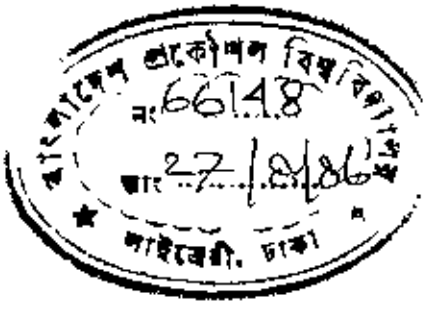
EFFECT OF CARBON
ON THE
NATURE OF THE LAYERS FORMED DURING ION-NITRIDING

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).



Md. Ekramul Haque

August, 1986.

BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY,
Dhaka, Bangladesh.

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.

Countersigned

Supervisor

Signature of the author

The undersigned recommend to the Department of Metallurgical Engineering the acceptance of the thesis "EFFECT OF CARBON ON THE NATURE OF THE LAYERS FORMED DURING ION-NITRIDING" submitted by Md. Ekramul Haque, B.Sc. Engg. (Metallurgical) in partial fulfilment of the requirements for the Degree of Master of Science in Engineering (Metallnrgical).

1. Dr. A.S.W. Kurny — Chairman (Supervisor)
   Associate Professor
   Dept. of Metallurgical Engg.
   BUET, Dhaka.

2. Prof. Md. Serajul Islam — Member
   Head
   Dept. of Metallurgical Engg.
   BUET, Dhaka.

3. Prof. M. Ibrahim 13.8.86. — Member
   Dept. of Metallurgical Engg.
   BUET, Dhaka.

4. Prof. Ehsanul Haque — Member
   Dept. of Metallurgical Engg.
   BUET, Dhaka.

5. Prof. Iqbal Mahmud — Member (External)
   Dept. of Chemical Engg.
   BUET, Dhaka.

ACKNOWLEDGMENTS

The author wishes to express his heartfelt gratitude and sincere thanks to his research supervisor, Dr. A. S. W. Kurny for his inspiring guidence and constant encouragement throughout the whole period of this work.

The author is indebted to Prof. M. Ibrahim, Prof. M. Serajul Islam, Prof. Ehsanul Haque and other teachers of the Department of Metallurgical Engineering for their inspiration and for the many helpful discussions he had with them during the course of this work. Thanks are also due to Mr. Lutfur Rahman, Senior Craft Instructor and Babu Binoy Bhushan Shaha, Senior Laboratory Instructor for their valuable help in the preparation of the specimens and in the printing of the micrographs.

Finally the author expresses his gratitude to his wife Mrs. Nazneen Haque for her continued inspiration throughout the whole period of this undertaking.

BUET, DHAKA

THE AUTHOR

ABSTRACT

Plain carbon steels of different carbon contents have been ion-nitrided in the temperature range of 475-525^{o}C in a 75 H_2: 25 N_2 gas mixture to study the effect of carbon on the nature of the layers formed during ion-nitriding. The effects have been studied by optical metallography and microhardness measurement techniques.

Optical metallographic studies on transverse sections of the ion-nitrided samples have shown that the thickness of compound layer increases with increasing carbon content in the steels.

Microhardness measurements on the surface of the nitrided samples were performed and also the hardness versus penetration distance profiles of the ion-nitrided samples were determined. From the hardness-penetration distance profiles it has been observed that the case-depth (i.e. the depth of nitrogen penetration into the specimens) decreases with increasing carbon content in the steel.

CONTENTS

Chapter-1
INTRODUCTION

Components with a hard wear-resistant surface and a tough ductile core find wide applications in industries. Various methods like carburizing, cyaniding, carbonitriding and nitriding are commonly used for the commerical attainment of this highly desireable combination of properties, the nomenclature depending on the saturating element involved.

The surface hardness obtained by the process of carburizing, cyaniding and carbonitriding depends upon the heat treatment performed after the chemical composition of the surface has been changed. But in the case of nitriding the composition of the surface layers is so altered that the compounds formed are inherently hard and for this reason no further heat treatment is required. Nitriding gives very high surface hardness and wear-resistance which are not attainable by any other surface hardening process. Moreover nitriding of steels is performed at much lower temperatures and so the properties of the core are not changed and the nitrided part are free from internal stresses (and therefore free from aging effects) making them especially suitable for crankshafts, gears, gauges etc.

The atomic radii of the two elements carbon and nitrogen (0.77Å for carbon and 0.71Å for nitrogen) seems to exert a similar influence on the polymorphism of iron on the binary constitution diagram. The micro-structure of both Fe-C and Fe-N alloys after

both slow and rapid cooling are similar. So the properties of the surfaces impregnated with either C or N would be expected to be similar or at best show marginal variation. But in practice, the properties of the nitrided and the carburized layers differ very substantially. The difference in properties is due to the difference in impregnation parameter and in the condition of iron during each of the treatment.

In carburization, the high temperature modification of iron i.e. γ-iron is impregnated with carbon in the temperature region of its stability and impregnation takes place below the solubility limit of carbon in γ-iron. The carbon impregnated layer is subsequently quenched resulting in the formation of a metastable phase, martensite, which is directly responsible for the high hardness. But in nitriding, the low temperature modification, α-iron is impregnated with nitrogen and the impregnation with nitrogen occurs above the solubility limit of this element in α-iron causing precipitation of nitrides. The surface hardness of nitrogen impregnated layer is caused by this highly dispersed nitride precipitates whose quantity and dispersion influence the attainable hardness. The two phase micro-structure of nitrided layer of steel is responsible for its better properties.

Nitriding is more expensive, more complex and more time consuming than any other surface hardening technique, even then the process of nitriding has received considerable attention from both

industrial as well as scientific community, because of its ability to offer superior properties. The possibility of iron reacting with nitrogen to form nitrides was first 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] and its further development by subsequent investigators throughout the world. As a result nitriding can now be performed in different saturating media like solid, liquid for gaseous and numerous modifications of the technique have been evolved to suit specific requirements in service.

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 adaptability appears to have a broader range of applications than any of the other nitriding techniques. The first studies [2,3] of this process were carried out in 1932 and ever since the process has received increasing attention.

Over the past 50 years numerous investigations [4-12] on the ion-nitriding of steels have been made. Most of these studies concern the effect of process variables such as time and temperature of treatment, applied voltage, gas composition and gas pressure on the nature and properties of ion-nitrided steels. Exhaustive investigations on the effects of such alloying elements as Chromium, Molybdenum, Vanadium, Aluminium etc. (commonly known as nitride-formers) have also been made. However, little information regarding the effects of carbon, the most important alloying

element in steels, exists. Moreover some of these observations appear contradictory.

Keller [13] has studied the structure of compound layers produced by ion-nitriding with and without carbon enriched plasmas. On the basis of these investigations, Edenhofer [14] contends that in carbon free plasmas only γ'-nitride is formed. The monophase γ'-nitride layer, because of its narrow range of stability, can grow to a maximum thickness of 6-8 μ. Kurny,[15] on the other hand,related the nature of the compound layers to the gas composition used. He also reported an increase in the thickness of the compound layer with an increase in the carbon content in the material.

Cho & Lee [16] observed that the compound layer was mono-,or polyphase depending on the level of carbon content in the material and an increase in carbon content in the material increases the compound layer thickness.

One of the reasons for this apparent contradiction could be that none of the investigations were designed to study the effects of carbon on the ion-nitrided steels. Sufficient details regarding the experimental variables leading to these observations are also not available. As a result a clear understanding of the effects of carbon on the nature of the layers formed during

ion-nitriding has been rendered difficult. Consequently it was considered desireable to investigate the effects of carbon on the ion-nitriding of steels under identical treatment conditions. Plain carbon steels of two different carbon levels e.g. 0.45%C & 0.53%C were chosen for this study. Except for carbon all other alloy contents in these two steels were identical. Pure iron specimens were also ion-nitrided so as to be able to compare the results obtained.

Chapter-2

ION-NITRIDING-A SURVEY

2.1 The Principle of Ion-Nitriding

The concept and the principle of Ion-nitriding were first established in Germany by Bernerd Berghaus [2] in the early 1930's. The principle of ion-nitriding process is similar to that of galvanic plating, where a current-carrying substance between an anode and a cathode supplies the coating material for the cathode. In ion-nitriding, the current-carrying substance is a low pressure nitrogen gas introduced into a vacuum chamber (1-10 torr). Under the influence of a high d.c. voltage (about 400-1000V) the gas is ionised and becomes electrically conductive. Positive nitrogen ions are attracted by the cathodic workpice where, on hitting its surface, they cause the nitriding action. The energy transferred to the workpices by the ion-bombardment is largely used to heat the workpice to the necessary treatment temperature (between 400-600^{o}C). The temperature of the work load is measured and controlled by means of thermocouples which are inserted in the charge.

2.2 Generation of Plasma and Ionisation Technique.

A plasma consists of electrically charged particles, i.e. ions and electron. In other words, the plasma state is reached by ionizing gas atoms or molecules. In a purely thermal process, the plasma state can be reached by heating the gas to a temperature at least some thousand degrees. But if electricity is used the plasma state can easily be reached as in the glow discharge.

Moreover, ionisation by itself does not cause accelerated nitriding. This occurs only in the presence of an ion-current.[6,7]

The small numbers of charge carrier which are present in any gas are accelerated in the voltage drop between cathode and anode, collision process involving other gas particles dissociates molecules of the treatment gas as well as excite and ionize atoms and molecules. New charge carriers are thus continuously produced, the electrons being accelerated towards the anode and the positive ions towards the cathodically connected workpiece.

The voltage applied does not drop in a linear way between the electrodes as it would in extremely high vacuum, but is greatly modified by the positive space charge which builds up in front of the workpiece. Accordingly, almost the entire applied voltage drops on a few mm in front of the cathode. This is why the voltage drop is called "cathode-fall". The collision and ionization processes which are an essential features of this type of surface treatment take place within the region of the cathode fall. Thus, the perfect plasma state of the treatment gas is only produced immediately in front of the workpiece surface (within the cathode-fall region), while the remaining treatment space in the vacuum chamber is filled with normal treatment gas which is somewhat enriched in charge carriers. The positive space charge has the effect of a projecting anode so that surface treatment in the plasma of the glow discharge is practically independent of the distance between the workpiece and the wall of the chamber.

The cathode luminous phenomena which is called "glow seam" is also limited to a narrow space around the workpiece. The glow seam follows each individual contour of the workpieces, so that all surfaces including notches and bores are submitted to uniform ion-bombardment, creating a uniform hardness. Fig. 2.1 shows the voltage required for the ionization of various gases. These curves are known as Paschen curves. For the majority of gases the minimum breakdown voltage is between 100 and 500 volts and corresponds to pd values of 0.1 to 10 torr-mm, where "p" is the pressure in "torr" (mm-Hg) and "d" is the distance in "mm" between electrodes. Gas mixtures generally have a lower break-down voltage than the pure gases.

2.3 Technique and Control of Glow Discharge and Type of Discharge Used for Ion-Nitriding.

A glow discharge is produced by the shock excitation of gas atoms or molecules in an electric field in accordance with physical laws. The pre-requisites of the appearence of glow discharge are the presence of a low pressure gas (medium-high vacuum) and the application of a suitable d.c. voltage between the electrodes.

The type of discharge that results upon spark breakdown of a gap in an ionisation chamber depends on gas pressure, the gap length and the applied voltage. Fig. 2.2 shows the voltage-current characteristics of different types of discharge. The regions A-B (range of Geiger-counter tube), B-C (Townsend discharge), E-F (normal glow-discharge) etc. where the current is extremly low are of no interest here.

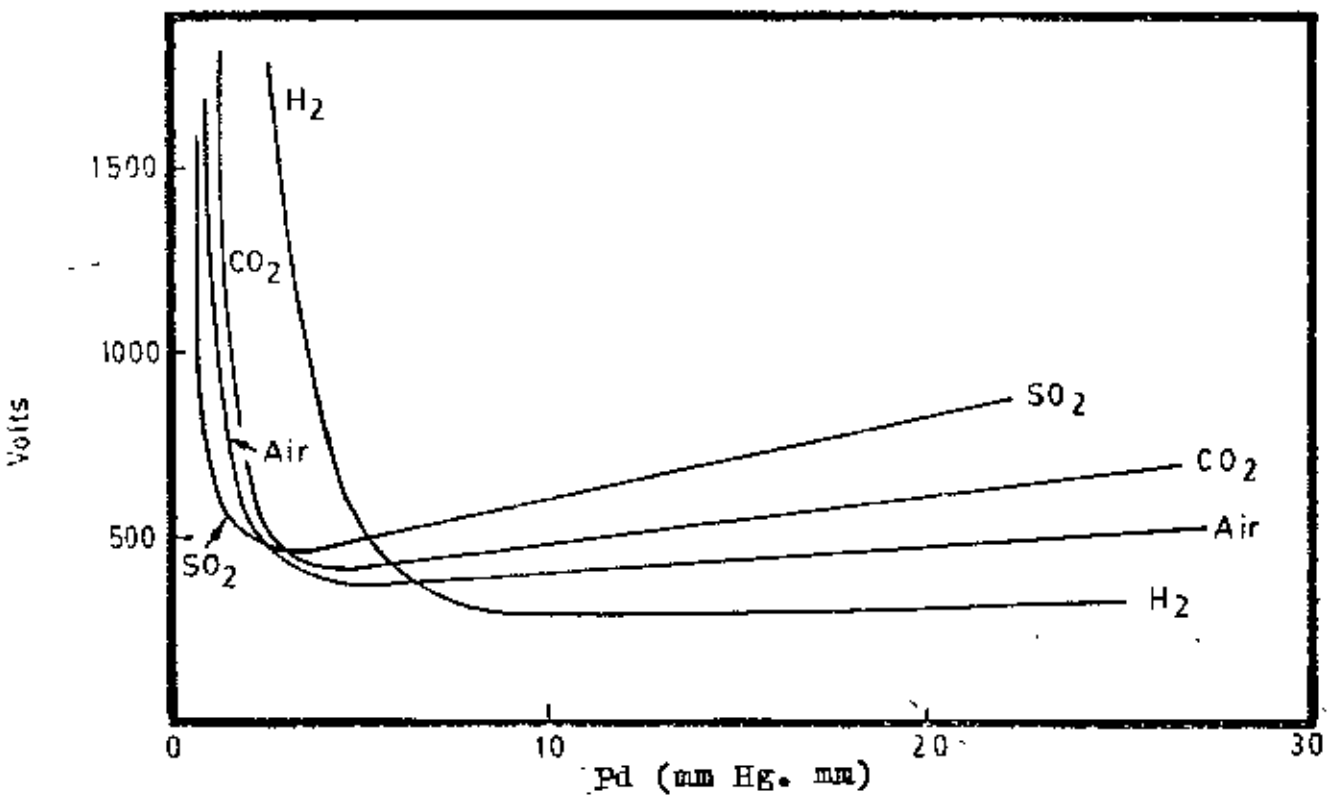


FIG.2.1 CURVES SHOWING THE DEPENDANCE OF BREAKDOWN VOLTAGE ON THE PRESSURE IN THE CHAMBER AND THE DISTANCE BETWEEN THE ELECTRODES.

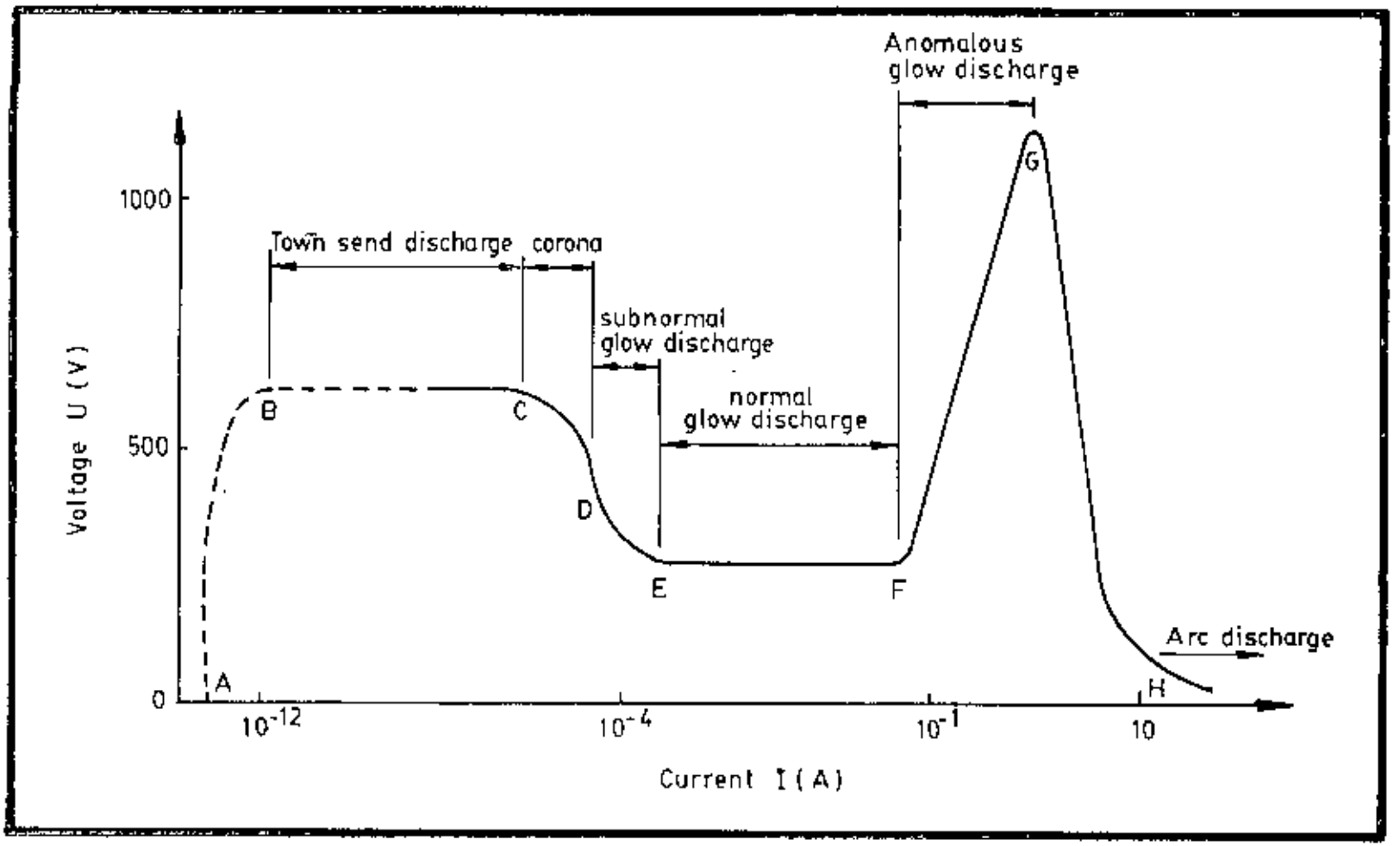


FIG. 2·2 VOLTAGE CURRENT CHARACTERISTICS OF DIFFERENT TYPES OF DISCHARGE

Ion-nitriding processes are associated with higher current and power densities and occur in the region of the abnormal, unstable and current-intensive glow discharge (F-G). The production and control of this unstable, abnormal glow discharge is the most essential feature in the production of truly ion-nitrided surface layers.

