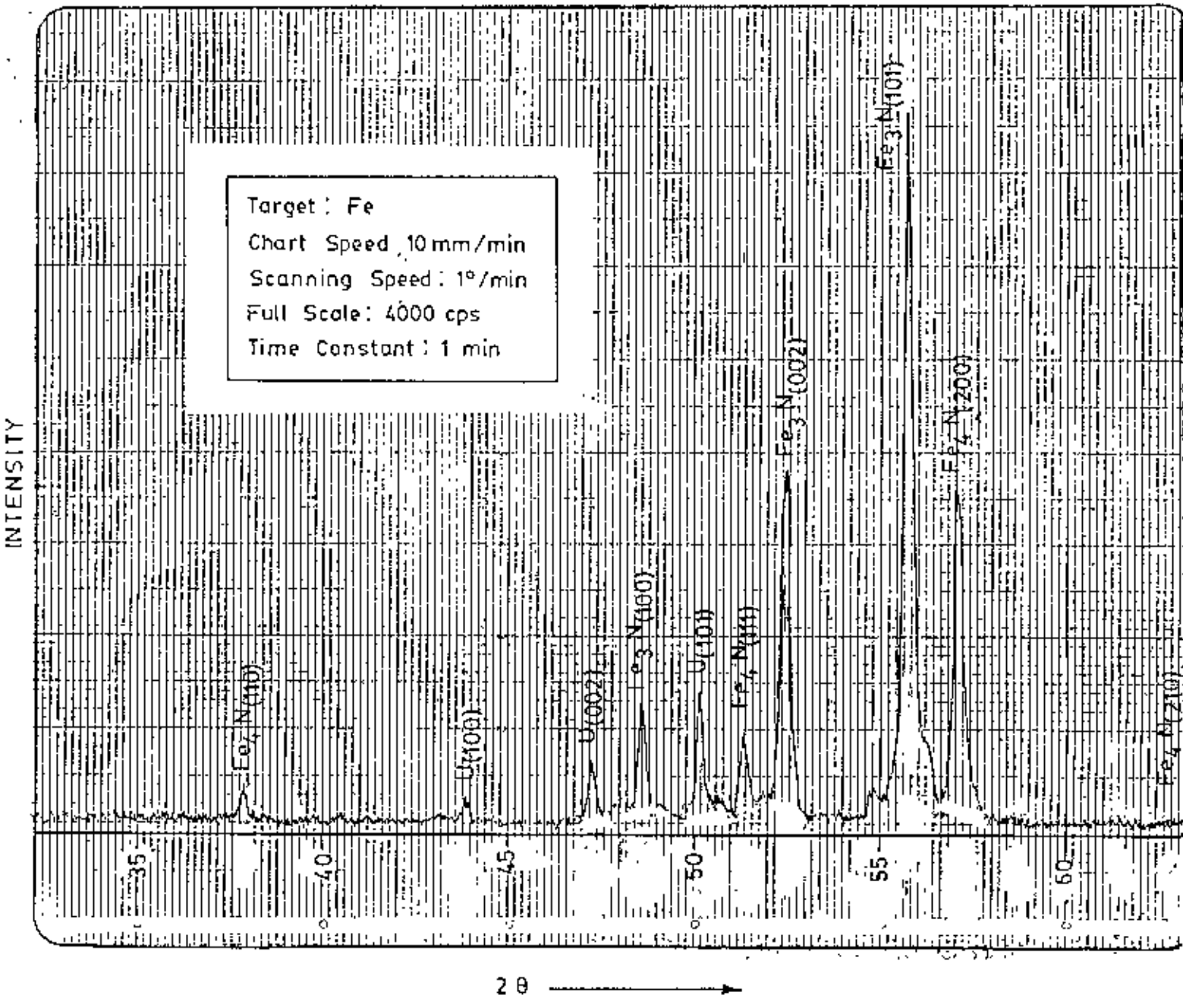


FIG.417 : X-RAY DIFFRACTION PATTERN OF A MILD STEEL SPECIMEN LIQUID NITRIDED FOR 3 HRS. AT 550°C IN UREA-SODA BATHS.

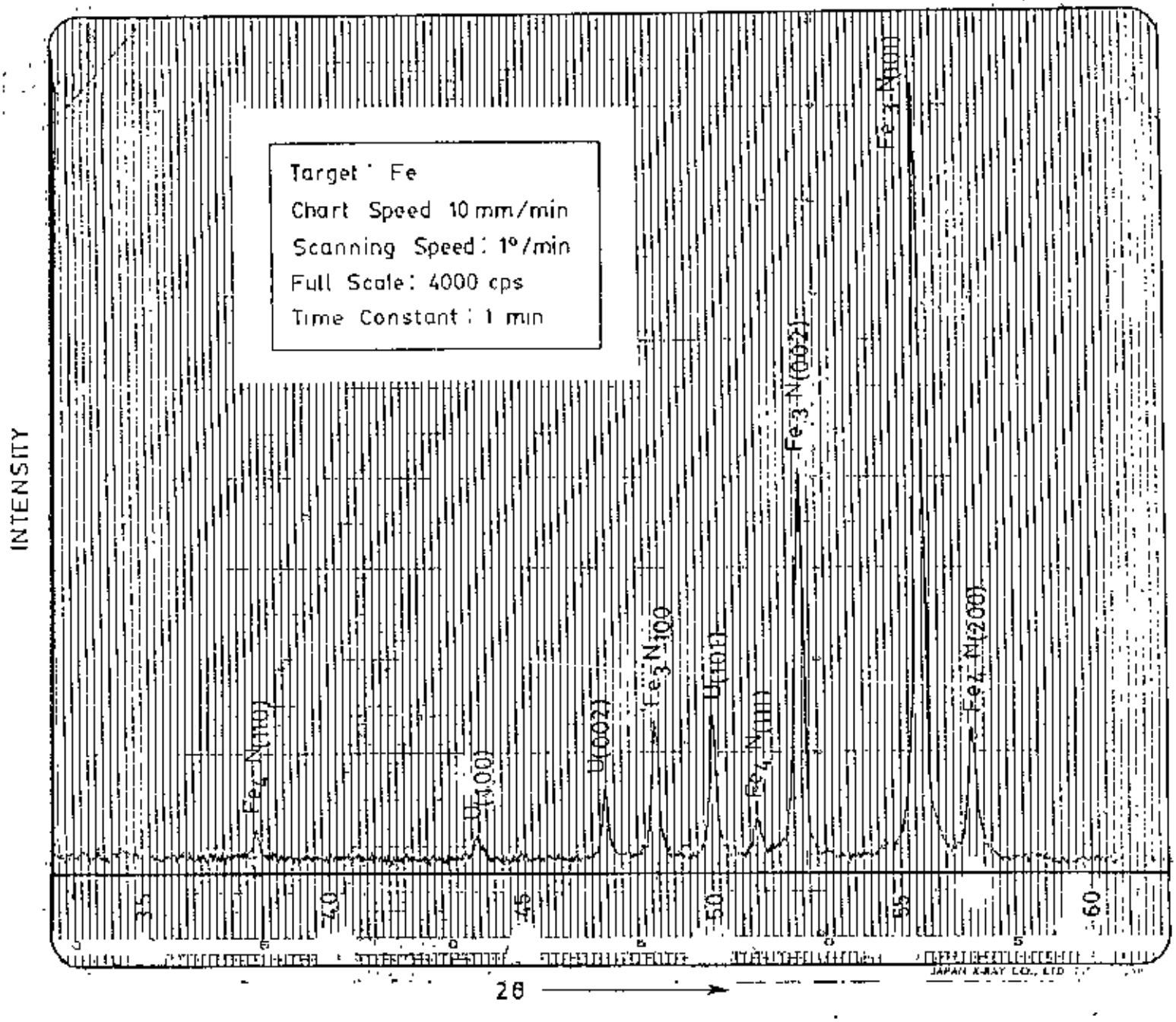


FIG. 4.18 : X-RAY DIFFRACTION PATTERN OF A MILD STEEL SPECIMEN LIQUID NITRIDED FOR 5 HRS. AT 550°C IN UREA + SODA BATHS.