2.4 Advantages of Ion-Nitriding

Since the inception of the process in 1932, a number of investigators [4-14] have studied the technique and almost all of these studies independently agree to several major advantages of ion-nitriding process as compared to the conventional nitriding techniques. These advantages are listed below.

i) The first laboratory tests showed that ion-nitriding reduced the time required for nitriding. The essential factor leading to this short treatment time was the accelerated diffusion of the nitrogen in ion-nitriding which could be attributed to (a) the high surface concentrations of nitrogen which is of particular importance at the beginning of the process and (b) the increased rate of nitrogen penetration due to the different diffusion paths and (c) higher energy of the nitrogen ions in ion-nitriding as compared to that in gas nitriding.

ii) During ion-nitriding, the glow uniformly covers all surfaces of the workpiece irrespective of its size and shape and also the distance from the anode. This guarantees uniform and complete transfer of nitrogen into all the surfaces of the workpiece.

iii) The amount of active nitrogen that can be obtained in gas and liquid nitriding techniques is strongly temperature dependent. This renders them unsatisfactory at temperatures below 500°C. In ion-nitriding, on the other hand, the highly active plasma state is created by the application of an electric field and nitriding potential of the low pressure-treatment gas is practically independent of temperature, over a wide range of temperatures. This permits nitriding at very low temperatures. Nitriding at low temperatures has three distinct advantages: (a) this yield high core hardness, (b) gives increased surface hardness and (c) has better dimensional stability.

iv) Careful control of the ion-nitriding process variables enables one to get a monophase layer of required thickness leading to superior properties. Apart from this, the virtual absence of porosity in the ion-nitrided layer is remarkable, which results in superior wear and corrosion resistance.

v) The process with its high degree of variability and adaptability appears to have a broader range of application than any other nitriding process. For example, cast irons (normally not nitrided by conventional techniques) can be ion-nitried to yield a monophase ε-nitride, giving good wear and gliding properties.

vi) In commercial nitriding it is sometimes necessary to stop-off sections of the part being processed. In ion-nitriding, this can be easily done by using sheet-stock or a di-electric in conjunction with and formed around the areas to be protected from the glow. It is held in position by spot-welding or by clamps.

vii) Ion-nitriding technique requires a much higher capital cost as compared to conventional nitriding techniques. However, the following reasons lower the cost of ion-nitriding:

1. Low consumption of gas and electrical energy
2. Production of heat directly on the surface of workpiece
3. Shorter treatment time and
4. Quick and easy masking methods.

Moreover ion-nitrided parts can be put to use without any after treatment, this saves the cost of washing, cleaning, lapping etc. As a result, when all costs are taken into account, ion-nitriding is much cheaper as compared with conventional techniques. Al Taylor, [23] Chief metallurgist of Advanced Vacuum Systems, USA compared the cost figures for gas and ion-nitriding of 500 lbs of nitroalloy 135M to a case depth of 0.017-0.002 inch with a white layer of 0.0005 inch. He puts directly associated costs of gas nitriding at $ 463.80 and only $ 83.10 for identical ion-nitriding load. To these direct cost savings one has to add the indirect cost savings produced by longer service life, special layer properties and better dimensional tolerence obtained in ion-nitrided components.

Chapter-3
MATERIALS AND METHODS

3.1 Preliminery Considerations:

It has been observed [14] that during ion-nitriding iron atoms are detached (sputtered) from the workpiece surface, combine with reactive nitrogen atoms near the workpiece and are redeposited on the workpiece surface as FeN. This FeN is unstable and decomposes into lower nitrides generating nitrogen ions.

These two processes sputtering and condensation, occuring during ion-nitriding depend to a great extent on the type of gas used. Furthermore their mutual relationship can be influenced by varying other treatment parameters such as pressure and voltage. An increase in the treatment voltage at constant pressure increases the rate of sputtering [14,17] leading to a decrease in the thickness of the compound layer, while an increase in gas pressure (voltage remaining constant) increases the rate of redeposition thus causing an increase in the thickness [14].

It has also been observed [15,18] that the thickness of the compound layer depends on the percentage of hydrogen in the treatment gas and decreases with an increase in hydrogen in the treatment gas. To eliminate uncertainities caused by the variation in the rates in these two processes identical treatment conditions were employed in this investigation. Therefore a treatment gas containing $25N_2$: $75H_2$, at a total pressure of 7.25 torr was used throughout this study. The voltage between the electrodes was also kept constant.

3.2 The Experimental Set-up

A laboratory model ion-nitriding unit Fig. 3.1(a) and (b) designed and fabricated at the Department of Metallurgical Engineering at BUET, Dhaka has been used in these studies. The essential features of this unit are:

1. a high voltage d.c. power supply.
2. a vacuum chamber with a suitable pumping system.
3. a gas dispensing system.

3.2.1 The Power Supply

The power supply used (0-4 KV dc, IA) was capable of providing the required voltage and current in the discharge gap 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.

3.2.2 The Vacuum Chamber

The vacuum chamber, where nitriding actually takes, place, is shown in Fig. 3.2. A 400 mm long, 80 mm internal diameter pyrex glass tube was used in the fabrication of this chamber. Two aluminium flanges, with circular gooves for seating the glass tube, were fixed to the ends of this tube with epoxy resin (araldite).

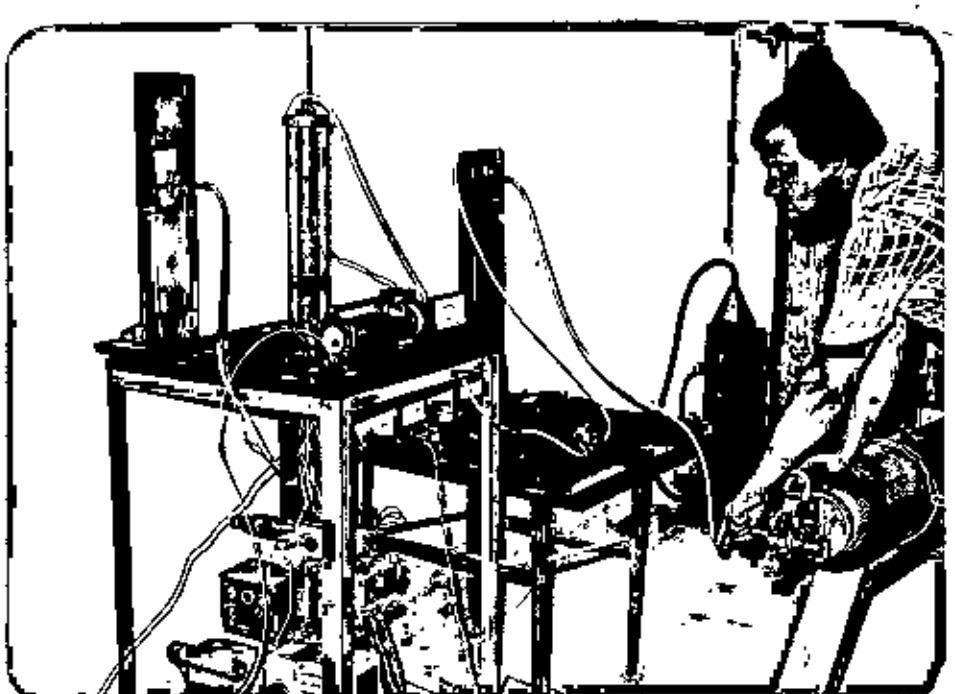


FIG. 3.1(a): A general view of the Ion-nitriding unit.

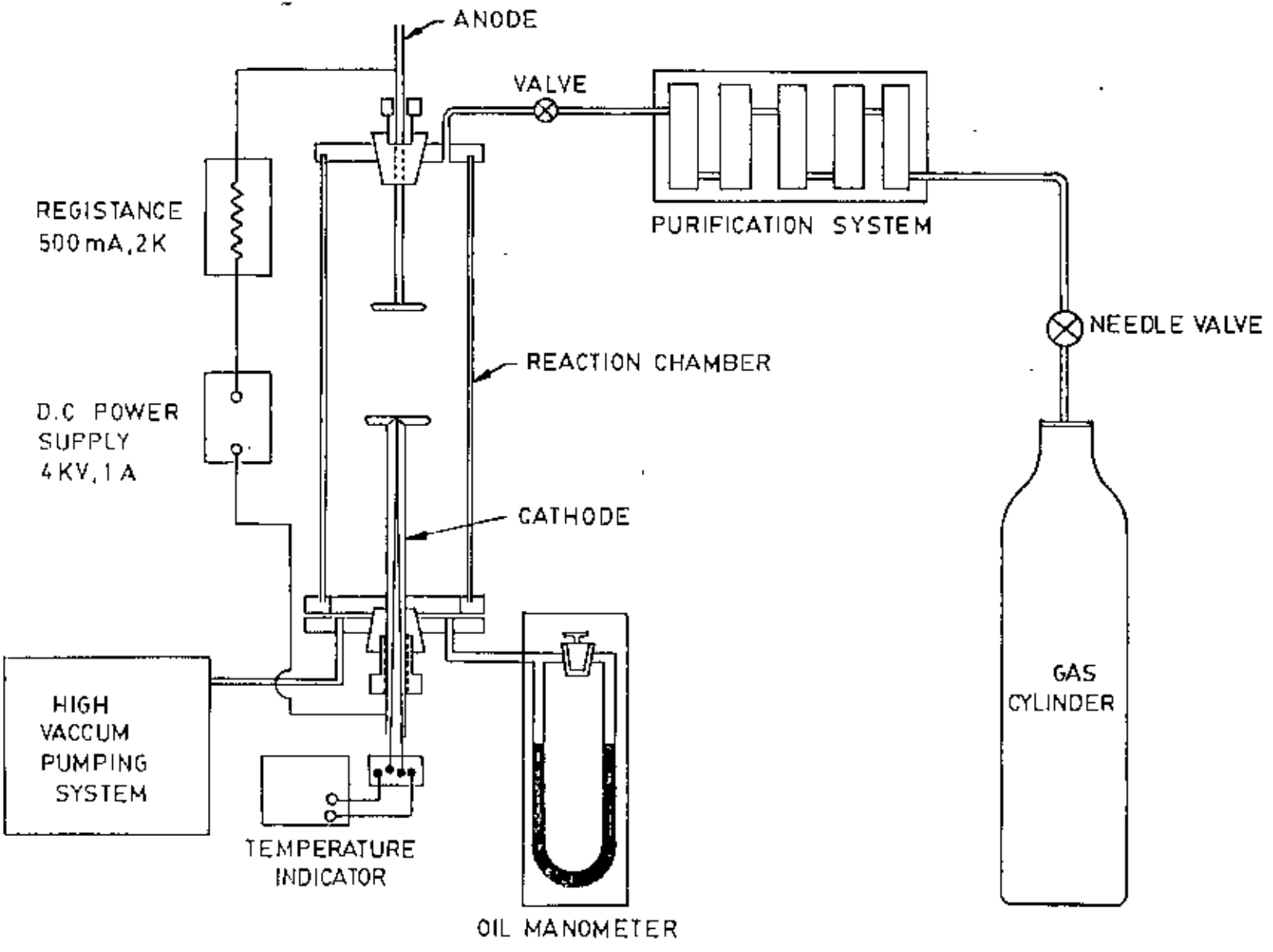


FIG. 3·1(b) EXPERIMENTAL SETUP FOR ION-NITRIDING

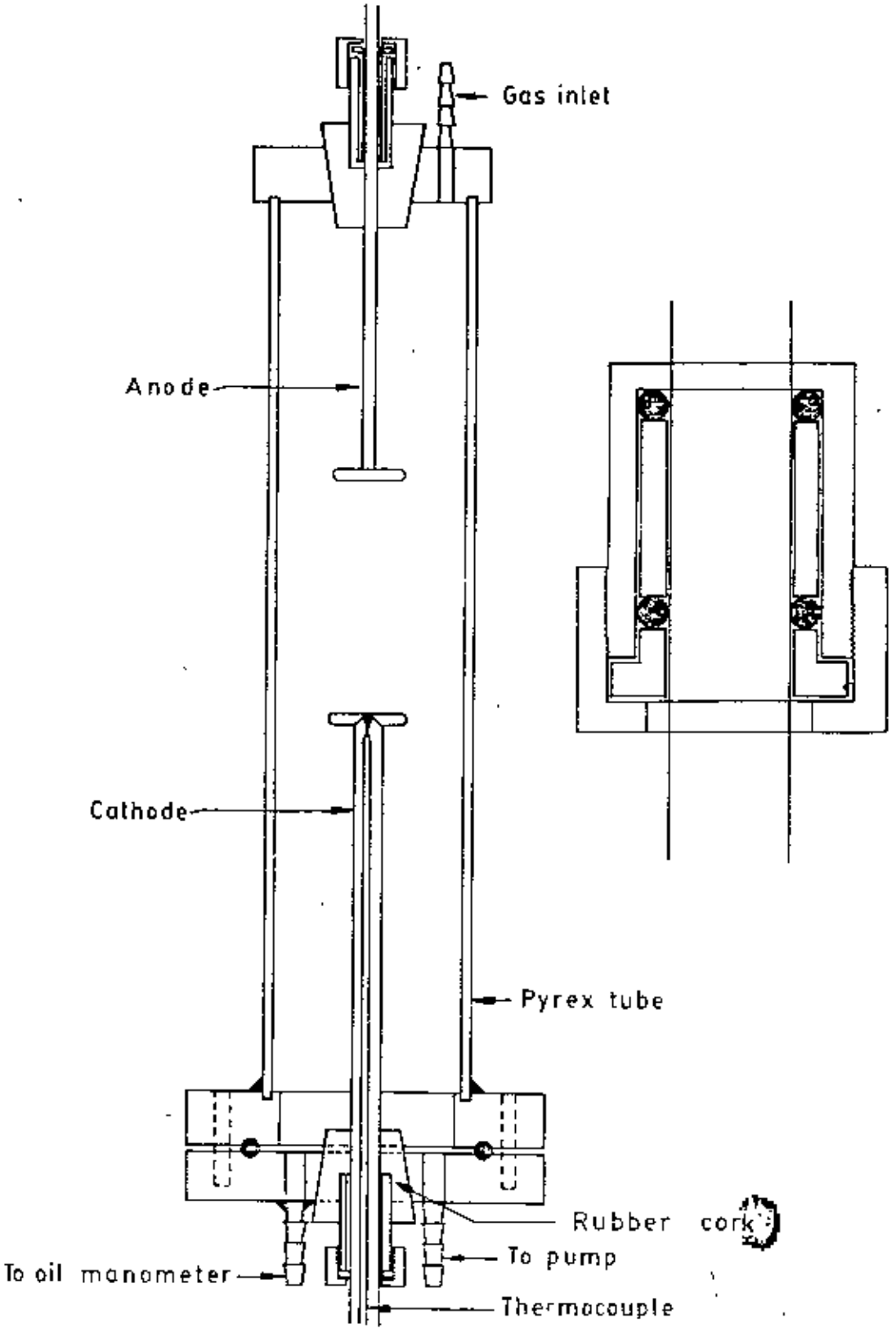


FIG. 3·2 THE VACUUM CHAMBER

The top flange is 90 mm in diameter and 20 mm thick, with a tapered hole 30/35 mm diameter at the centre. A rubber cork machined to slight oversize was press-fitted into this hole. A 5 mm hole at the centre of this rubber cork allows the anode to extend outside the chamber through a double O-ring seal. This double O-ring seal (inset, Fig. 3.2) allows the vertical movement of the anode without breaking the vacuum. A stainless steel rod, 6 mm in diameter, was silver brazed to a 25 mm diameter, 3 mm thick stainless steel disc to form the anode. This top flange is also provided with a port for introducing the treatment gas mixture.

The bottom flange, 140 mm in diameter and 20 mm thick is provided with a 70 mm diameter hole in the centre. This flange is secured to the base plate through allen screws. A 80/88 mm O-ring groove is provided on the base plate and an O-ring seal has 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.

3.2.3 The Base-plate Assembly

The base plate assembly, illustrated seperately in Fig. 3.3 is made of a nickel plated mild steel. Similar to the top flange this also has a tapered hole, 30/35 mm diameter at the centre and a rubber cork was press-fitted into this hole. The cathode, inserted through this hole, extends beyond the chamber through a double O-ring seal which allows vertical movement of the cathode.

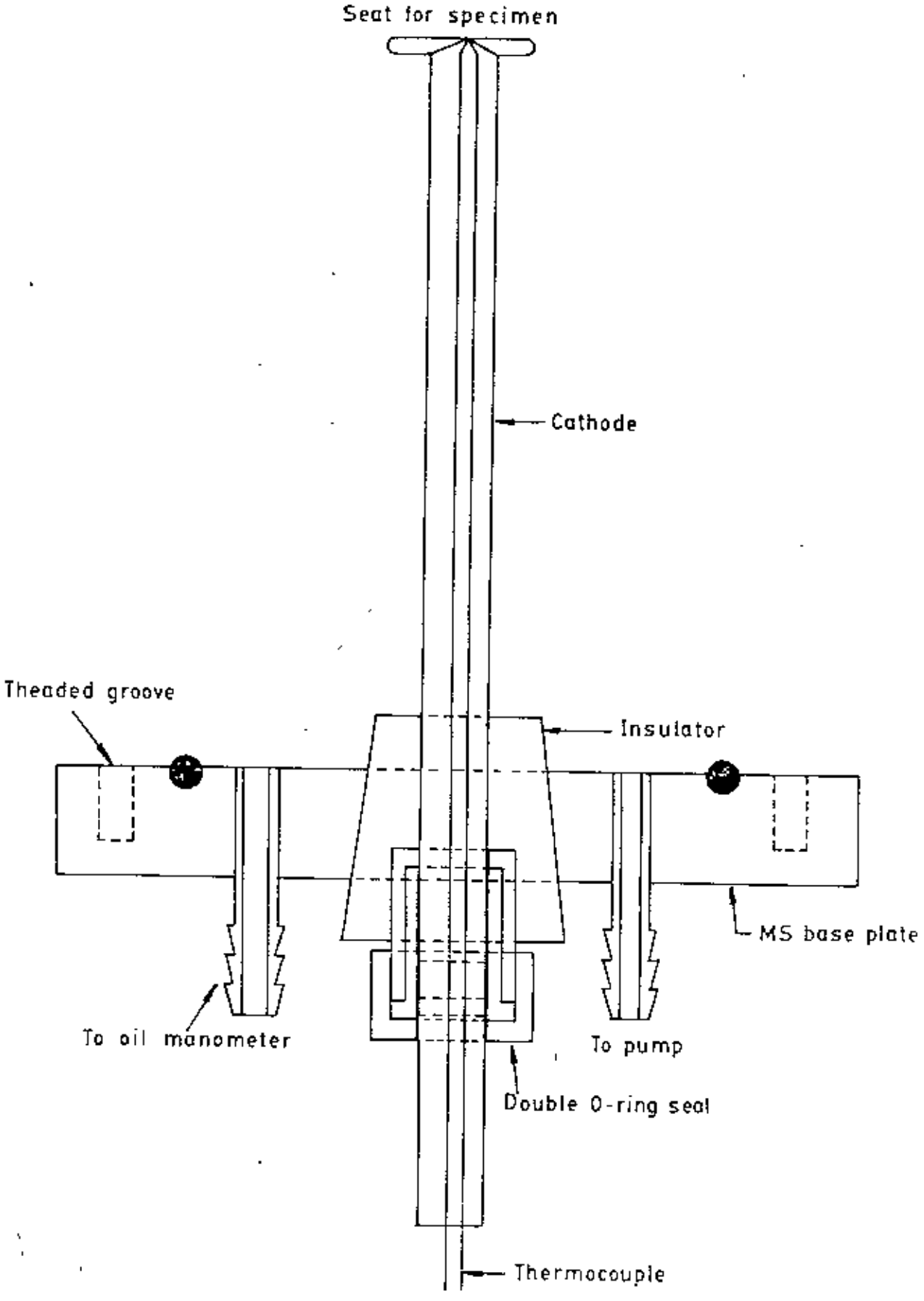


FIG. 3·3 BASE PLATE ASSEMBLY

A 10 mm diameter stainless steel tube was silver brazed to a 25 mm diameter 3 mm thick 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 to an arc discharge.

A protected chromel-alumel thermocouple was introduced through the cathode and embedded in the steel disc, as illustrated. 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 for measurement of pressures. The ports for introducing gas, pumping and for the measurement of pressures were all connected by epoxy resin.

3.2.4 The Pumping System

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^{-4} torr.

3.2.5 Gas Dispensing System

As already mentioned, composition of treatment gas has been found to affect the ion-nitriding process to a great extent. Hudis [6] observed that nitriding is faster in a nitrogen-hydrogen mixture than in pure nitrogen. James & Martins [19] indicated that hydrogen

in the treatment gas cleans the workpiece surface and accelerates the rate of nitriding. Soccorsy and Ebihara [18] observed that after initial cleaning of the substrate, hydrogen reacted wtih 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 25 N_2 : 75 H_2 throughout this study. Gas mixtures 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 and a flow-meter. The gas mixture flowing out of the flowmeter were made to enter into the chamber. A needle-type valve between the flowmeter and the nitriding chamber was used to control the flow-rate of the gas mixture.

3.3 Preparation of Specimen

Since it was intended to study the effect of carbon content in the material on the ion-nitriding of steels, two commercial grade steels having two different carbon levels were chosen for this study. A simple system, pure iron, was also chosen for this study to facilitate easy interpetation of the results obtained. The actual chemical analysis of these steels, code named CS-1 and CS-2, are presented in Table 3.1 Specimens measuring 20 mm dia and 3 mm thick were machined from the commercial grade hot rolled rods. No heat treatment of the samples were performed. Before nitriding the specimens were polished on emery papers and degreased in acetone.

Table 3.1: Chemical composition of the steels investigated.

Material	C%	Si%	Mn%	S%	P%
CS-1	0.45	0.25	1.31	0.037	0.028
CS-2	0.53	0.25	1.30	0.036	0.029

3.4 Ion-Nitriding

The cleaned and degreased workpiece was placed on the cathode and the chamber was then evacauted to about 1×10^{-3} torr. During this evacuation the limbs of the oil manometer, which was used to measure the system pressure during nitriding, were also evacuated by properly operating the stop cock. After the desired vacuum had been reached, the diffusion pump and one limb of the manometer were isolated and a mixture of 25 percent nitrogen and 75 percent hydrogen was introduced through the needle valve. The pressure inside the chamber, measured with the manometer was maintained at 7.25 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. The voltage was adjusted and maintained at a constant voltage and the current was adjusted to maintain a constant nitriding temperature. The temperature was read off on a temperature indicator, using a chromel-alumel thermocouple.

After nitriding for a specified time (this includes the time to reach the nitriding temperature, which was usually 5-6 minutes) at the desired temperature the power supply was switched off and the specimen cooled to room temperature in a stream of the treatment gas. The workpiece was then taken out and stored in a desiccator.

The treatment conditions for CS-1 and CS-2 and pure iron are presented in Table- 3.2.

Table 3.2: Ion-Nitriding conditions of the steels investigated.

Material	Temperature ^{o}C	Time of treatment (hr.)
Pure iron	450	0.5,1.0 and 3.0
	475	0.5,1.0 and 3.0
	500	0.5,1.0 and 3.0
	525	0.5,1.0 and 3.0
CS-1	475	0.5,1.0 and 3.0
	500	0.5,1.0 and 3.0
	525	0.5,1.0 and 3.0
CS-2	475	0.5,1.0 and 3.0
	500	0.5,1.0 and 3.0
	525	0.5,1.0 and 3.0

3.5 Optical Metallography

The nitrided workpieces were cut off into small pieces at 90 degrees to the nitrided surface by using silicon-carbide cut-off wheel for optical metallography work. 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. A 5 pct nital was used as an etchant to reveal the structure of pure iron, CS-1 and CS-2 grade steels.

The microstructures were observed and photographed on an optical metallograph.

3.6 Hardness Measurements

Microhardness measurements on the surfaces of the nitrided specimens were made on a Shimadzu microhardness tester using a 100 g load. No further treatment of the nitrided specimens were done for these microhardness measurements.

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 on nitriding.

The measurements in this study were made with a 50 g load and started at the point of closest approach to the edge. The distance between two successive indentations were kept constant as far as possible. The zero-point on distance scale in the figures presented in this dissertation corresponds to the extreme outer surface of the specimen and includes the compound layer.

Chapter - 4

RESULTS AND DISCUSSION

4.1 Introduction

The effects of carbon on the nature of the layers formed during ion-nitriding in a $75H_2:25N_2$ gas mixture in temperature range of 475-525°C have been investigated by optical metallography and microhardness measurement techniques. In this chapter the results of this investigation have been presented and discussed.

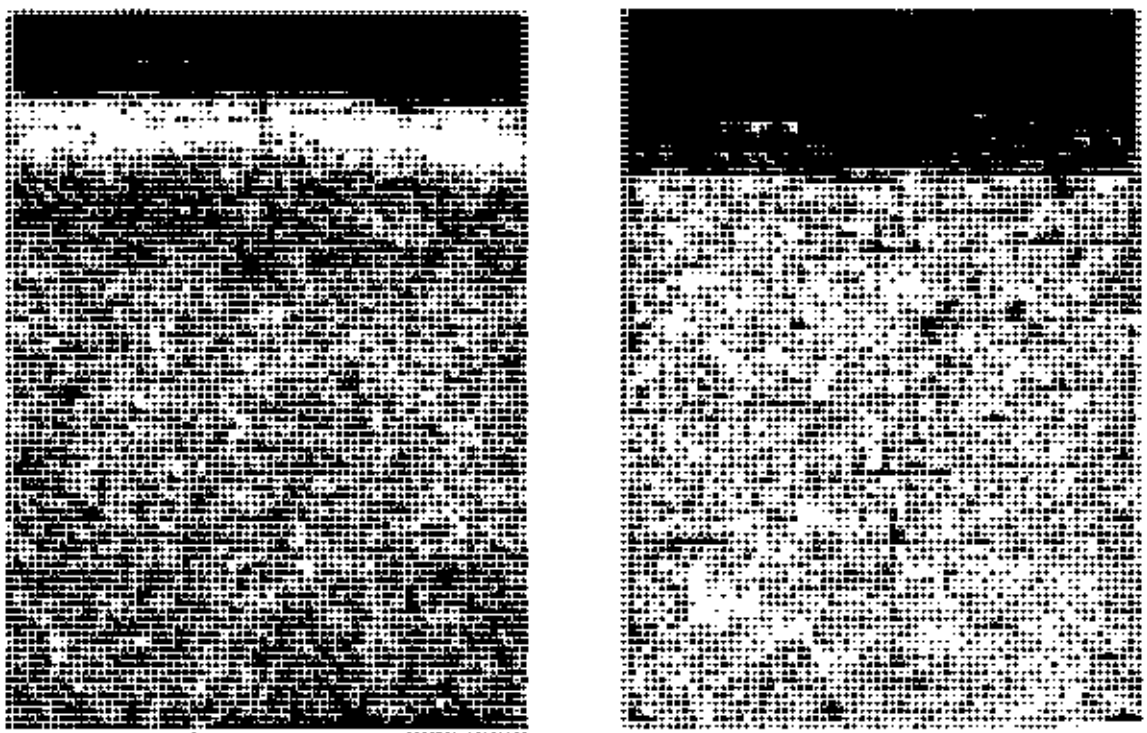
4.2 Optical Metallography

The microstructural changes occuring in the steels and in pure iron during ion-nitriding were followed by optical microscopy. Transverse sections of nitrided specimens were mounted in thermo-setting resin and were prepared by using standard technique. The structures were observed and photographed on an optical metallograph. The microstructures of the specimens are presented in Fig. 4.1 to Fig. 4.3 and Fig. 4.5 to Fig. 4.6.

The study of the microstructures leads to the following general observations.

1) The compound layer, also known as the white layer, do not etch with nital. The thickness of the compound layer increases with time at temperature and also with temperature at constant time.

2) The compound layers are compact and free from pores.



5% nital 100x (a)

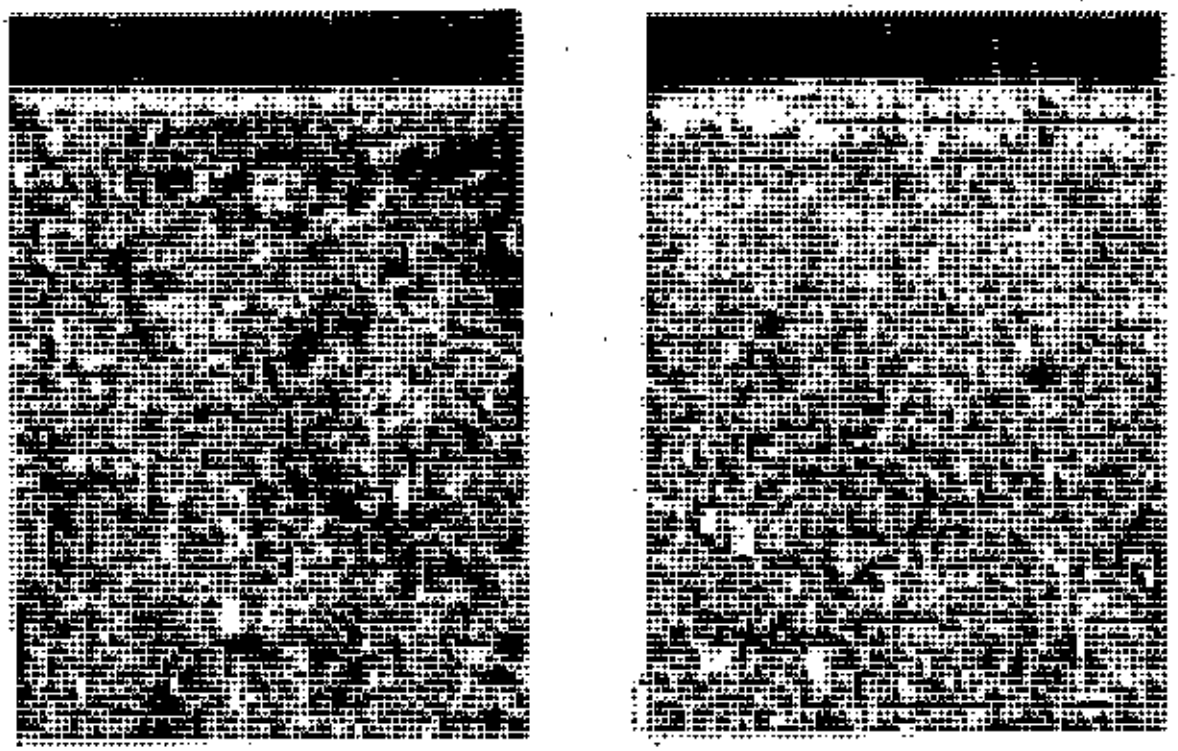
5% nital 100x (b)

FIG. 4.1: Optical micrographs* of

(a) Ion-nitrided ($75H_2$:$25N_2$, 7.25 torr) for 1.0 hour at 500°C for the steel Cs-1.

(b) Ion-nitrided ($75H_2$:$25N_2$, 7.25 torr) for 1.0 hour at 450°C for pure iron.

*Magnified 2.5 x during reproduction.



5% nital 100x (a)

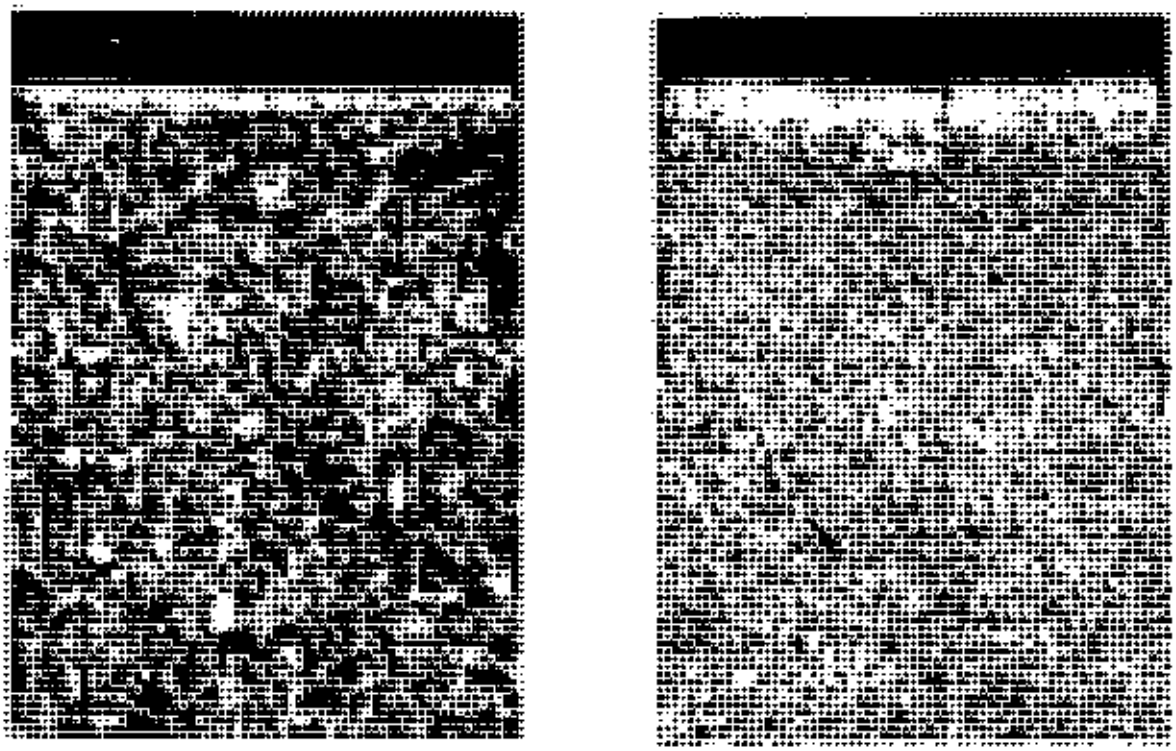
5% nital 100x (b)

FIG. 4.2: Optical micrographs* of the steel CS-1 ion-nitrided ($75H_2:25N_2$, 7.25 torr) for

a) 0.5 hour at $475^{o}C$

b) 3.0 hours at $475^{o}C$

*Magnified 2.5x during reproduction.



5% nital 100x (a)

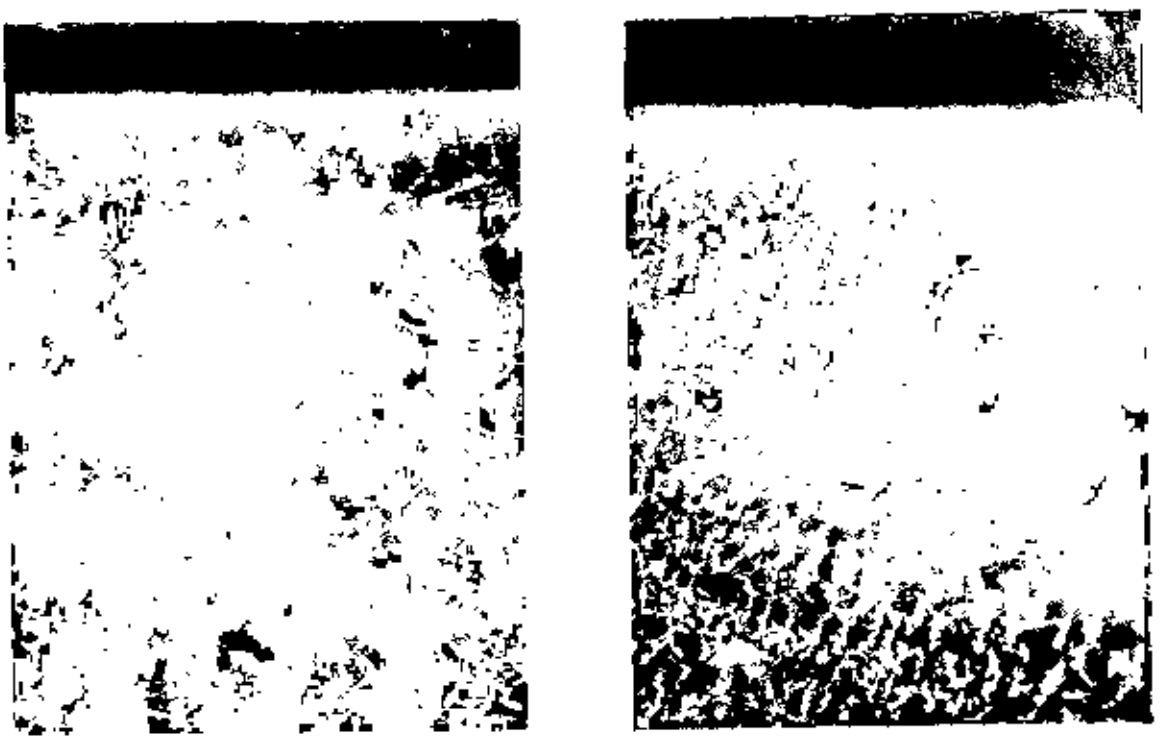
5% nital 100x (b)

FIG. 4.3: Optical micrographs* of the steel CS-1 ion-nitrided ($75H_2:25N_2$, 7.25 torr) at

a) 475°C for 0.5 hour

b) 525°C for 0.5 hour

*Magnified 2.5x during reproduction.



5% nital 100x (a)

5% nital 100x (b)

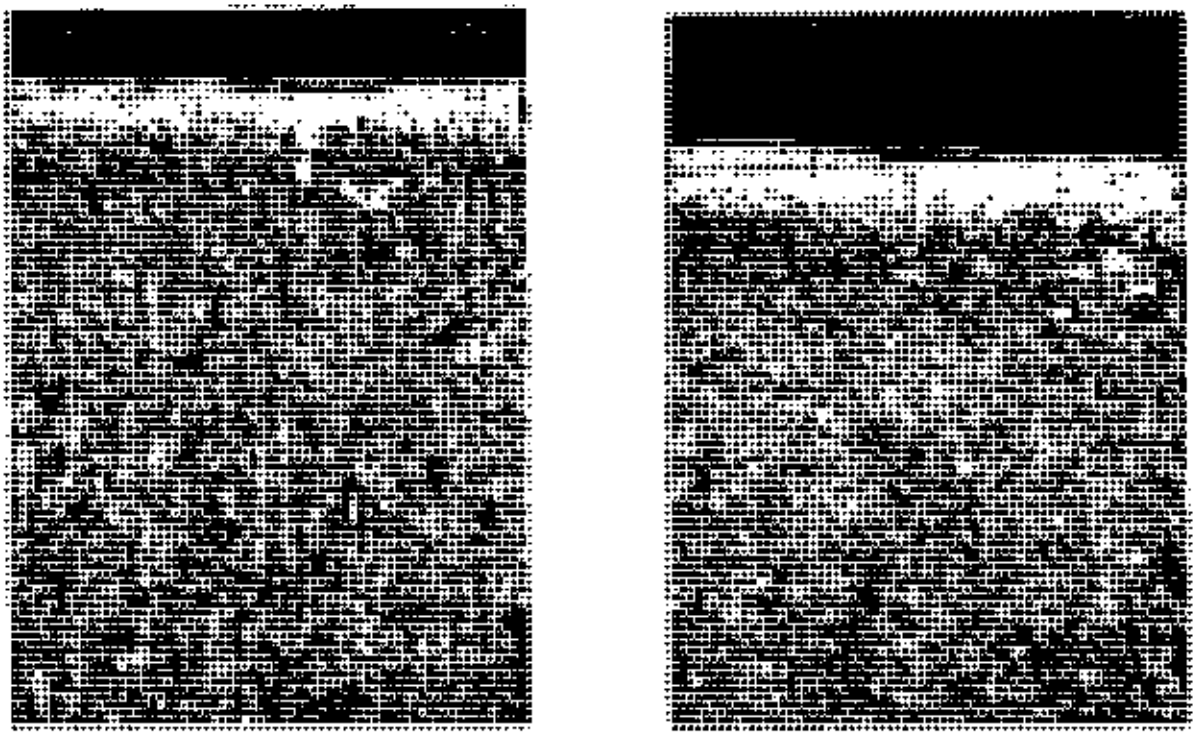
FIG. 4.5: Comparison of the microstructures* of the steels

a) CS-1

b) CS-2

Ion-nitrided ($75H_2:25N_2$, 7.25 torr) at $475^{o}C$ for 0.5 hour.

*Magnified 2.5x during reproduction.



5% nital 100x (a)

5% nital 100x (b)

FIG. 4.6: Comparison of the microstructures* of the steels

a) CS-1

b) CS-2

Ion-nitrided ($75H_2$:$25N_2$, 7.25 torr) at 525°C for 1.0 hour.

*Magnified 2.5x during reproduction.

3) Nitride needles are clearly visible in the ion-nitrided pure iron. On the contrary, no nitride needle could be observed on the steels investigated. Seybolt[8] also observed that these needles either cannot nucleate in the presence of carbides or they cannot grow beyond a very small size. In almost all steels therefore, the nitride needles are not visible under an optical microscope.

4) The core of the steel specimens remains unaltered during nitriding as seen by metallography.

5) A nital etch do not reveal the depth of nitrogen penetration.