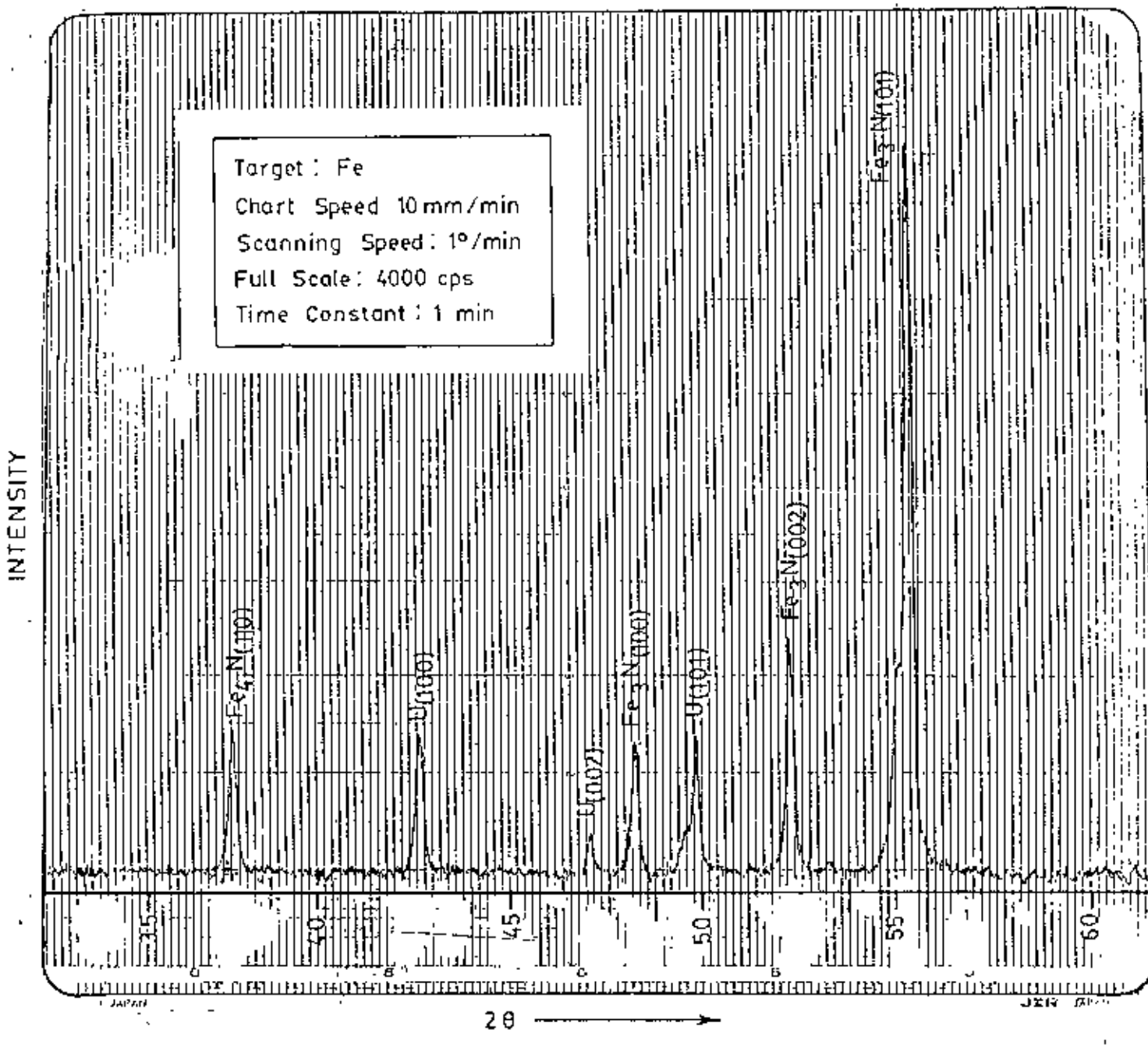


FIG.4.19: X-RAY DIFFRACTION PATTERN OF A MILD STEEL SPECIMEN LIQUID NITRIDED FOR 0.5 HR. AT 575°C IN UREA-SODA BATHS.

ding in these baths, this phase is perhaps an iron-carbonitride phase.

4.4.3 Effect of Time on the Nature of Layers

Both Fe_3N and Fe_4N was found to have formed under all treatment conditions investigated. A comparison of Figs. 4.15 and 4.16 and also Figs. 4.17 and 4.18 show that both at 525°C and 550°C the intensity of the diffraction line $Fe_4N_{(111)}$ gradually decreased with increasing treatment time indicating a decrease in the amount of this phase in the nitrided layers. Similar results were also obtained by other investigators.[19-21]

The intensity of diffraction lines can be and has been used to indicate the amount of a phase in a mixture of phases. The results obtained show that although both Fe_3N and Fe_4N form, the nitride layers consist predominantly of Fe_3N nitride.

It has been observed[22] that in the presence of carbon higher nitrides tend to form. This has been attributed to the increase in the fields of stability of higher nitrides in the presence of carbon. It is to be noted that in the absence of carbon, nitrides form according to the binary Fe-N system whereas in the presence of carbon the structure is determined by the Fe-C-N ternery system.

With increasing treatment time at a particular temperature, nitrogen concentration at or near the surface of the nitrided samples increases gradually and thus leads to the gradual transformation of the lower nitride Fe_4N to the higher nitride Fe_3N.

4.4.4 Effect of Sulfur on the Nature of Layers

Fig. 4.20 shows the diffraction pattern of a mild steel specimen liquid nitrided in urea soda baths in which 2 per cent sulfur was added as Na_2S. The phases present were identified and indexed by using the procedure described in Appendix-A. Sulfur was found to be definitely present in the compound layer, possibly as FeS_2 but unfortunately the lines could not be indexed clearly.

There has been some controversy regarding the presence of sulfur in the compound layer. Mitchell and Dawes[16] could not detect the presence of sulfur in the compound layer, whereas Cahn[23] observed that traces of sulfur was present in the compound layer. The amount of sulfur added in this bath (2%) was considerably higher than those (0.6%) cited above[16,20]. The addition of a large quantity of sulfur in these experiments possibly led to its clear detection. It may therefore be concluded that compound layers on the samples nitrided in baths containing sulfur do contain some sulfur.

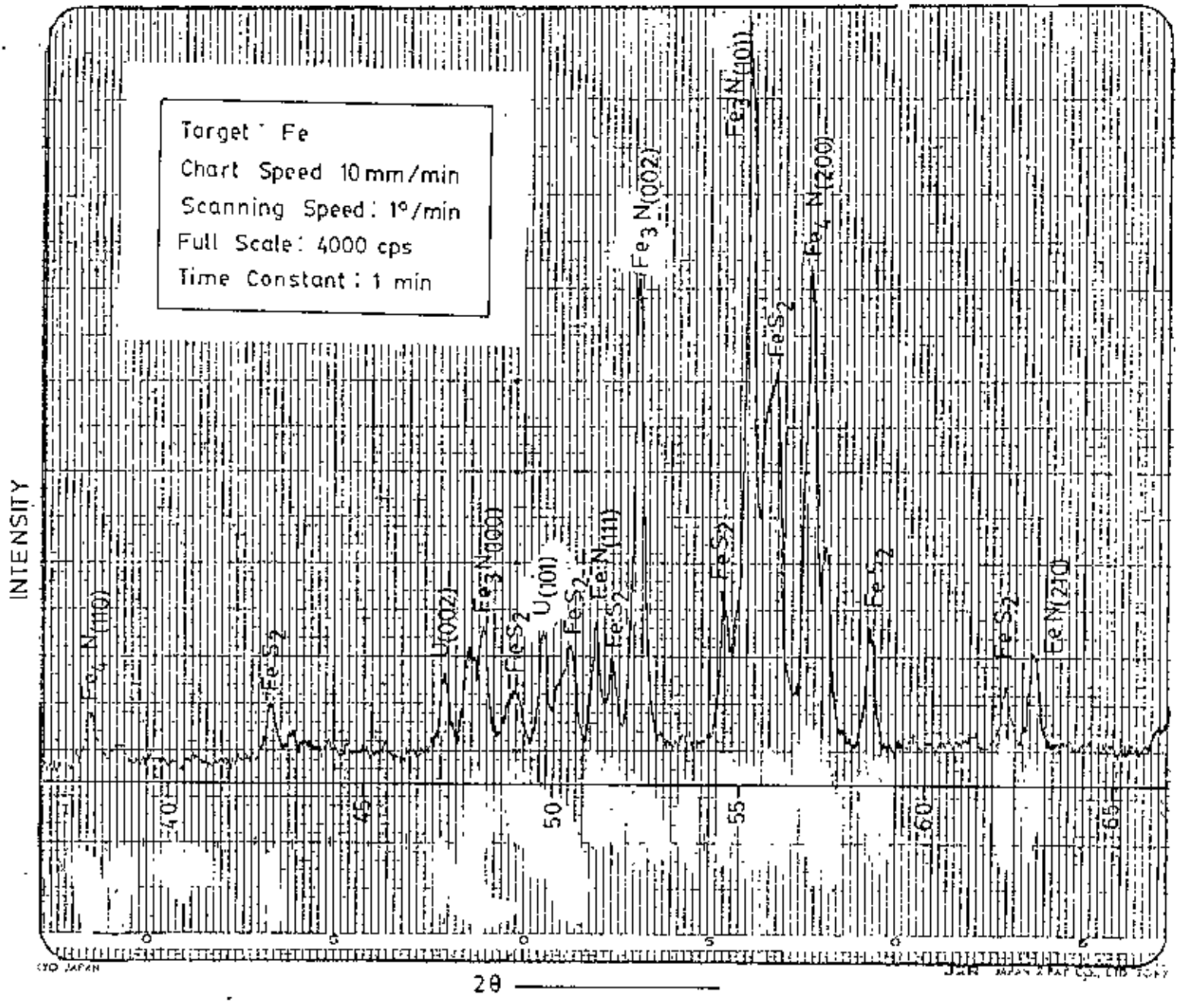


FIG. 4.20: X-RAY DIFFRACTION PATTERN OF A MILD STEEL SPECIMEN LIQUID NITRIDED FOR 5 HRS. AT 575°C IN UREA-SODA BATHS CONTAINING 2 PCT SULPHUR

4.5 Wear Studies

4.5.1 Introduction:

Liquid nitriding of mild steel specimens was investigated in the temperature range of 525 - 575°C and for times upto 5 hours of treatment in urea-soda baths.

Two samples were nitrided at each treatment time and temperature for wear studies. Wear rates were determined on a pin-on-disc type test ring. A constant load of 1.485 kg was used and all the samples were tested for a constant contact distance of 198.86 meters. The results of these tests, reported as weight loss (mg) per unit area (mm^2) of specimen contact area are presented and discussed below.

4.5.2 Effect of time and temperature:

Nitriding in urea-soda baths was found to increase the wear resistance significantly. The maximum wear rate of the nitrided sample was found to decrease to 0.06 mg/mm^2 of contact area where as the rate of wear in the unnitrided condition was found to be 0.78 mg/mm^2. Increasing treatment time and a decrease in treatment temperature was found to result in a reduction in wear loss (Fig. 4.21). It is to be noted that a decrease in treatment temperatures result in an increase in the surface hardness values (Fig. 4.6). Edenhofer and Bowley[24] also reported a dramatic increase in wear resistance as the temperature of