4.2.1 Variation in Thickness of the Compound Layer

Fig. 4.4 shows the variation in thickness of the compound layer formed on the steel CS-1. It can be seen that thickness of the compound layer increases with time at temperature and also with temperature at constant time. A similar trend in the variation in the thickness of the compound layer formed was also noted on the steel CS-2.

4.2.2 Comparison of the Thickness of the Layers on CS-1 & CS-2

A closer examination of the micro-structures (Fig. 4.5 and 4.6) reveals that under identical treatment conditions, the thickness of the compound layer formed on the steel CS-2 is more as compared to the thickness of the compound layer formed on the steel

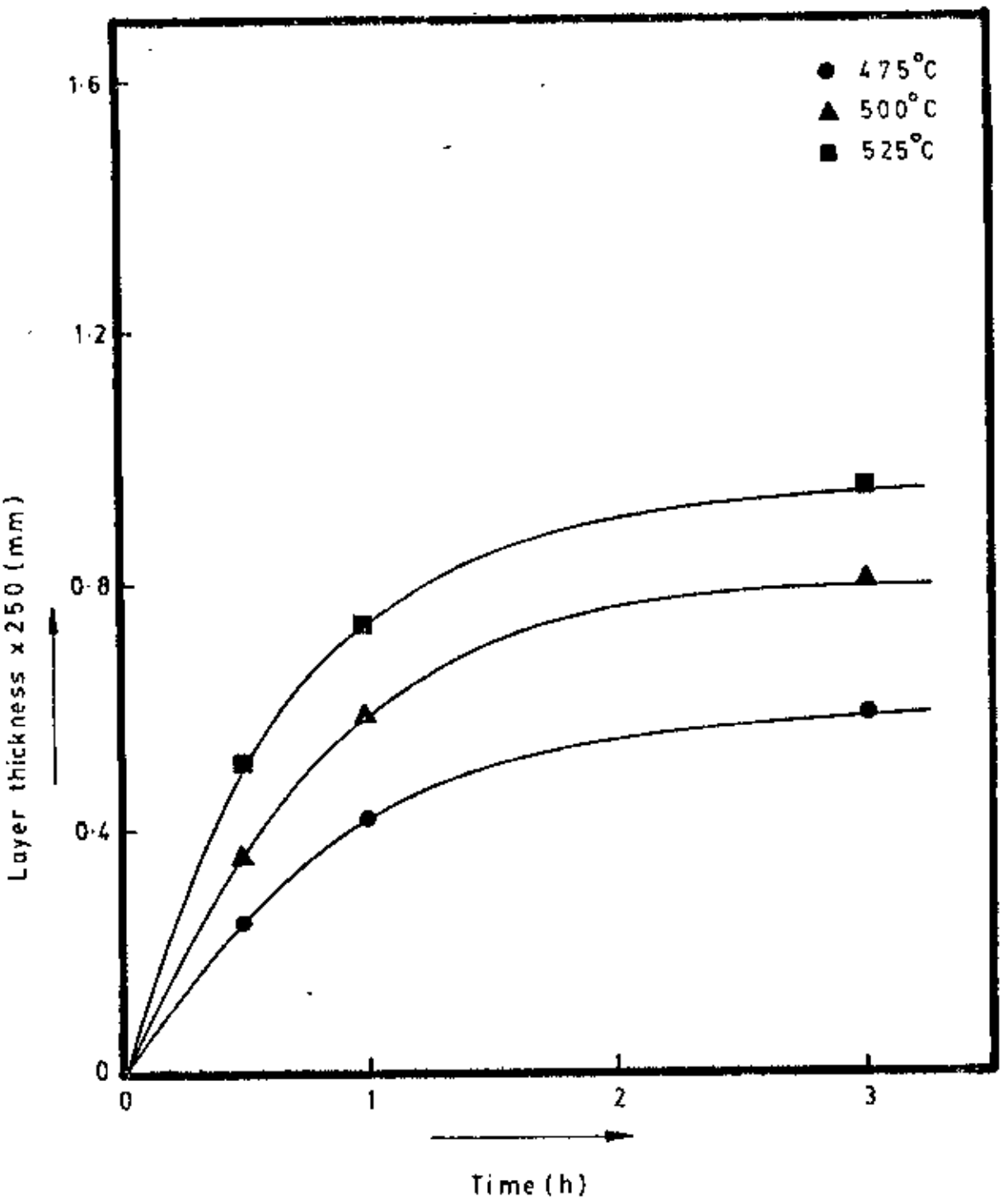


FIG. 4.4 VARIATION IN THE THICKNESS OF THE COMPOUND LAYER WITH TREATMENT TIME AT DIFFERENT TEMPERATURES FOR THE STEEL CS-1 [ION NITRIDED $75H_2 : 25N_2$; 7·25 TORR]

CS-1. The carbon content in the steel CS-2 (0.53%C) was more than the content of carbon in the steel CS-1 (0.45%C). It can be thus seen that the thickness of the compound layer formed on the steel increases with an increase in the amount of carbon in the steel.

Fig. 4.7 shows the dependence of the thickness of the compound layer formed during ion-nitriding on the carbon content in the material. This figure is related to a specified treatment time (0.5h). From this figure also it can be noted that the thickness of the compound layer is greater in the steel containing a higher amount of carbon. This is in good agreement with the results obtained by Cho & Lee [16] and also by Kurny[15].

The increase in the thickness of the compound layer with increasing carbon content could possibly be explained by the increased activity of nitrogen in the presence of carbon in the material. From a study on the nature of the dark component in carbonitrided steels Akhantev et al observed [20] that the activity of nitrogen is increased in the presence of carbon. Kurny [21] has shown that a higher partial pressure of 7.14×10^{-3} atm is required for the formation of higher nitrides (ε-nitride) in pure iron whereas in the presence of carbon (0.35%C) a partial pressure of 2.38×10^{-3} atmoshpere was adequate for the formation of ε-nitride. He attributed the formation of a higher nitride in steels at partial pressures of nitrogen which leads to the formation of only γ'-nitride in pure iron to the increased activity of nitrogen in the presence of carbon.

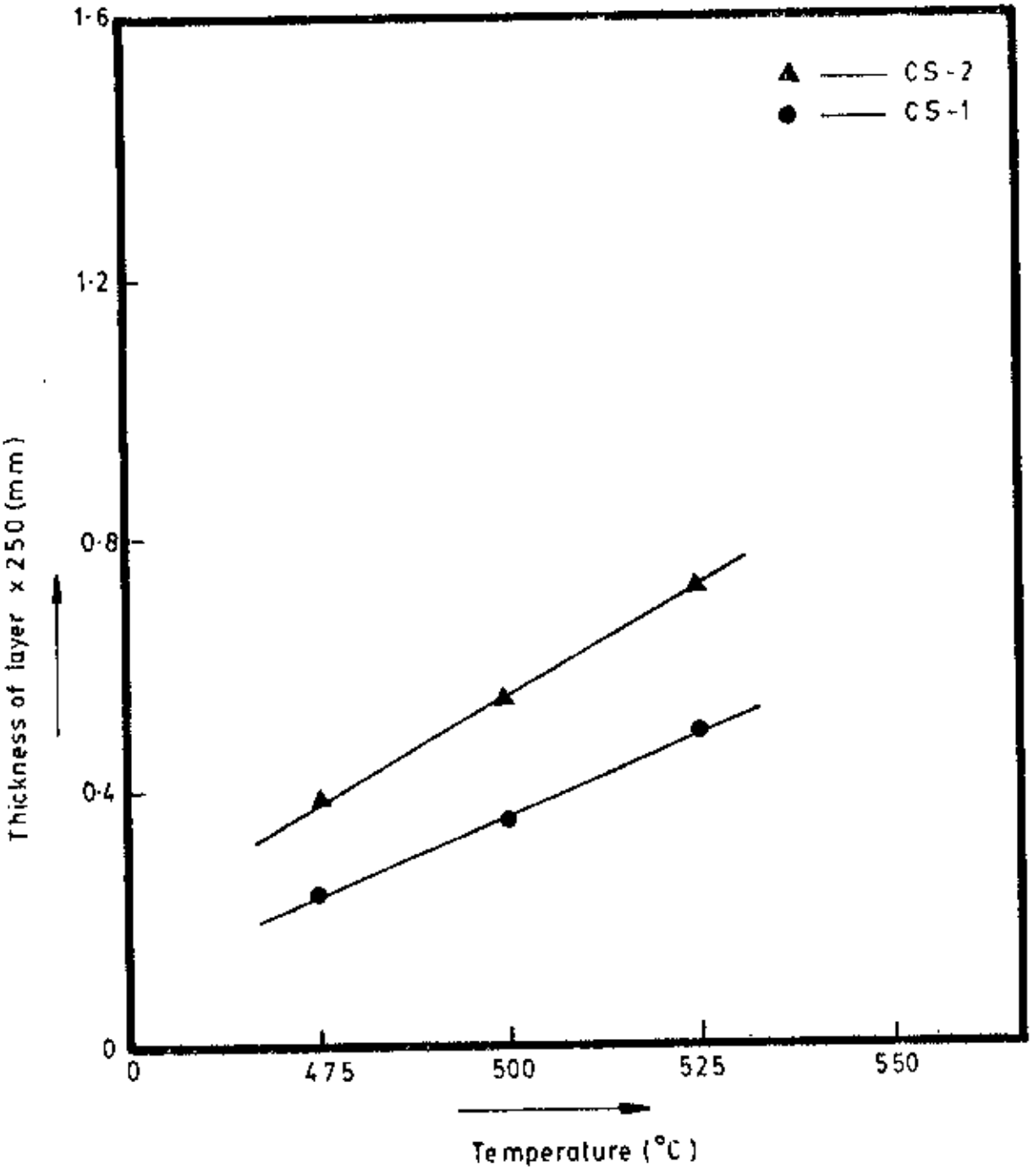


FIG. 4·7 COMPARISON OF THE THICKNESS OF THE COMPOUND LAYER FORMED ON THE STEELS CS-1 AND CS-2 [ION NITRIDED, 0·5HR 7·25 TORR, 75 H_2 : 25 N_2]

4.3 Surface Hardness

Surface hardness measurements were carried out on all ion-nitrided specimens, using a 100 g load. Small variations in hardness values were noted on the samples. The surface hardness values reported here, are the averages of 5 random hardness values and are intended to serve as a measure of hardening achieved.

Fig. 4.8 shows the relationship between surface hardness and treatment time at various temperatures for the CS-1 steel. It can be seen that at all temperatures investigated, the hardness values show an increasing trend.

The hardening in nitriding is caused by finely dispersed nitrides within the matrix. The hardening is dependent on the size of the nitride precipitates. Philips and Seybolt [22] studied the precipitation of alloy nitrides using electron microscopy and noted that coarse nitrides caused small to moderate hardening. They identified very fine particles, which were hard to resolve, to be the principal source of hardening.

The growth of the nitrides is time and temperature dependent. These experiments were of short durations and were performed at low and moderate temperature and hence the nitride particles grow in size causing an increasing in hardness. These particle, however, could not grow beyond a certain critical value and thus

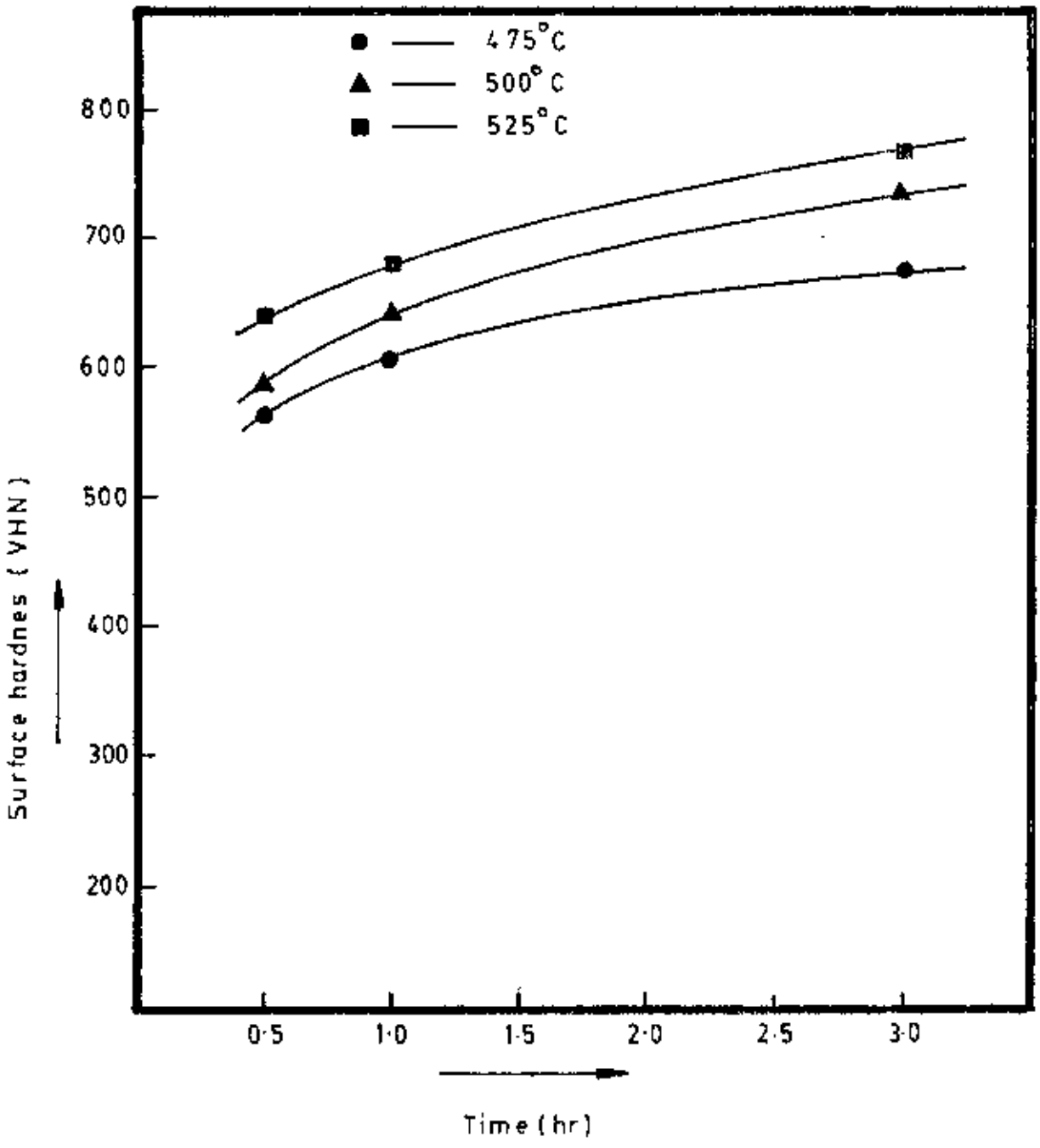


FIG. 4·8 VARIATION IN SURFACE HARDNESS WITH TREATMENT TIME AND TEMPERATURE FOR THE STEEL-CS-1 [ION NITRIDED, 75 H_2 : 25 N_2 ; 7·25 TORR]

the hardness values showed a continuously increasing trend. Fig. 4.9 shows the variation in surface hardness with treatment time at various temperatures for the steel CS-2.

In this case also the hardness values increased continuously. Fig. 4.10 and Fig. 4.11 show comparison of the surface hardness values for the two steels. It can be seen that under identical treatment conditions, higher surface hardness is obtained on the steel containing higher amount of carbon. It is to be noted that steel CS-2 contains 0.53% carbon while CS-1 contains 0.45% carbon. The higher hardness at the surface is related to the thicker layer of the compound layer formed on the steel containing higher amount of carbon.

4.4. Hardness Versus Penetration Distance

Fig. 4.12 to Fig. 4.14 show the variation in the hardness versus penetration distance profiles with the treatment time for the steel CS-1. Each of these figures corresponds to a particular temperature and contain profiles for different treatment times as specified. Fig. 4.15 to Fig. 4.17 show variation in the harness versus distance profiles with treatment temperature at constant time.

From these figures it can be observed that the 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 nitriding time. Fig. 4.18 shows the variation in case-depth with time and temperature of treat-

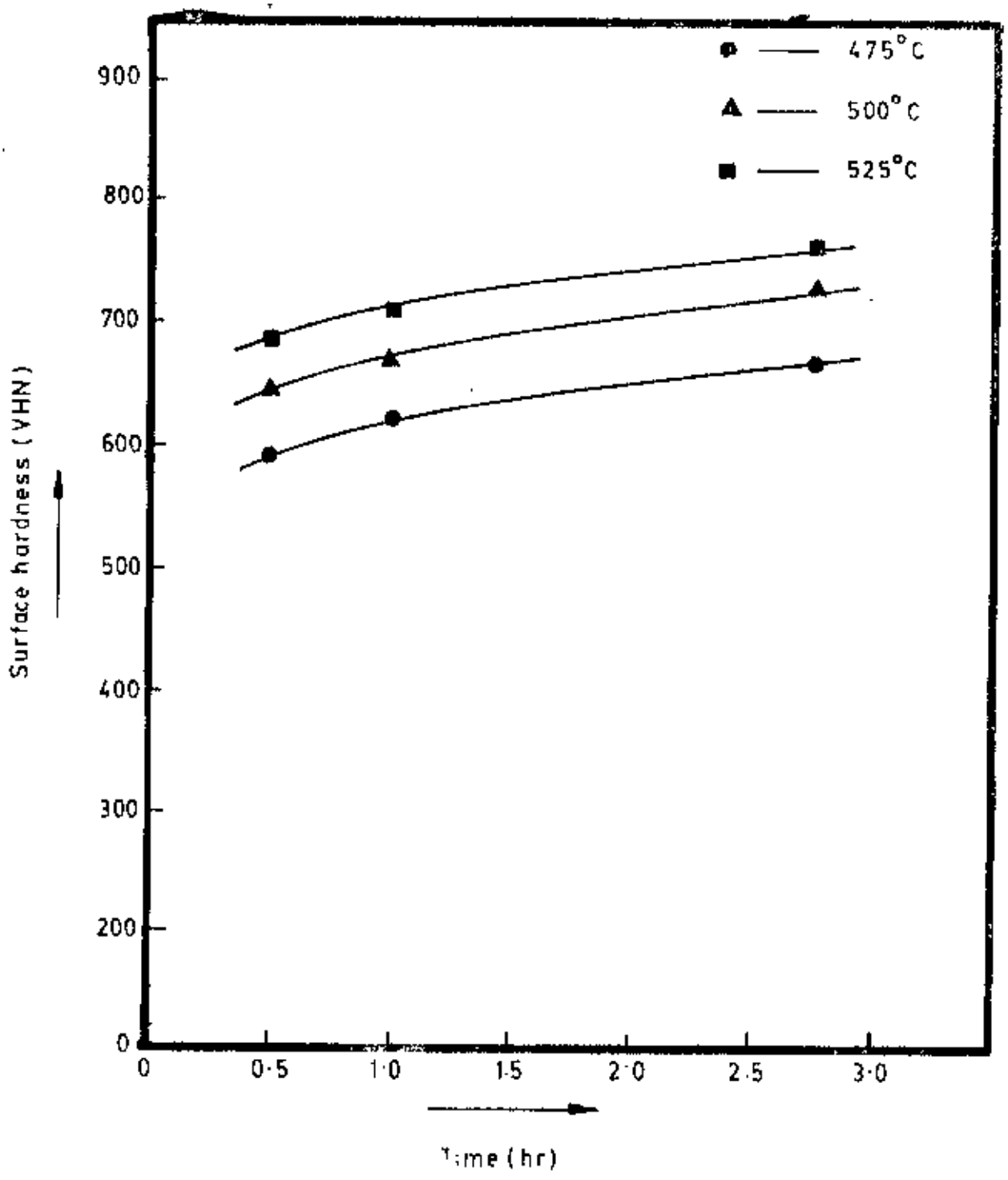


FIG. 4·9 VARIATION IN SURFACE HARDNESS WITH TREATMENT TIME AND TEMPERATURE FOR THE STEEL CS-2 [ION NITRIDED, 75 H_2 : 25 N_2 ; 7·25 TORR]