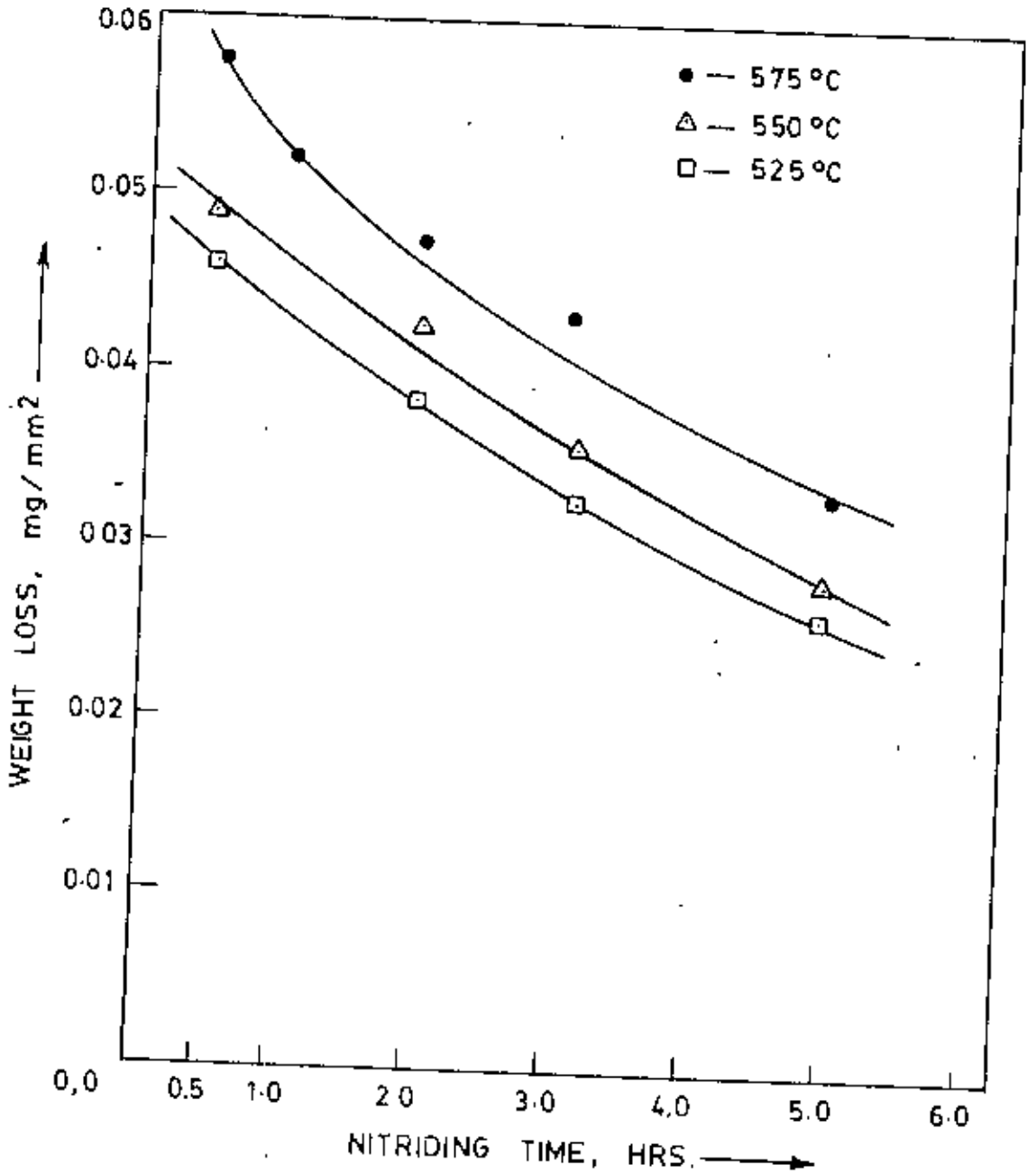


FIG.4.21 VARIATION IN WEAR RATES OF MILD STEEL SPECIMENS LIQUID NITRIDED IN UREA-SODA BATHS.

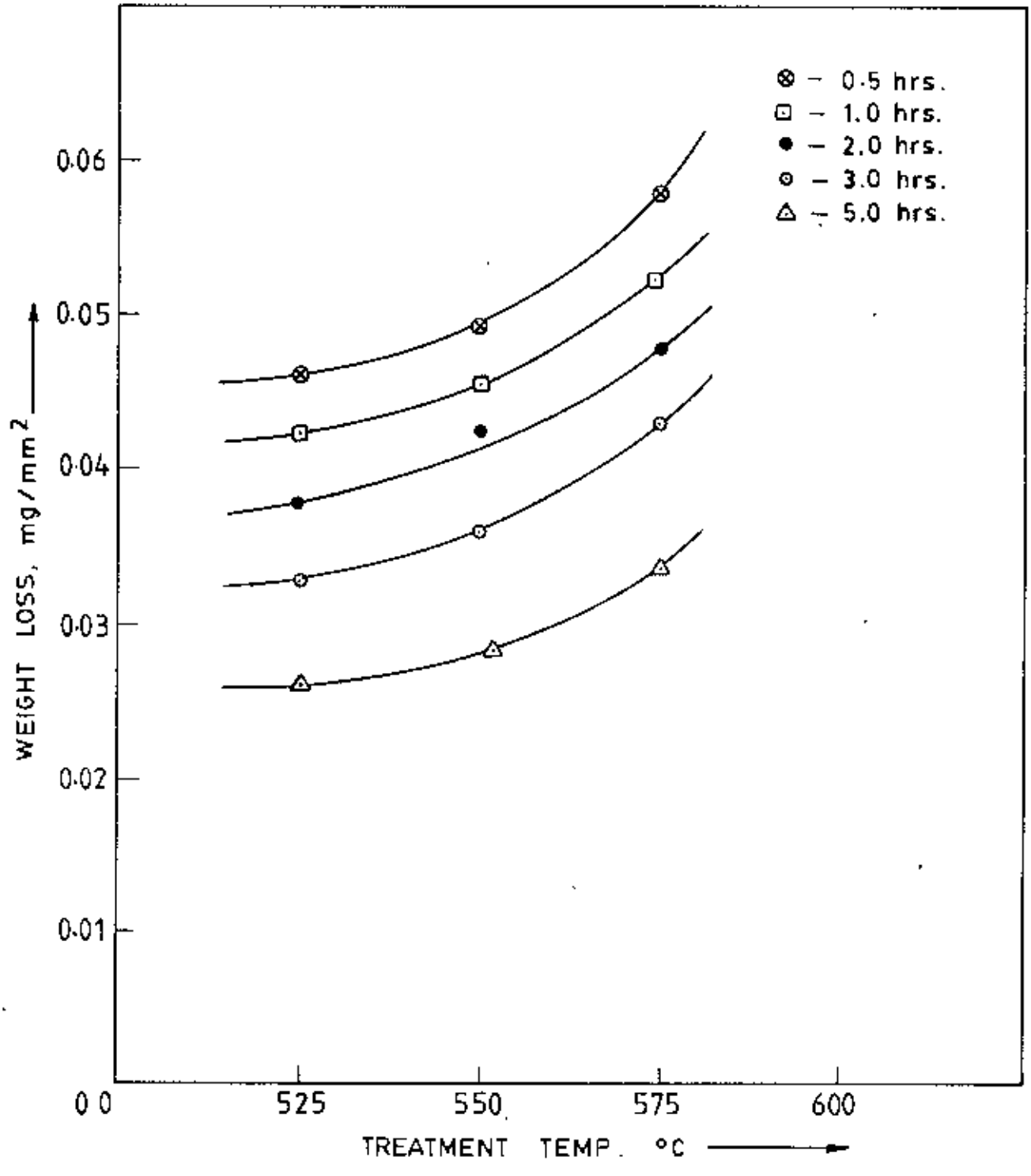


FIG. 4.22 VARIATION IN WEAR-RATES WITH TREAMENT TEMPERATURES OF MILD STEEL SAMPLES, LIQUID NITRIDED IN UREA-SODA BATHS.