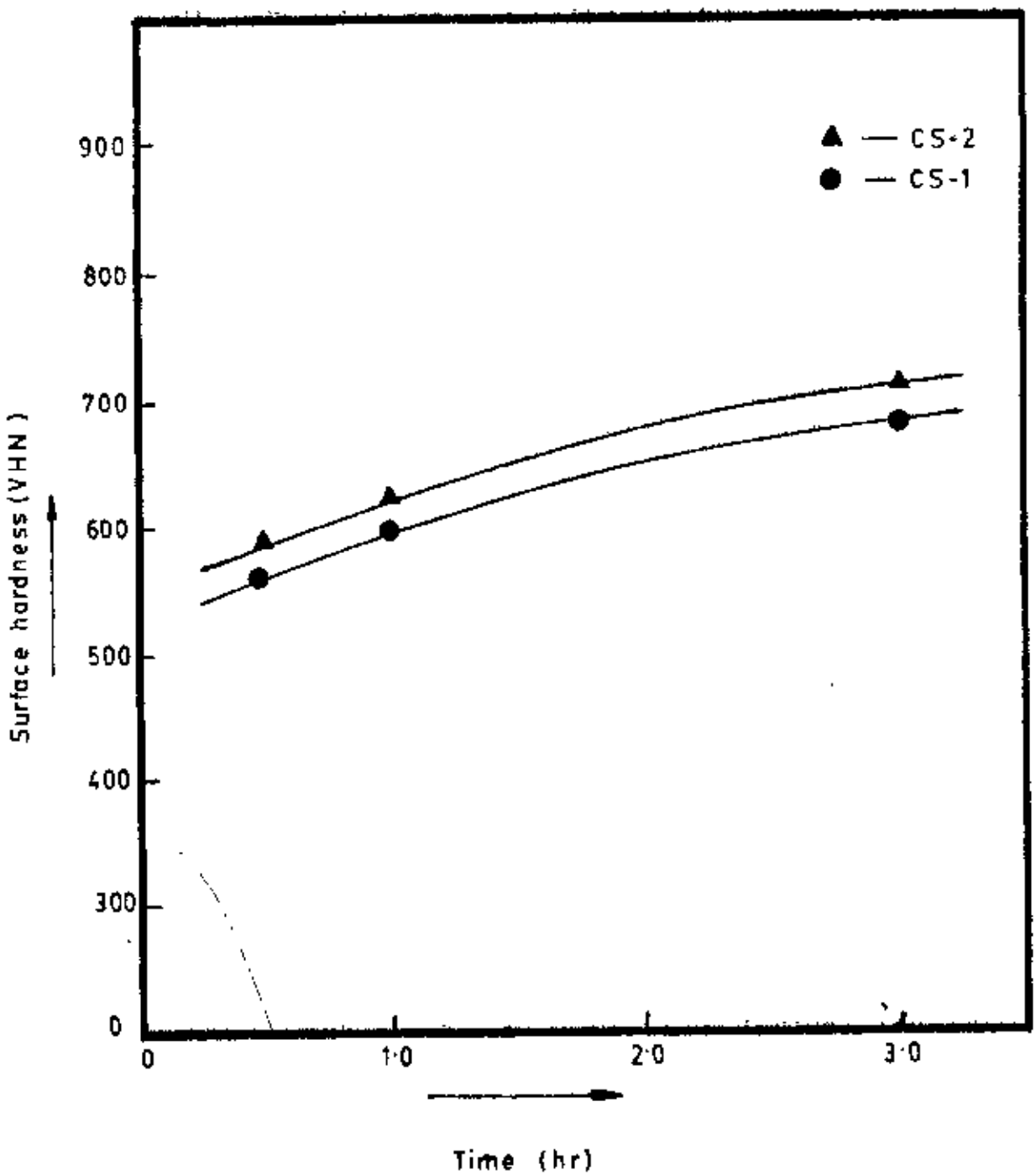


FIG. 4·10 COMPARISON OF SURFACE HARDNESS OF THE TWO STEELS [ION NITRIDED AT 475°C, 75 H_2 : 25 N_2 ; 7·25 TORR]

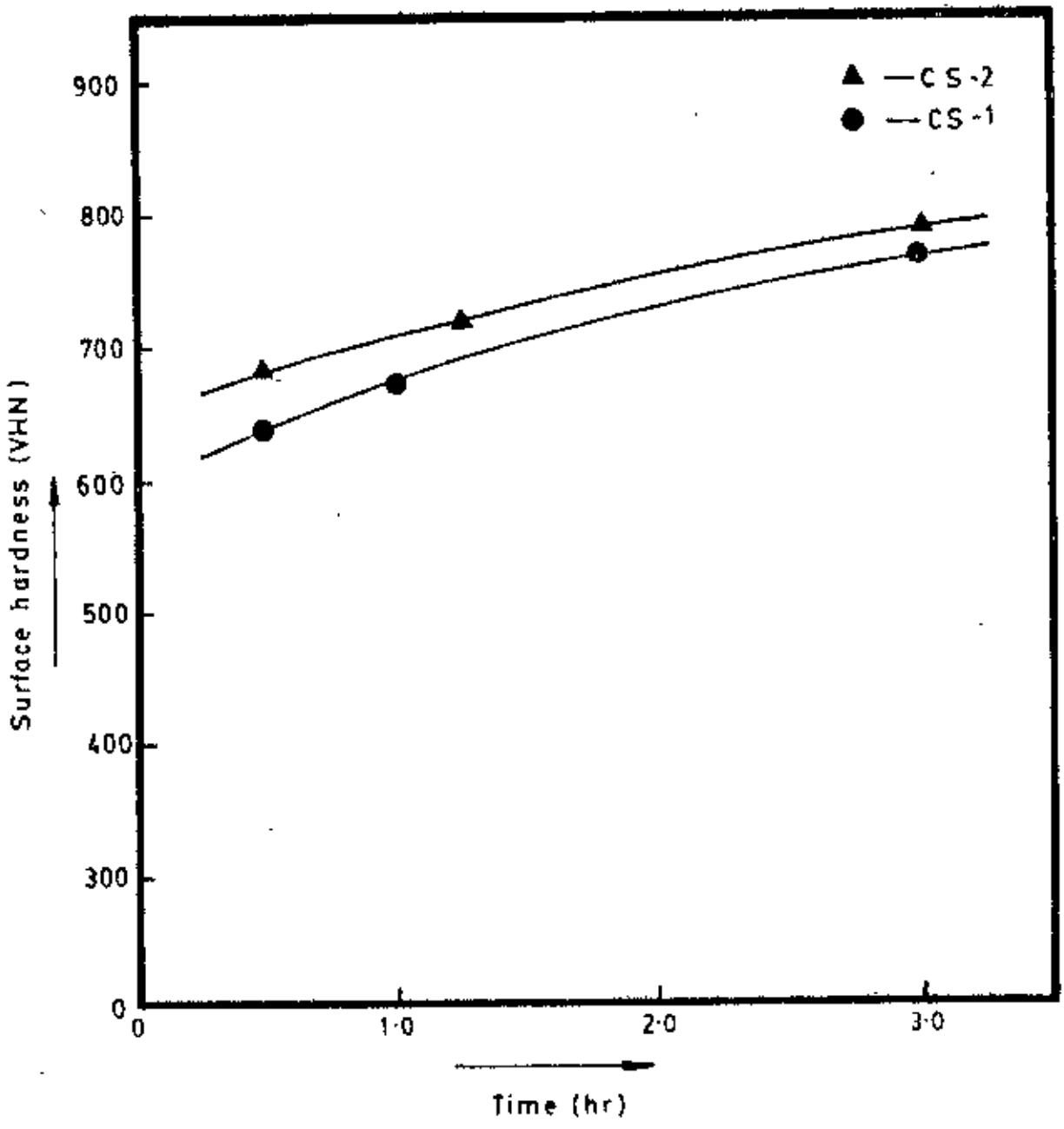


FIG. 4.11 COMPARISON OF SURFACE HARDNESS OF THE TWO STEELS [ION NITRIDED, 525°C, $75H_2 : 25N_2$; 7·25 TORR]

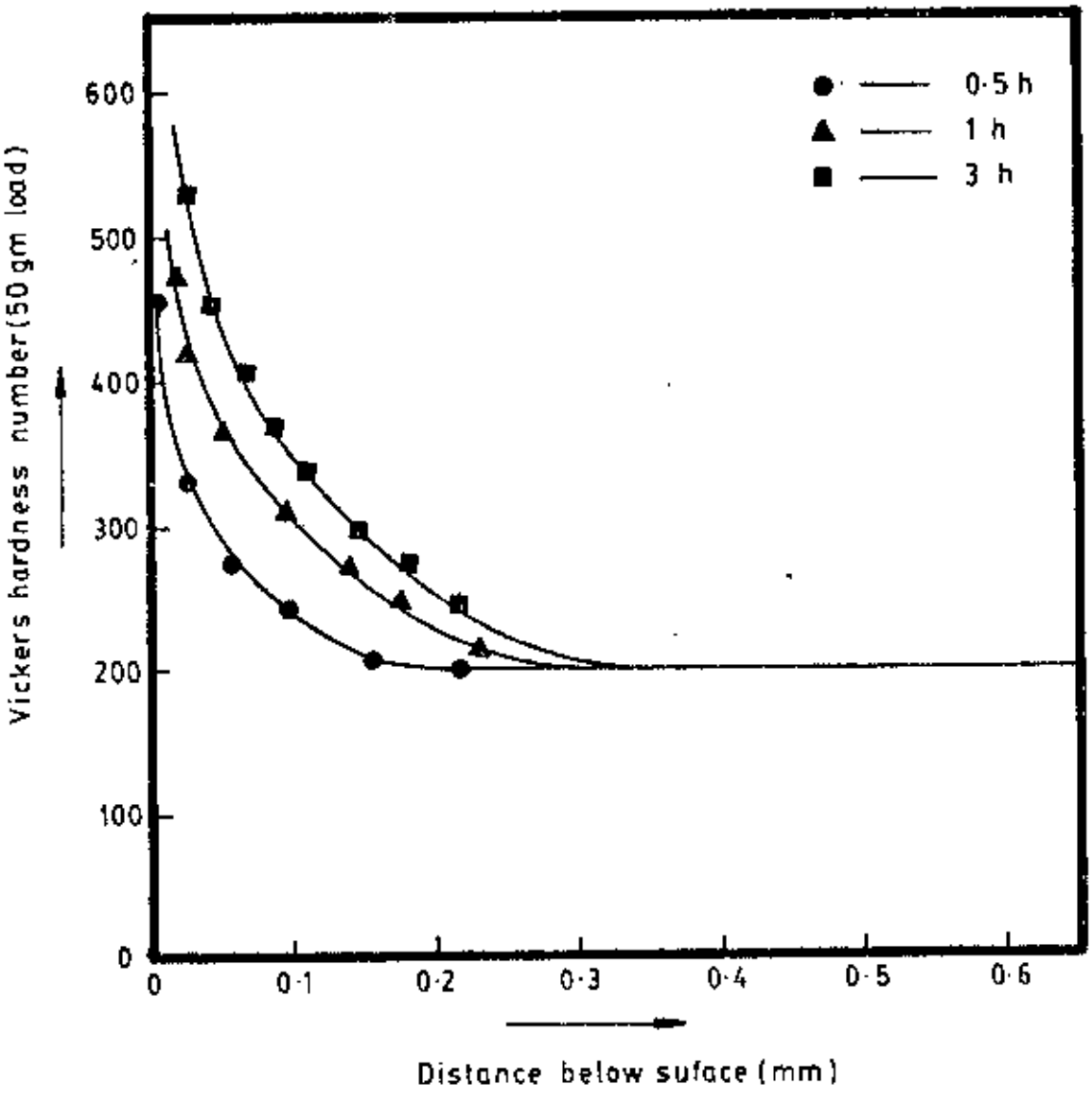


FIG. 4·12 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME AT 475°C FOR THE STEEL CS-1 [ION NITRIDED , $75H_2 : 25N_2$; 7 25 TORR]

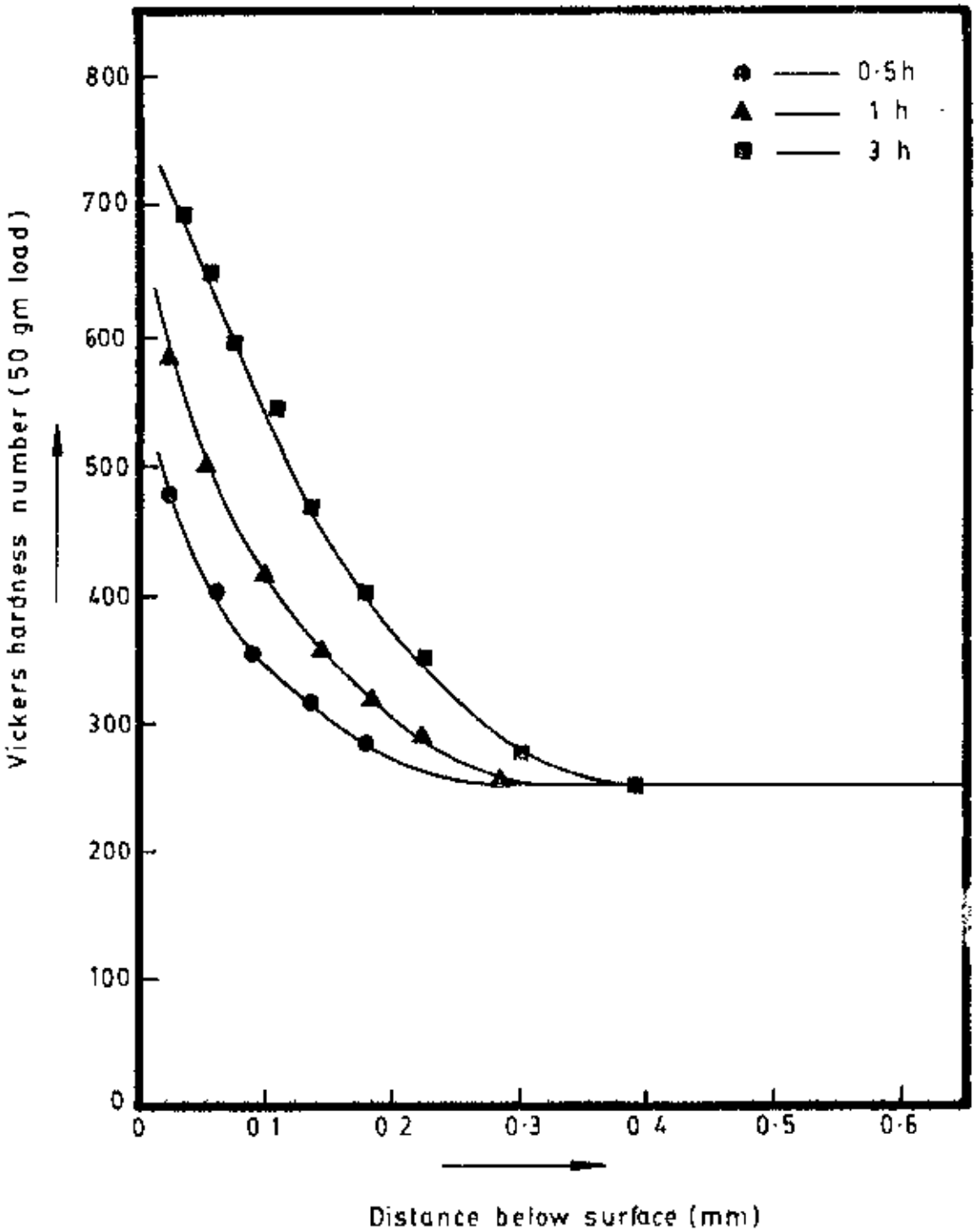


FIG. 4·13 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME AT 500°C FOR THE STEEL CS-1 [ION NITRIDED, $75H_2 : 25N_2$; 7·25 TORR]

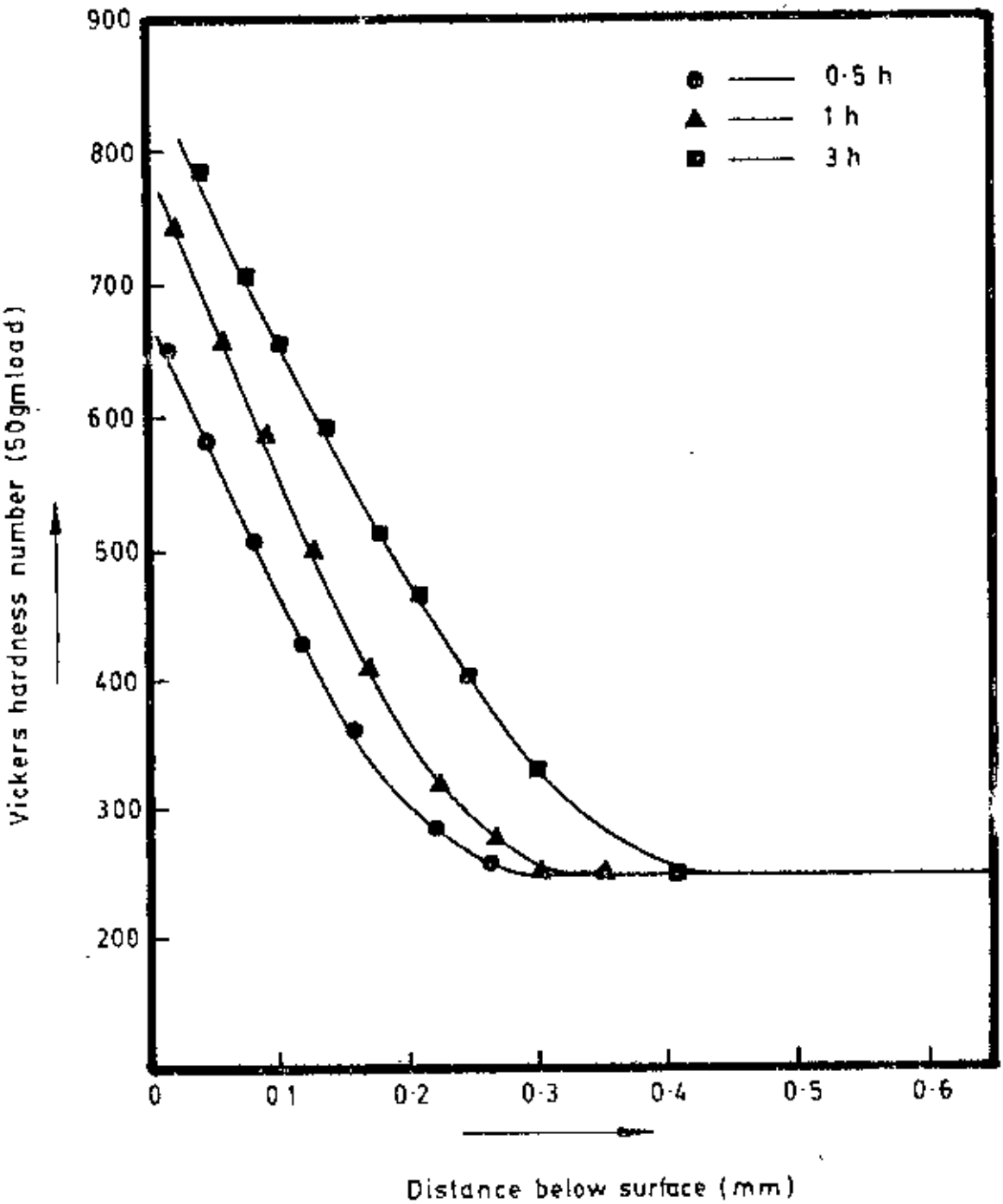


FIG. 4 14 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME AT 525°C FOR THE STEEL CS - 1 [ION NITRIDED, 75 H_2 : 25 N_2 ; 7·25 TORR]