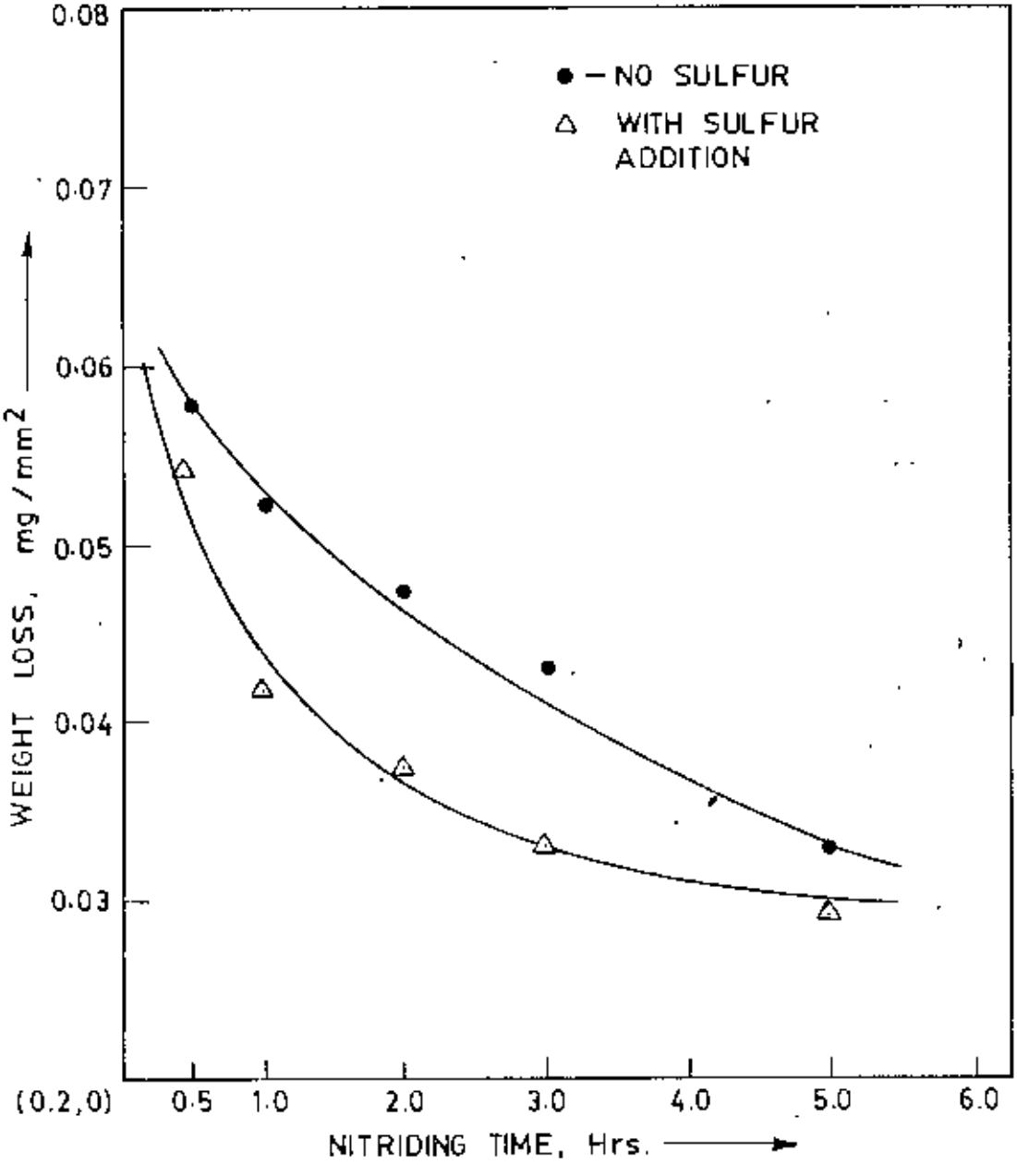


FIG.4.23 COMPARISON OF WEAR-RATES OF MILD STEEL SAMPLES LIQUID NITRIDED AT 575 °C IN UREA-SODA BATHS WITH AND WITHOUT THE ADDITION OF SULFUR.

nitriding was lowered. The wear rate was also found to decrease with treatment time at all temperatures investigated (Fig. 4.22). It is to be noted that the wear samples had a varying thickness of the nitrided layer (compound layer and the case-depth), this is because the depth of nitrogen penetration increases with treatment time at a specified temperature. Thus the chances of the hardened layer of a test piece to be in contact with the sliding surface for a increasingly longer period of the wear study increases with increasing treatment time at any temperature therefore resulted in a decrease in the wear rate. The maximum wear resistance in these studies was found to coincide with the maximum surface hardness of the nitrided samples. As in other liquid nitriding baths a predominantly monophase nitride layer was found to form (discussed in a later section) on samples nitrided in urea-soda baths. Monophase nitride layers, because of less stress in the compound layers, have been reported[22] to be more wear resistant than those layers consisting of more than one nitride.

The decrease in wear rate with increasing treatment time at a particular temperature therefore seems logical. It therefore appears that for maximum wear-resistance, nitriding in these baths should be performed for a longer time at lower temperatures.

4.5.3 Effect of Sulfur on Wear Resistance

Fig. 4.23 shows the effect of addition of sulfur to the urea-soda baths on the wear-resistance of ;mild steel specimens nitrided in these bath. Addition of sulfur seems to cause a decrease in the wear-rate of mild steel specimens nitrided in these baths. It may be mentioned that addition of sulfur causes an increase in surface hardness values of mild steel specimens liquid nitrided in urea-soda baths, and therefore an increase in wearresistance of mild steel specimens liquid nitrided in urea-soda baths is perhaps not unexpected. An increase in wear resistance in presence of sulfur has also been noted by other investigators.[4,16] X-ray diffraction studies (Fig. 4.20) showed that sulfur was definitely present in the compound layer and is responsible for this increase in wear resistance. A detailed study is, however, necessary to determine the exact amount of sulfur additions capable of producing the best results.

Chapter – 5

SUMMARY AND CONCLUSIONS

5.1 SUMMARY AND CONCLUSSIONS

5.1.2 SUMMARY

Liquid nitriding in urea-soda baths is a recent development in the field of nitriding in liquids and have been used in these experiments. Mild Steel samples have been liquid nitrided in a urea-soda baths in the temperature range of 525°C-575°C and for time of upto 5 hrs. of treatment. The effects of nitriding in this bath have been followed by optical metallography, microhardness measurements and X-ray diffraction techniques. Relative wear measurements have also been performed on a 'pin-on-disc' type apparatus. Effects of addition of 2% sulfur in the form of sodium sulphide to this bath have also been investigated. Optical metallographic studies showed that the thickness of the compound layer increases with treatment time at a constant temperature. A comparatively thin compound layer is formed on the steels treated at a low temperatures, where as a thicker layer was obtained on samples nitrided at higher temperatures. The thickness of the compound layer increases with treatment time at any temperature.

It was also observed that a comparatively thin compound layer is formed on mild steel samples nitrided in urea-soda baths containing 2% sulfur as compared to a thicker layer formed on mild steel specimens treated under otherwise indentical conditions in the baths containing no sulfur.

Case depths determined from hardness - penetration distance profiles showed that case-depth increases with increasing time at a constant temperatures and also with increasing temperatures at a constant treatment time. It was also observed that a lower case depth was produced in the samples nitrided in the bath containing sulfur than those nitrided at the same temperature in the bath containing no sulfur.

Measurements of wear rates on the nitrided samples have shown that an increase in treatment time and a decrease in the treatment temperature result in a reduction in wear loss. It was also observed that the addition of sulfur to the urea-soda baths increases the wear resistance of mild steel specimens nitrided in this bath.

X-ray studies on the steels liquid nitrided in urea-soda baths showed that Fe_3N and Fe_4N nitrides forms at all treatment temperatures and times investigated. Diffraction lines belonging to an unknown phase was also observed. It was found to have a close-packed hexagonal structure. The phases formed during nitriding were found to be dependent on treatment time and temperature. The intensity of the diffraction line $Fe_4N(111)$ was found to decrease gradually with treatment time indicating a decrease in the amount of this phase in the nitrided layers. With increasing treatment time at a particular temperature, nitrogen concentration at or near the surface of the nitrided samples increases gradually thus leading to the gradual transformation of the lower nitride Fe_4N to the higher nitride Fe_3N.

5.1.3 CONCLUSIONS

The following conclusion may be drawn from this study on liquid nitriding of mild steels in urea-soda baths:

(1) Although both Fe_3N, Fe_4N nitrides form in the nitrided layers, the layers consist predominantly of Fe_3N nitride.

(2) The hardness values obtained on samples treated at lower temperatures are always higher than the surface hardness obtained on samples treated at higher temperatures.

(3) Addition of sulfur increases the surface hardness but decreases the depth of nitrogen penetration.

(4) For maximum wear resistance, nitriding of mild steel samples in this bath should be performed for a longer time at lower temperatures.

(5) Sulfur has been definitely identified in the nitrided layers of the mild steel samples nitrided in baths containing sulfur.

Appendix-A
IDENTIFICATION OF PHASES

APPENDIX-A

X-ray diffraction was used to identify the phases formed during nitriding in urea-soda baths. Diffraction data cards of the possible nitrides, that may form according to the Fe-N diagram is presented at the end of this section. A detailed method of analysis of x-ray diffraction patterns and the assumptions involved therein are described by Cullity. The method of identification of the phases is illustrated below using the pattern of the mild steel specimen nitrided for 3 hrs at 525°C.

The θ, Sin θ and $Sin^2\theta$ values of the diffraction lines observed on the dirfractograms were listed as in Table A-1. Since it was expected that only nitrides are formed, the diffraction lines were tentatively identified using 2θ values calculated from x-ray data cards for the radiation used for these studies. The nitrides that seemed to have formed during nitriding of mild steel in urea-soda was Fe_3N and Fe_4N. There were however other lines present on the pattern.

To confirm the identification of the diffraction lines belonging to the Fe_3N, the diffraction lines belonging to this phase were listed as shown in Table A-2. Fe_3N has a close packed hexagonal structure and the lines belonging to this phase was indexed analytically. The analytical method used for the identification of the phases involves arithmatic manipulation of the observed $Sin^2\theta$ values, to find certain characteristic relations between

them. Once this relationship is recognised, the diffraction lines in the pattern can be indexed.

This characteristic relationship for hexagonal lattice is

$$\sin^2\theta = A\,(h^2 + hk + k^2) + Cl^2.$$

$$\text{where, } A = \frac{\lambda^2}{3a^2} \; ; \; C = \frac{\lambda^2}{4c^2}$$

Permissible values of $(h^2 + hk + k^2)$ can be obtained from tables (Fig. A-1) and are 1,3,4,7,9 etc.

The θ, $\sin\theta$, $\sin^2\theta$ values of the diffraction lines identified as the Fe_3N-nitride are listed in Table A-2. The first step is to divide the $\sin^2\theta$ values by the integers 1,3,4,7 etc. and tabulate the results as shown. Then the quotients which are equal to one another or equal to one of the observed $\sin^2\theta$ values are found out. In this case, the two starred entries, 0.1658 and 0.1655 are the most nearly equal and it was assumed these lines were hk0 lines. Then it was tentatively put as A=0.1658, which is equivalent to saying that line 1 is 100. Since the $\sin^2\theta$ value of line 5 is very nearly 3 times that of line 1, line 5 must be 110. To find the value of C, the following equation was used:

$$\sin^2\theta - A\,(h^2 + hk + k^2) = Cl^2$$

From each $Sin^2\theta$ values, the values of A(=0.1658), 3A(=0.4794), 4A(=0.6632) etc. were subtracted and the remainders which were in the ratio of 1,4,9,16 etc. were identified . These values are listed in Table A-3. Here the 3 starred numbers are of interest, because these numbers (0.0488, 0.1930 and 0.433) are very nearly in the ratio 1,4 and 9. Therefore putting $0.0488=C(1)^2$ and $0.1930=C(2)^2$ and $0.433=C(3)^2$ gives C=0.0488 and identifies line 2 as (002). Since line 3 has a $Sin^2\theta$ value equal to the sum of A and C, its indices must be 101. Similarly indices of line 4 and line 6 were found to be 102 and 103 respectively. In this way, indices were assigned to all lines belonging to Fe_3N nitrides. It was thus confirmed that the tentative identification, regarding these line were correct.

The other nitride that formed appeared to be γ'-nitride (Fe_4N). Electron diffraction studies of this phase has shown that the structure is deficient in Fe with absences in the face centre sites. The γ'- phase has a face centred cubic close packing of iron atoms with nitrogen atoms equidistant from each other and occupying one fourth of the number of octahedral interstices in a completely ordered manner. Because of this speciality, this phase, although face centred cubic, contains reflections from planes having mixed indices. It may be mentioned here that face centred cubic crystals can, in general, have reflections only from planes having unmixed indices, e.g. (111), (200) ... and not from planes having mixed indices like (110), (210) ... etc.

It was therefore not possible to confirm the tentative identification of the diffraction lines belonging to this phase (Table A-4) by actual calculations. Satisfactory match was however, obtained with the standard diffraction pattern for this phase published by the American Society for Testing Metals (ASTM).

In addition to the diffraction lines belonging to Fe_3N and Fe_4N nitrides, there were some other diffraction lines which could not be identified clearly. Attempts to match these lines with those of nitrides and carbides of all possible elements contained in the mild steel specimens remained unsuccessful. The mild steel specimens used in the present investigation, were also qualitatively tested for the presence of elements like Cr, Mo, V, W and Ni. These tests confirmed that these elements were not present in the samples used in these investigations and that the samples used were truly plain carbon steels.

Since nitriding in urea-soda baths caused simultaneous saturation of the mild steel specimens with carbon and nitrogen, it was thought that these lines could perhaps belong to the iron carbonitride phase. X-ray diffraction pattern for this phase could not be found in the alphabetical index to the data cards and therefore a match could not be attempted.

However, in order to determine the type of crystal to which they belong, these lines alongwith their $\sin\theta, \sin^2\theta$ values were then listed as shown in Table A-5. It was first checked whether these lines

belong to a cubic crystal. A cubic crystal gives diffraction lines whose $Sin^2\theta$ values satisfy the following equation (obtained by combining the Bragg law with the plane spacing equation for the cubic system)

$$\frac{Sin^2\theta}{h^2+k^2+l^2} = \frac{Sin^2\theta}{S} = \frac{\lambda^2}{4a^2}$$

and $\lambda^2/4a^2$ is a constant for any one pattern. Therefore, if these lines belonged to a cubic crystal any one of the 3 set of integers S listed (Fig. A-1) for each type of cubic crystal would have yielded a constant quotient when divided one by one into the observed $Sin^2\theta$ values, Since a constant quotient could not be obtained it was concluded that they did not belong to a cubic crystal.