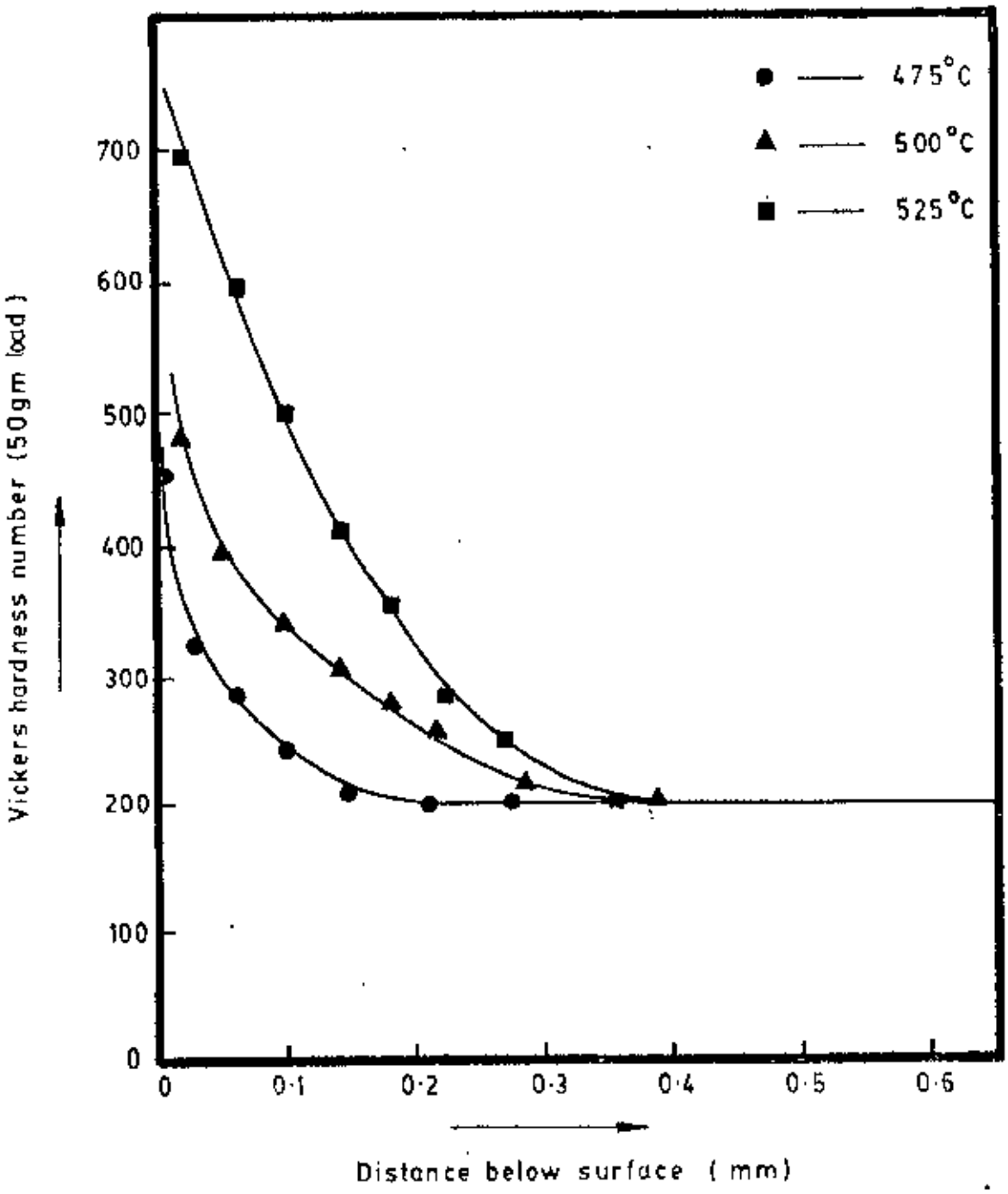


FIG. 4·15 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURE FOR THE STEEL CS-1 [ION NITRIDED FOR 0·5 HR, 75 H_2. 25 N_2 ; 7·25 TORR]

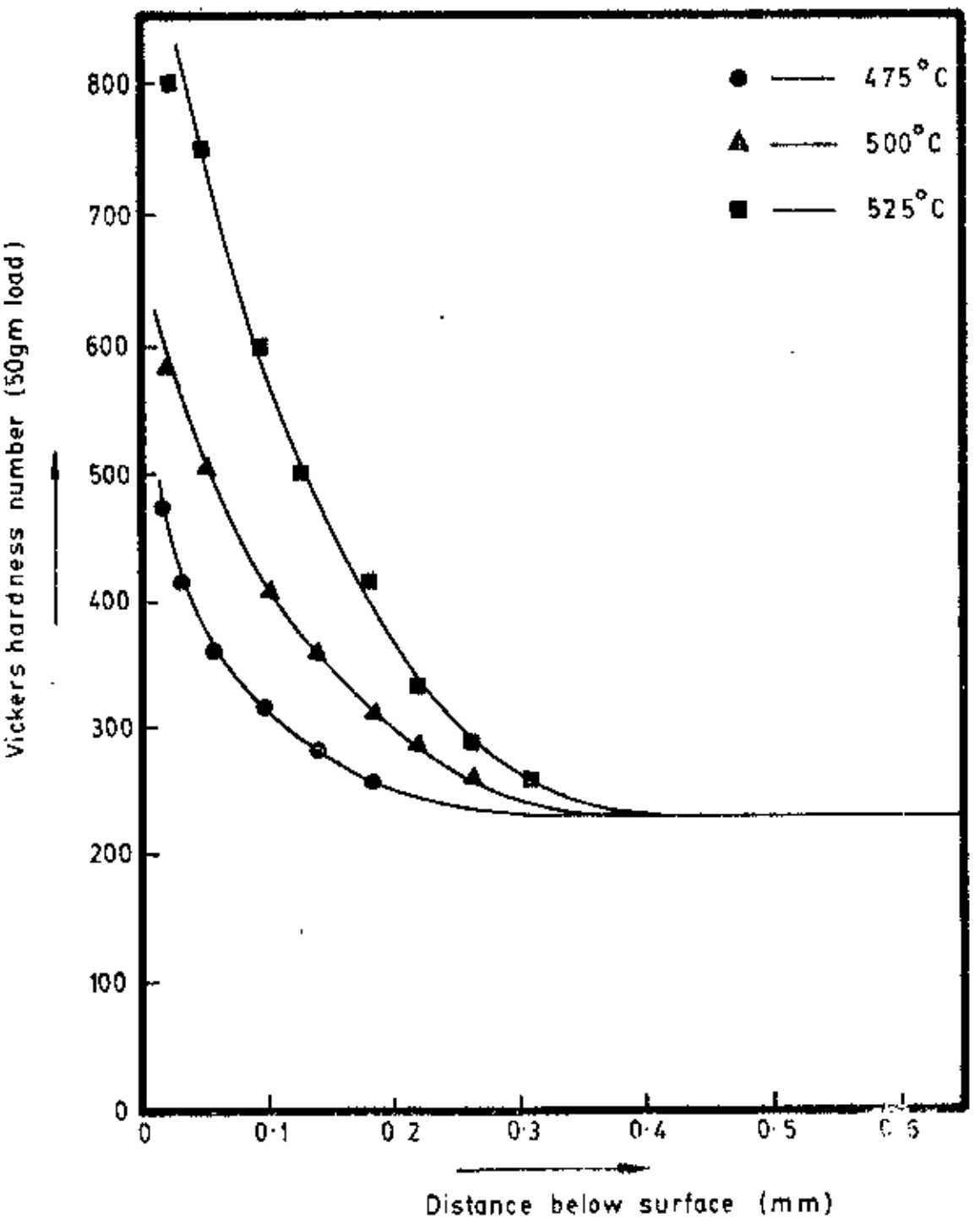


FIG. 4·16 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURE FOR THE STEEL CS-1 [ION NITRIDED FOR 1·0 HR, 75 H_2: 25 N_2; 7·25 TORR]

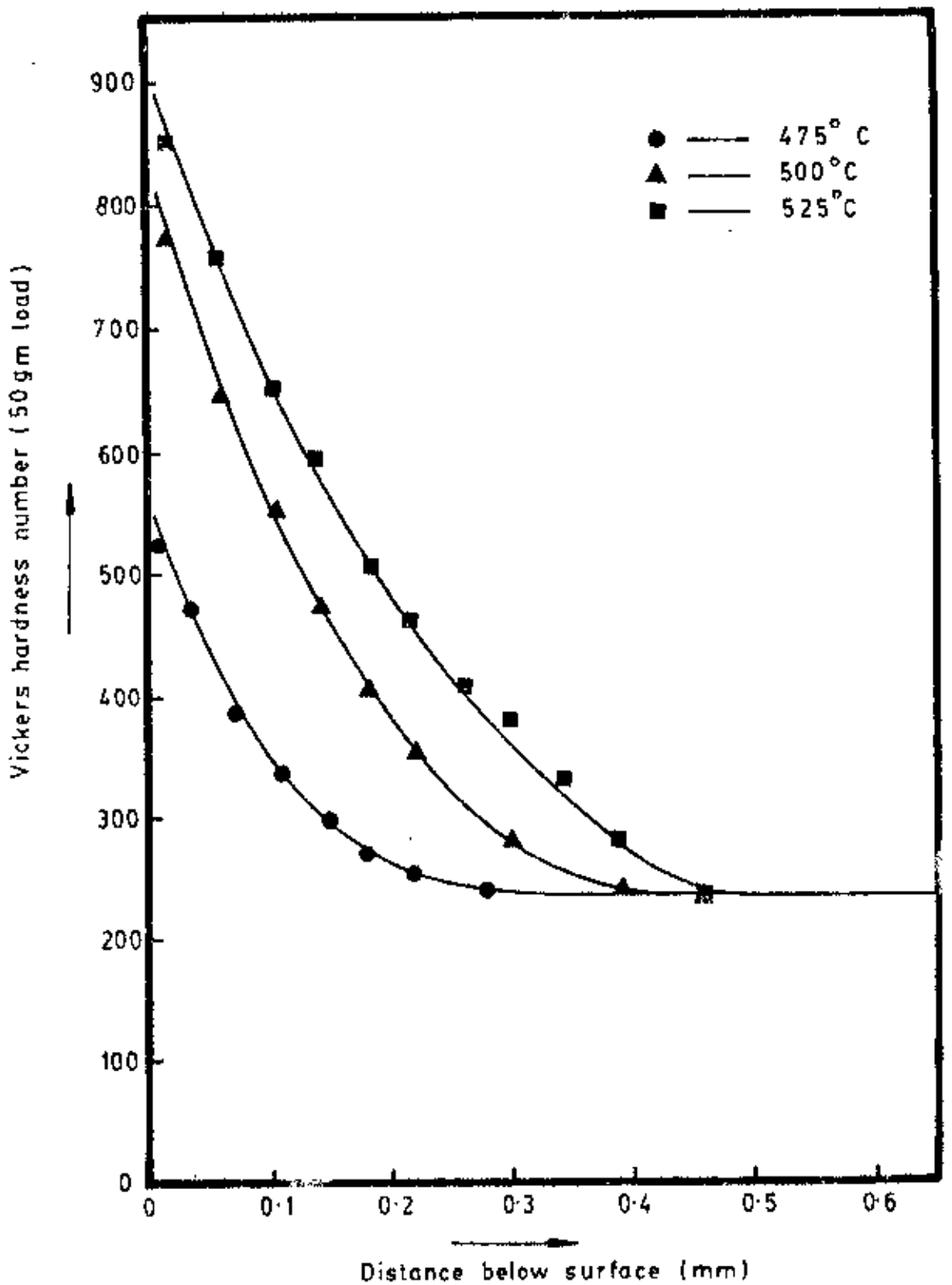


FIG. 4.17 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURE FOR THE STEEL CS-1 [ION-NITRIDED FOR 3 HRS. 75 H_2:25 N_2; 7·25 TORR]

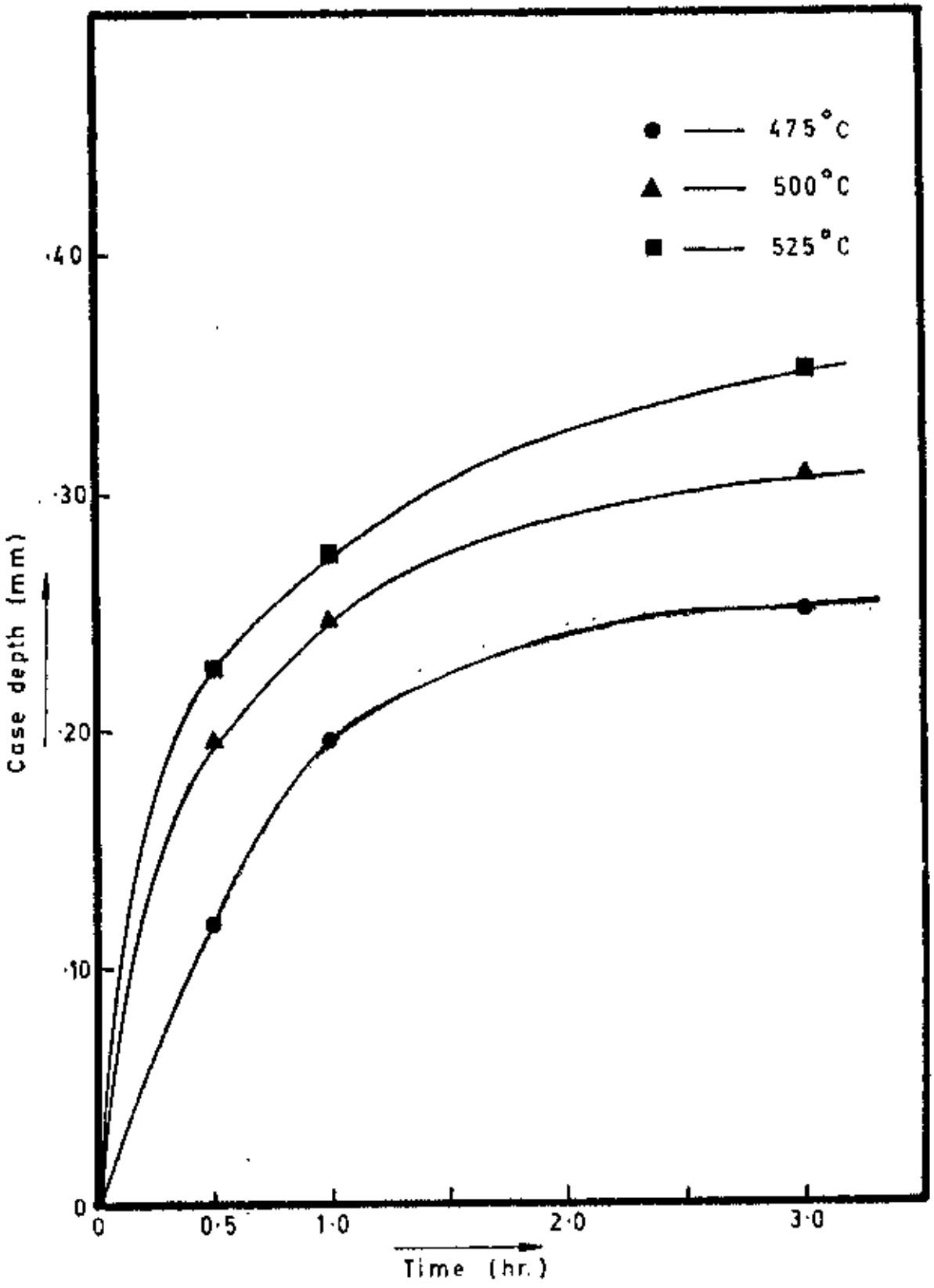


FIG. 4·18 VARIATION OF CASE DEPTH WITH TIMES AND TREATMENT TEMPERATURE FOR THE STEEL CS-1 [ION-NITRIDED, 75 H_2 : 25 N_2 ; 7·25 TORR]

ment for the steel CS-1. It can also be noted Fig. 4.12 to Fig. 4.14 that with increasing treatment time at a particular temperature, the hardness curves have a more gradual slope from surface to core. This is because of the decrease in the concentration gradient with increasing nitriding time and also with temperature.

Fig. 4.19 to Fig. 4.21 show the variation in the hardness versus penetration distance profiles with treatment time for the steel CS-2, Fig. 4.22 to Fig. 4.24 show the variation in the hardness versus penetration distance profiles with treatment temperature at constant time.

These figures also show that the case depths increases with time at temperature and also with temperature for a constant nitriding period. This, as already mentioned, is due to decrease in the concentration gradient.

Comparison of the depths of penetration for these two steels are shown in Fig. 4.25 to 4.27 . It can be seen that under identical treatment conditions the depth of penetration of nitrogen in the CS-1 is more as compared to the depth of penetration of nitrogen in the steel CS-2. Steel CS-1 contains less carbon (0.45%) than the CS-2 steel, which means that an increase in the carbon content in the steel causes a decrease in the depth of nitrogen penetration.

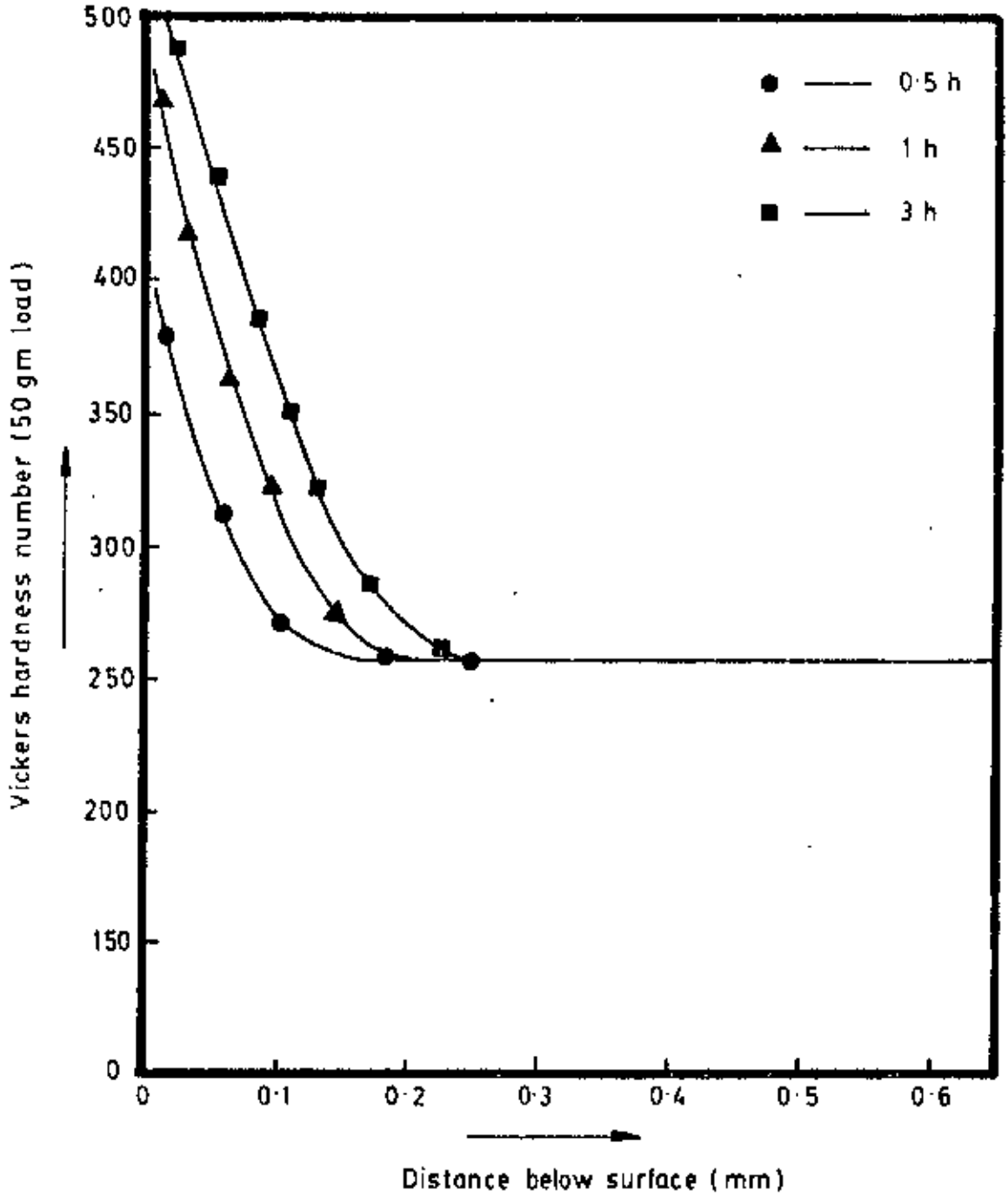


FIG. 4·19 VARIATION IN THE HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME AT TEMPERATURE 475 °C FOR THE STEEL CS-2 [ION NITRIDED, $75H_2 : 25N_2$; 7·25 TORR]