It was then assumed that they belonged to a hexagonal phase, and this was varified by using the procedure described earlier. A satisfactory result was obtained (Table A-6) and it was concluded that these lines belonged to a hexagonal phase. This phase could not however be identified clearly and has been marked as U (unknown) in the diffraction patterns. The lattice parameters a and c of this unknown hexagonal phase was calculated using the following relations

$$A = \frac{\lambda^2}{3a^2} \; ; \quad C = \frac{\lambda^2}{4c^2} \; .$$

and was found to be 2.763Å and 4.852Å respectively.

Finally the extra diffraction lines which appeared during nitriding in baths containing sulfur were listed as shown in (Table A-7). A preliminary match was obtained by referring to the index to the diffraction data file and they were found to belong to FeS_2. However, due to nonavailability of data cards and lack of information on the type of this crystal, further treatment of this data could not be performed.

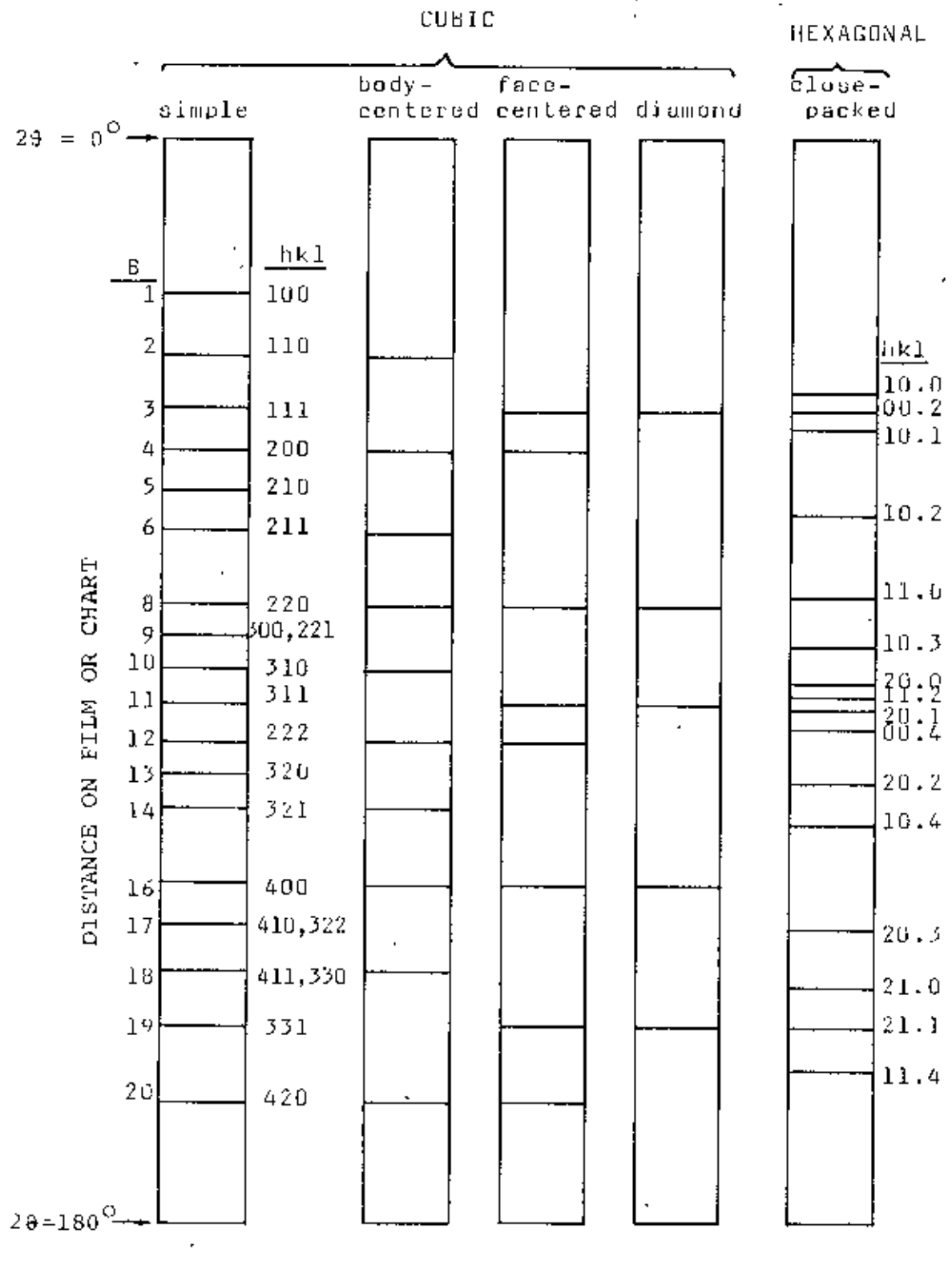


FIG. A-1 Calculated diffraction patterns for various lattices. $s = h^2+k^2+l^2$.

Table A-1: List of the diffraction lines observed on the diffractogram of a sample nitrided in urea-soda for 3 hr at 525°C.

LINE	θ	$Sin^2\theta$	Tentative Identification
1	18.69	0.1028	Fe_4N
2	21.65	0.1361	U
3	23.50	0.1590	U
4	24.03	0.1658	Fe_3N
5	24.80	0.1759	U
6	25.60	0.1866	Fe_4N
7	26.03	0.1925	Fe_3N
8	27.60	0.2146	Fe_3N
9	28.40	0.2262	Fe_4N
10	31.50	0.2730	Fe_4N
11	32.89	0.2948	U
12	36.80	0.3588	Fe_3N
13	39.70	0.4080	U
14	42.30	0.4529	Fe_4N
15	44.80	0.4965	Fe_3N
16	50.70	0.5988	Fe_3N
17	56.27	0.6916	Fe_3N

Table A-2: Identification of hk0 planes of the diffraction lines belonging to Fe_3N.

Line	θ	Sinθ	$Sin^2\theta$	$\frac{Sin^2\theta}{3}$	$\frac{Sin^2\theta}{4}$	$\frac{Sin^2\theta}{7}$	hkl
1	24.03	0.4072	0.1658*	0.0552	0.04145	0.0236	100
2	26.03	0.4388	0.1925	0.0642	0.0481	0.0275	
3	27.6	0.4633	0.2146	0.0715	0.0536	0.0306	
4	36.8	0.5990	0.3588	0.1196	0.0897	0.0512	
5	44.8	0.7046	0.4965	0.1655*	0.1241	0.0709	110
6	50.7	0.7738	0.5988	0.1996	0.1497	0.0855	
7	56.3	0.8319	0.6920	0.2306	0.1730	0.0988	

Table A-3: Identification of Diffraction lines belonging to Fe_3N.

Line	θ	$Sin^2\theta$	$Sin^2\theta$ -A	$Sin^2\theta$ -3A	$Sin^2\theta$ -4A	$Sin^3\theta$ -7A	hkl
1	24.03	0.1658	-	-	-	-	100
2	26.03	0.1925	0.0267	-	-	-	002
3	27.6	0.2146	0.0488*	-	-	-	101
4	36.8	0.3588	0.1930*	-	-	-	102
5	44.8	0.4965	0.3307	-	-	-	110
6	50.7	0.5988	0.433*	0.1014	-	-	103
7	56.27	0.6916	0.526	0.1944	0.0286	-	200

TABLE A.4: DIFFRACTION LINES BELONGING TO Fe_4N-NITRIDE.

LINE	θ	hkl
1	18.69	γ' 110
6	25.60	γ' 111
7	28.40	γ' 200
8	31.50	γ' 210
11	42.30	γ' 220

Table A-5: Identification of hko lines of the unknown phase

Line	θ	$\sin^2\theta$	$\frac{\sin^2\theta}{3}$	$\frac{\sin^2\theta}{4}$	$\frac{\sin^2\theta}{7}$	hkl
1	21.65	0.1361*	0.0454	0.0340	0.0194	100
2	23.50	0.1590	0.053	0.0397	0.0227	-
3	24.80	0.1759	0.0586	0.0439	0.0251	
4	32.89	0.2948	0.0982	0.0737	0.0421	-
5	39.70	0.4080	0.1360*	0.1020	0.0582	110

Table A-6: Indexing of diffraction lines which did not appear to belong to any of the known nitrides.

Line	θ	$Sin^2\theta$	$Sin^2\theta$-A	$Sin^2\theta$-3A	hkl
1	21.65	0.1361	-	-	100
2	23.5	0.1590	0.0229	-	002
3	24.8	0.1759	0.0398	-	101
4	32.89	0.2948	0.1581	-	102
5	39.7	0.4080	0.2713	-	110

Table A-7: Extra diffraction lines in Samples nitrided at 575°C for 0.5 hrs. in facts containing sulfur.

Line	2θ	θ	d°A	I	I/I_o	Tentative Identification
1	42.4	21.2	2.747	6	8	FeS_2
2	48.9	24.45	2.4	8.5	12	FeS_2
3	51.08	25-54	2:3	5.2	7	FeS_2
4	51.6	25.8	2.282	3.5	5	FeS_2
5	54.5	27.25	2.169	5.5	8	FeS_2
6	55.9	27.95	2.119	45	65	FeS_2
7	58.4	29.2	2.036	15	21	FeS_2
8.	62.09	31.045	1.92	6.1	8	FeS_2

1-1236

8478

d 2.09 2.19 1.61 2.38 Fa_3N

1-1241

I/J_1

1-1239 100 25 25 20 Iron Nitride

Rad. MoK 0.709 Filter $Zr\rho_2$

Dia. 16 inches Cut off Coll

I/I_1 Calibrated strips d corr.abs.? No

Ref. H

Sys. Hexagonal S.G. $D_6^6-P_3^622$

a_o 2.695 c_o 4.362A C 1.618

Ref. Wy

dÅ	I/I_1	hkl
2.38	20	100
2.19	25	002
2.09	100	101
1.61	25	102
1.37	25	110
1.24	25	103
1.16	20	200
1.14	10	112
1.10	3	004
1.04	5	202
0.92	5	203
.88	8	210
.86	8	211
.82	3	212,105
.76	3	213

6-0696

d	2.03	1.17	1.43	2.03	(Fe) 2B
I/I_1	100	30	20	100	Iron (α-phase)

Rad. CuK 1.5405 Filter Ni

Dia. Cut off Coll.

I/I_1 Counter Diffractometer d corr. abs.?

Ref. Swanson et al., NBS Circular 539, Vol. IV p3(1955)

dÅ	I/I_1	hkl
2.0268	100	110
1.4332	20	200
1.1702	30	211
1.0134	10	220
0.9064	12	310
.8275	6	222

Sys. cubic S.G. IM3M (229)

a_o 2.8664

Ref. Ibid

Total impurities of sample 0.0013%

each metal and non-metals.

X-ray pattern at 25°C. W structure type.

occurs as terrestrial "Iron" and in meteorites ans "Kamacite".

6-0627

d	2.19	1.90	1.34	3.79	(Fe_4N) 4.25C
I/I_1	100	75	65	10	Iron Nitride (λ'-phase)

Rad. CoK 1.7902 Filter Fe

Dia. 9.19cm Cut off Coll.

I/I_1 Microphotometer d corr. abs.? Yes

Ref. Jack, Proc. Roy. Soc. A 195 34-40 (1948

Sys. Cubic S.G.

a_o 3.795

Ref. Ibid.

Sample contains 6.1 wt.% N.

Homogeneity range 5.7 - 6.1 wt. % N

dÅ	I/I_1	hkl
3.79	10	100
2.684	20	110
2.191	100	111
1.897	75	200
1.697	20	210
1.549	20	211
1.342	65	220
1.265	20	221,300
1.200	10	310
1.144	85	311
1.095	40	222
1.053	20	320
1.014	20	321
0.949	45	400

6-0656

d	2.11	1.63	2.21	3.45	(Fe_2N) 120
I/I_1	100	25	20	2	Iron Nitride

Rad. CoK 1.7902 Filter Fe

Dia. 9, 19cm Cut off Coll.

I/I_1 Microphotometer d corr.abs? Yes

Ref. Jack, Proc.Roy.Soc., A 195 34-40 (1948)

Sys. Orthorhombic S.G

a_o 5.523 b_o 4.830 c_o 4.425 C 0.9161

Ref. Ibid.

Sample contains 11.3 wt. % N.

Homogeneity range 11.1 - 11.3 wt. % N.

dÅ	I/I_1	hkl
3.45	2	101
2.804	2	111
2.404	14	020,210
2.207	20	002
2.110	100	021,211
1.790	1	121
1.697	1	301
1.626	25	022,212
1.600	1	311
1.457	1	131
1.422	1	103
1.385	2	321,230
1.365	1	113
1.255	25	023,213
1.206	2	040
1.197	2	420
1.166	458	232,402
1.104	6	004
1.065	1	133
1.055	10	042,422
1.003	4	024,214
0.9299	358	333,043
.9103	4	250
.9074	4	440
.9026	4	610

3-0925

3215
d 2.34 2.19 2.06 2.34 Fe_3N-Fe_2N
3-0934

I/I_1
3-0923 100 100 100 100 Epsilon Iron Nitride

Rad.FaK 1.93597 Filter
Dia. Cut off Coll.
I/I_1 Visual d corr. abs.?
Ref. Hagg, N.Acta Reg.Soc.Sci.UPS.,IV 7 1.p16

Sys. Hexagonal S,G.
a_o 2.700 c_o 4.371Å C 1.619
Ref.Hagg,N.Acta Reg.Soc.Sci.Ups.,IV 7 1.p16

dÅ	I/I_1	hkl
2.34	100	100
2.19	100	002
2.06	100	101
1.59	100	102
1.34	100	110
1.23	100	103
1.17	60	200
1.15	100	112
1.13	100	201
1.09	60	004
1.03	80	202
0.989	60	104

The upper limit of N concentration (49.3N atoms to 100 Fe atoms) is less than for Fe_2N. The lower limit varies with temperature and at 700°C the N concentration is less than Fe_4N. At composition near Fe_3N and Fe_2N $a_o' = 3a_o$, $c_o = c_o$, where a_o and c_o are the hex. close-packed cell dimensions. Near Fe_4N and between Fe_3N and Fe_2N additional superstructure reflections which require the unit $a_o'=2\ 3a_o$, $c_o=c_o$ (Jack, Acta Cryst. 3 392(1950) see also Paranjpe et al., Trans AIME 188 307(1950).

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LIST OF THE FIGURES

LIST OF TABLES.