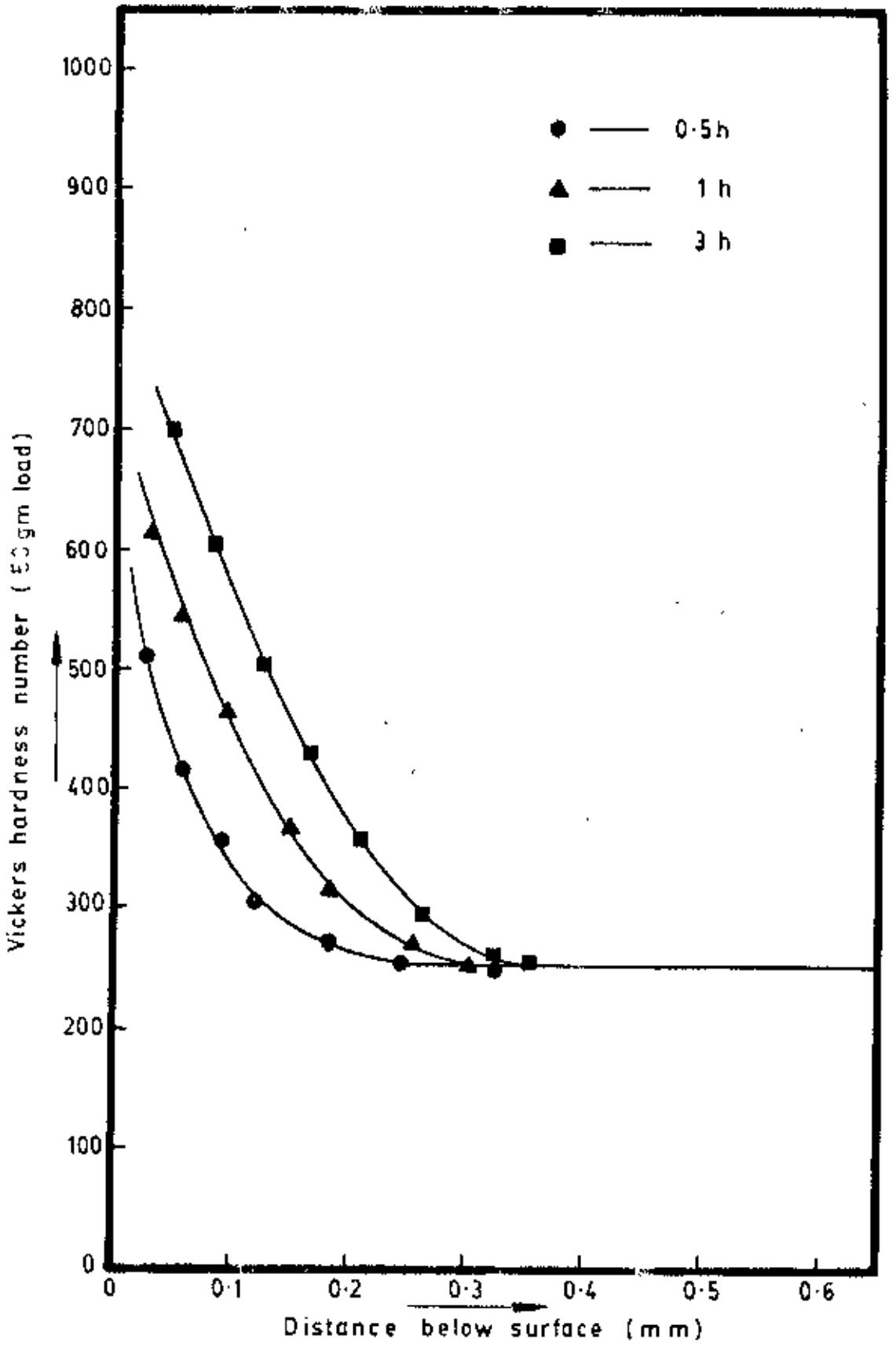


FIG. 4·20 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TIME AT 500°C FOR THE STEEL CS-2 [ION-NITRIDED, $75H_2 : 25N_2$; 7 25 TORR]

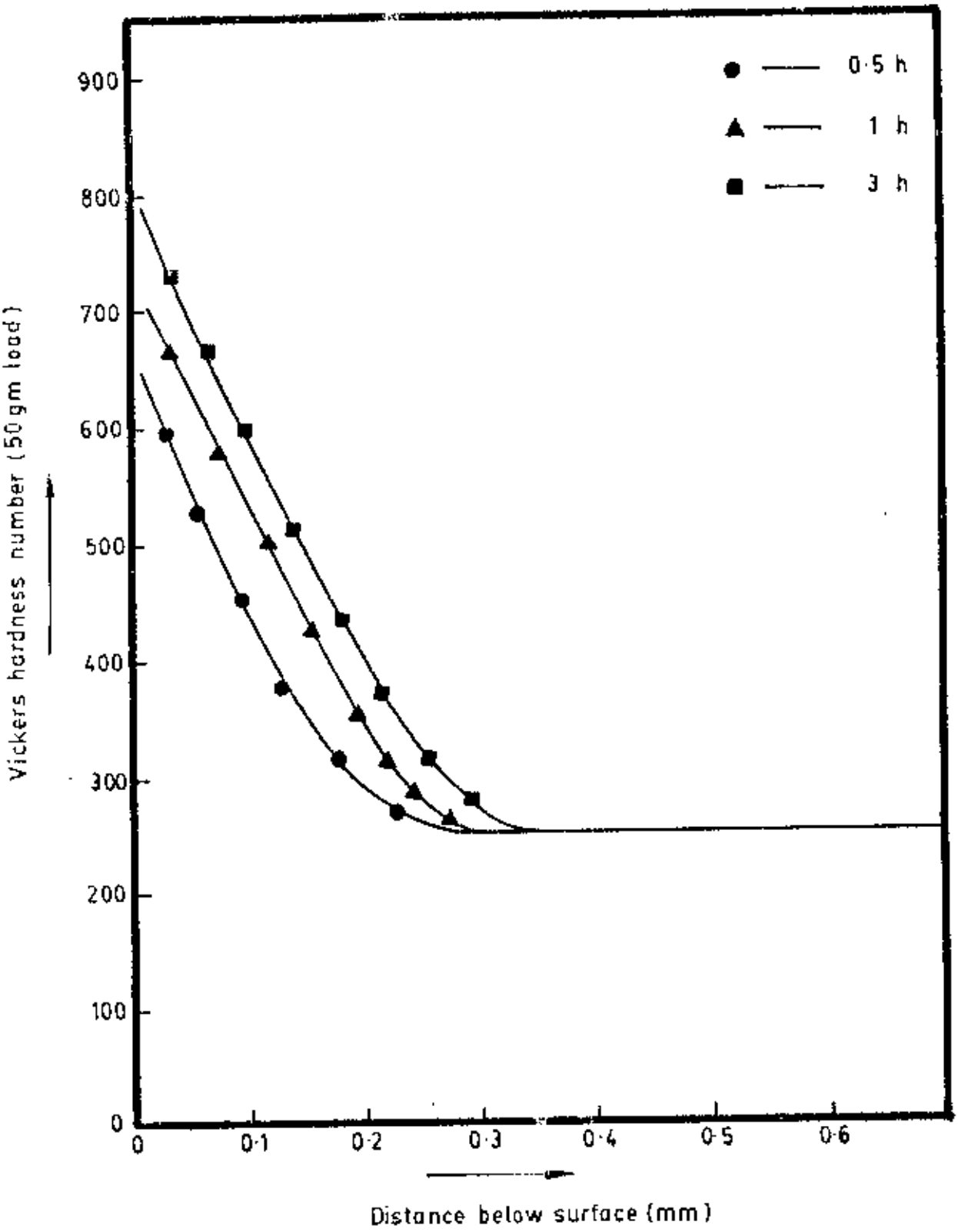


FIG. 4·21 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATM. .T TIME AT TEMPERATURE 525°C FOR THE STEEL CS-2 [ION NIT.. .ED, 75 H_2 : 25 N_2 ; 7·25 TORR]

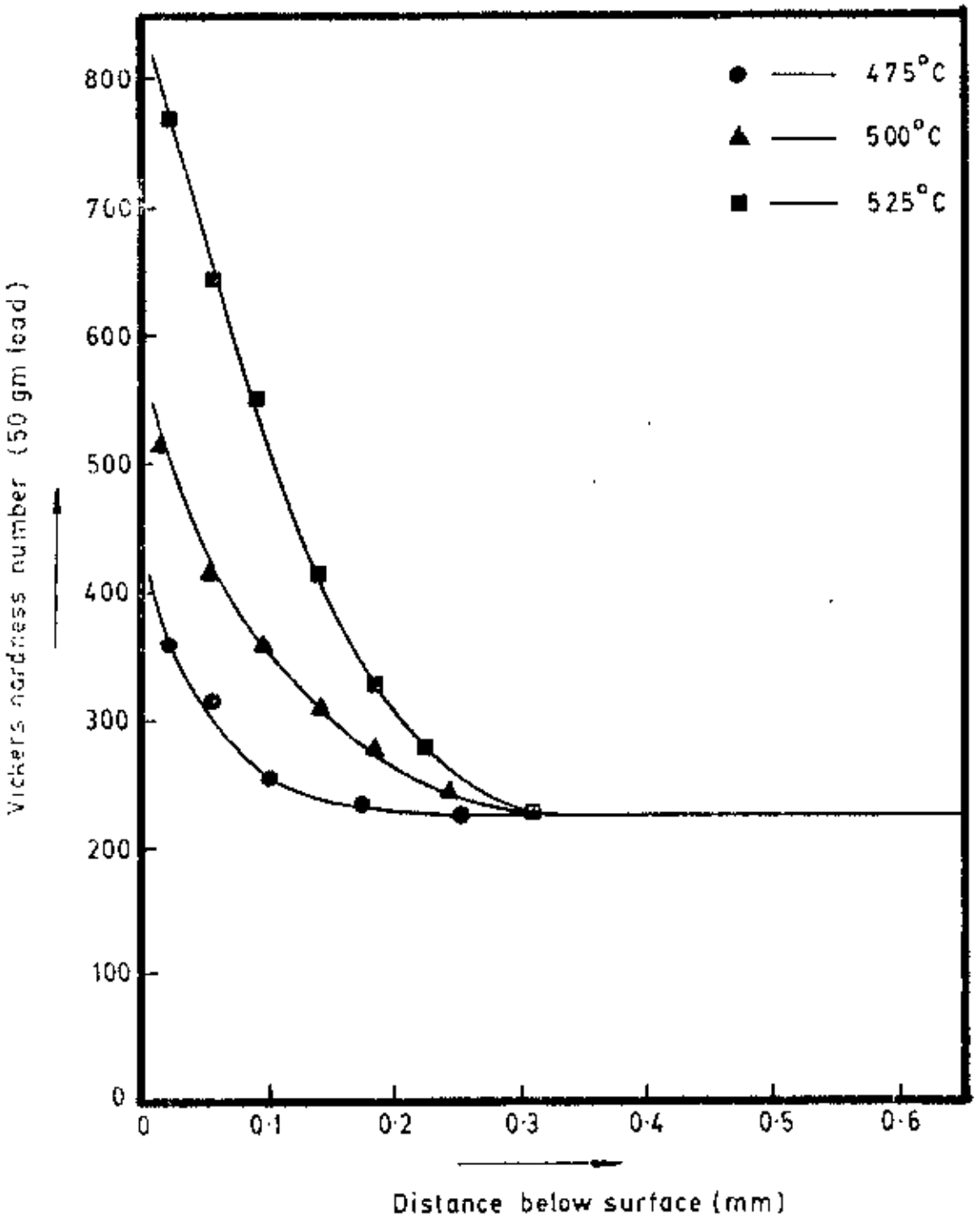


FIG. 4·22 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURE FOR THE STEEL CS-2 [ION NITRIDED, FOR 0·5 HR, $75H_2 : 25N_2$; 7·25 TORR]

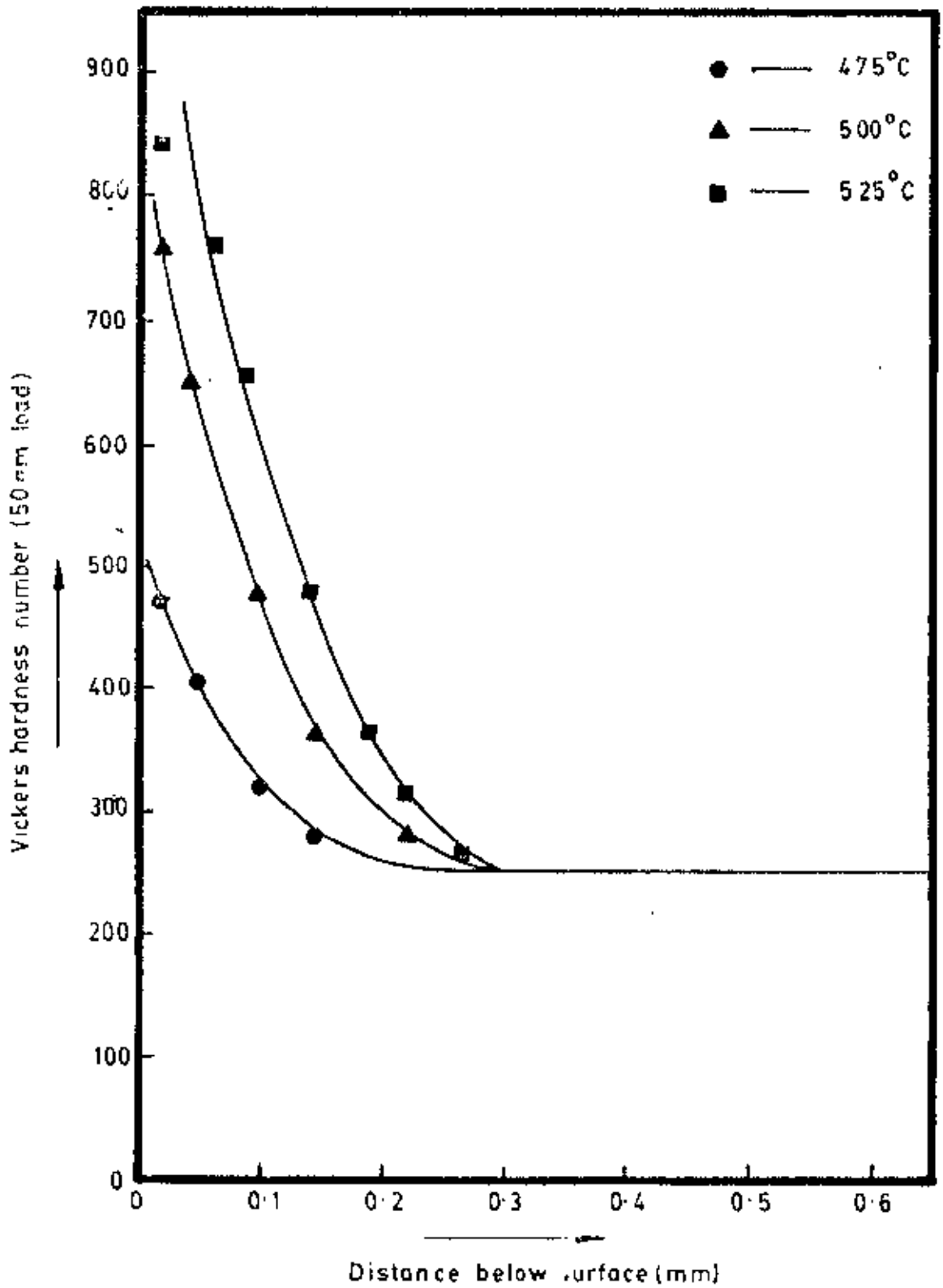


FIG. 4·23 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURE FOR THE STEEL CS-2 [ION NITRIDED FOR 1 HR, 75 H_2 : 25 N_2 ; 7·25 TORR]

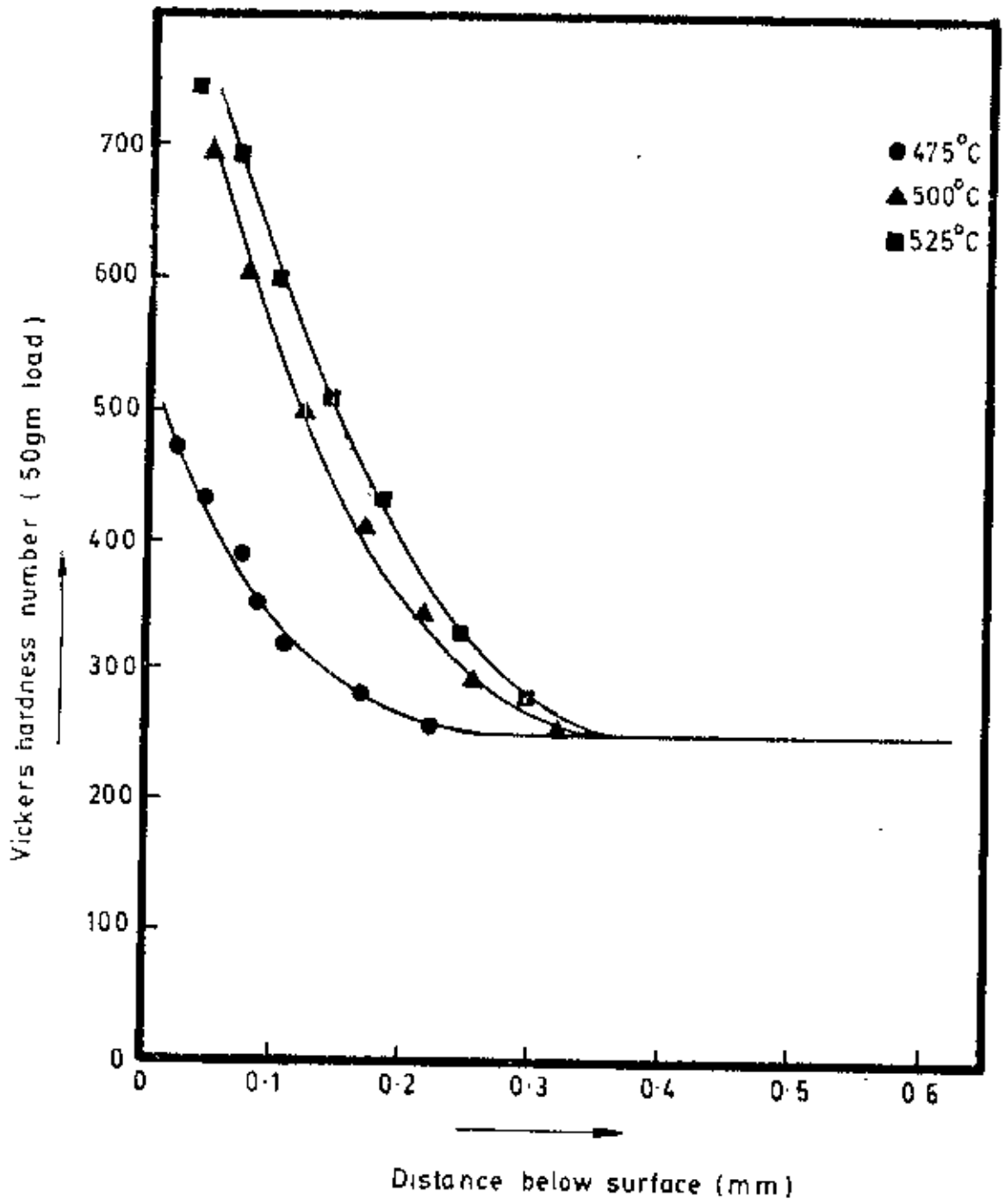


FIG. 4·24 VARIATION IN HARDNESS VERSUS PENETRATION DISTANCE PROFILES WITH TREATMENT TEMPERATURE FOR THE STEEL CS-2 [ION NITRIDED FOR 3·0 HRS, 75 H_2:25 N_2; 7·25 TORR]

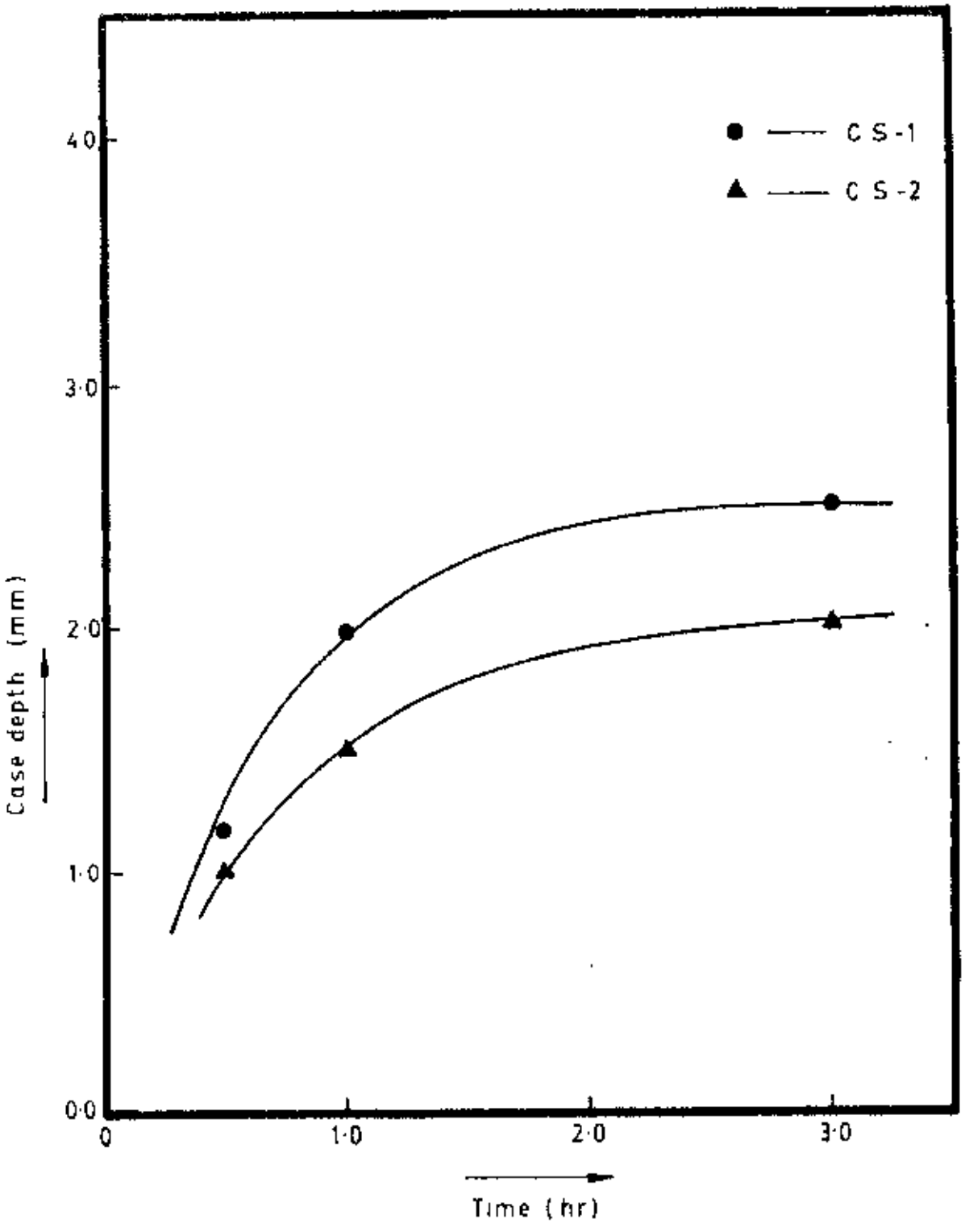


FIG. 4·25 COMPARISON OF CASE DEPTHS FOR THE STEELS CS-1 AND CS-2 [ION NITRIDED AT 475°C, 75 H_2 : 25 N_2; 7·25 TORR]

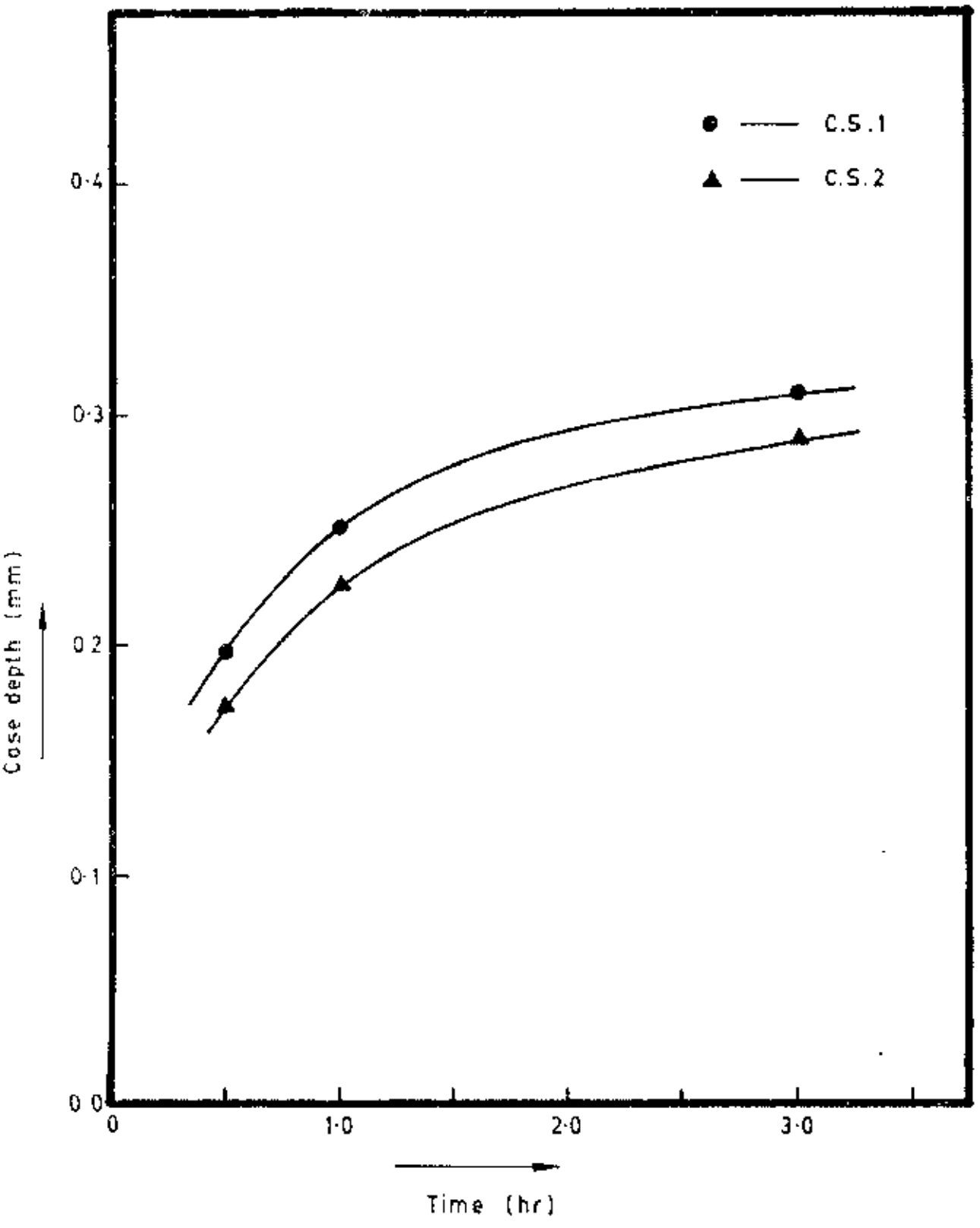


FIG. 4·26 COMPARISON OF CASE DEPTHS FOR THE STEELS CS-1 AND CS-2 (ION NITRIDED AT 500°C; 75 H_2 : 25 N_2; 7·25 TORR)

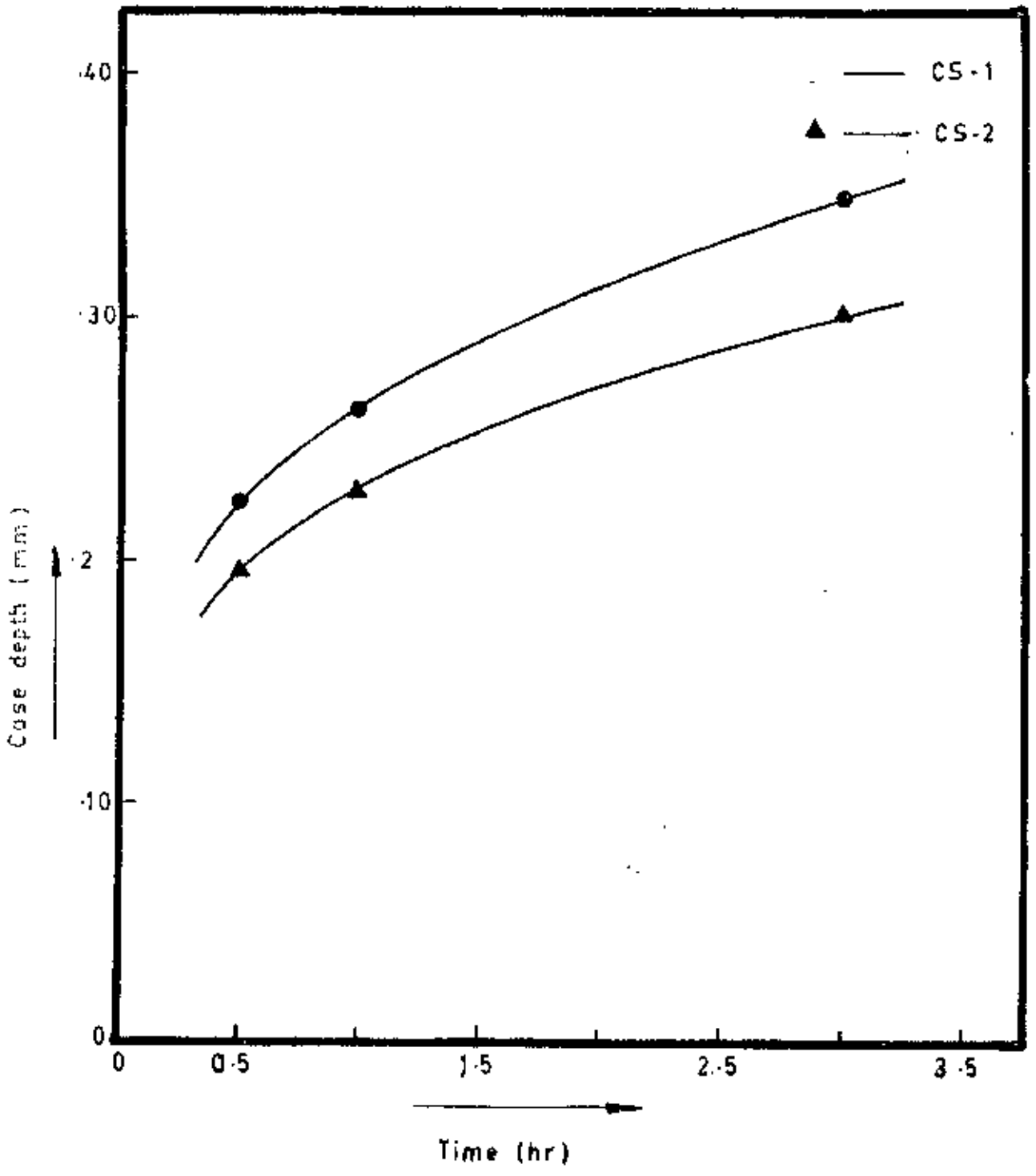


FIG. 4·27 COMPARISON OF CASE DEPTHS FOR THE STEELS CS-1 AND CS-2 [ION NITRIDED AT 525°C, 75 H_2 : 25 N_2; 7·25 TORR]

The results presented above can be summarised as follows:

i) The thickness of compound layer increases with increasing content of carbon.

ii) Case depths (depth of penetration) decreases with increasing carbon content and

iii) A higher hardness at the surface layers is obtained for the steel containing a higher amount of carbon.

These studies were performed under identical conditions leading to the generation and maintenance of identical nitrogen concentration at the surface of the specimen. It is therefore evident that carbon in the steels resists the penetration of nitrogen into the steels. This causes a higher concentration of nitrogen at or near the surface of the steels and leads to the formation of thicker compound layer.

Edenhofer [14] observed carbonitride precipitation along grain boundaries in steels. The precipitation of carbonitrides along the grain boundaries retard grain boundary diffusion of nitrogen thus causing a higher concentration in areas near the surface.

In the steels containing lower amount of carbon, the amount of carbonitride precipitation along the grain boundaries is less and there is less resistance to the grain boundary diffusion of nitrogen deeper into the steel. Deeper penetration of nitrogen into the steel leads to a lower concentration of nitrogen.

The compound layer is composed of two nitrides, Fe_3N and Fe_4N containing about 11 pct and 6 pct nitrogen (by weight) respectively. Thus a higher concentration of nitrogen at or near the surface layers leads to the formation of a thicker compound layer.This is perhaps the reason for the formation of a thicker compound layer on steels containing a higher amount of carbon. Lower concentration of nitrogen resulting from the deeper penetration of nitrogen, on the other hand, cannot lead to the formation of compound layer and a thinner layer is obtained on low carbon steels.

The nitrides are very hard particles and therefore the formation of a thicker compound layer leads to a higher hardness at the surface.

4.5 Results Obtained on Pure Iron

A thin nitride layer formed on the ion-nitrided pure iron specimens. Surface hardness measurements (Fig. 4.28) showed only a marginal increase in hardness. This is because the layer formed on pure iron was very thin and the soft matrix below could not support the load used to cause the indentations. A thicker compound layer at higher temperatures led to a slight increase in surface hardness values. No further processing of these data could therefore be made. Hardness-penetration distance profiles

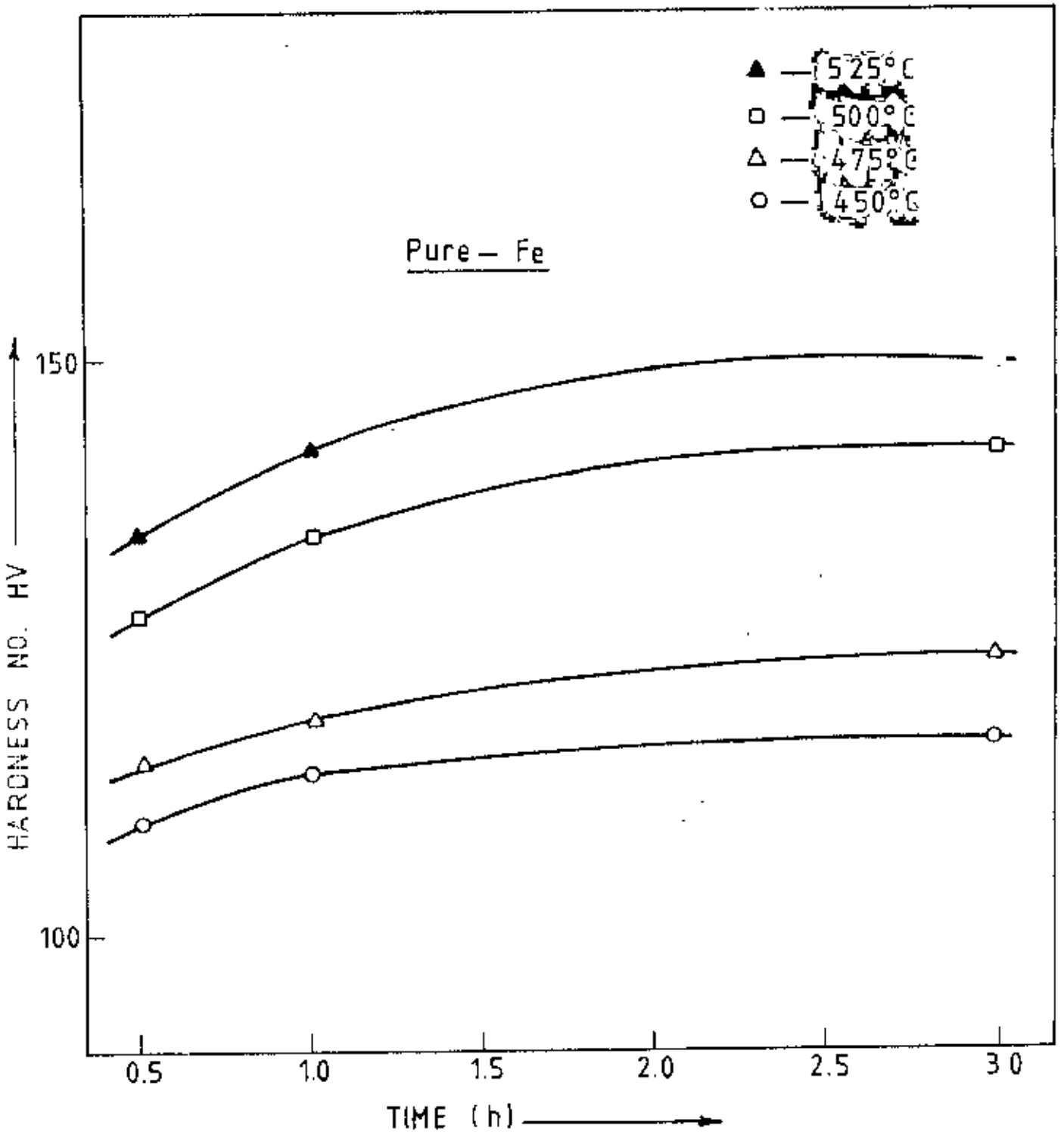


Fig. 4-28 Variation in surface hardness with treatment time at temperature.

also could not be determined as the increase in hardness was very small. However, optical micrographs Fig. 4.1(b) show that nitrogen penetrated deep into the specimen and during cooling nitrides precipitation took place even at considerable depths. This is logical, because in the absence of carbon, the grain boundary diffusion took place readily and led to deep penetration of nitrogen.

Chapter-5

SUMMARY AND CONCLUSIONS

5.1 Summary

The effect of carbon on the nature of the layers formed during ion-nitriding has been investigated under identical treatment conditions. Plain carbon steels of two different carbon levels were chosen for this study. Except for carbon all other alloy contents were identical in these two steels. Pure iron specimens were also ion-nitrided so as to be able to compare the results obtained.

A laboratory model ion-nitriding unit, designed and fabricated at the Department of Metallurgical Engineering at BUET, Dhaka has been used in this study. Ion-nitriding was performed for different times at specified temperatures. The effects were investigated by optical metallography and microhardness measurements on the surface and also across the transverse section of the nitrided specimens.

Optical metallographic studies have shown that the thickness of the compound layer increases with time at temperature and also with temperature for a specified time of treatment. The steel containing a higher amount of carbon has been found to give a thicker compound layer as compare to steels containing lower amount of carbon. It has been concluded that the thickness of the compound layer is directly proportional to the carbon content in the steel.

Hardness versus penetration distance profiles have shown that the depth of nitrogen penetration is higher in the steel containing a lower amount of carbon.

A higher hardness has been obtained on the surface of the steel containing a higher amount of carbon. This has been attributed to the greater thickness of the compound layer together with a lower depth of penetration leading to a higher concentration of nitrogen at and near the surface of the steel containing a higher amount of carbon. In good agreement with other investigations, nitride-needles could be clearly observed on the ion-nitrided pure iron specimens whereas these needles could not be observed on the steels.

Marginal increase in hardness values in pure iron rendered its further processing difficult. However, nitride needles detected at considerable depths led to the conclusion that nitrogen penetrates deep into pure iron.

5.2 Conclusions

From this study on the effects of carbon on the nature of the layers formed during ion-nitriding it can be concluded that

a) the thickness of the compound layer increases with increasing carbon content in steel,

b) case-depths decreases with increasing carbon content.

iii) A higher hardness at the surface layers is obtained for the steel containing a higher amount of carbon.

iv) Nitride-needles do not form in the steels under the conditions investigated.

5.3 Suggestion for Future Work

1. Effects of carbon in treatment gas on the nature of the layers formed on steels should be an interesting topic for investigation. Pure iron and a steel specimen could be nitrided in a treatment gas mixture containing various amounts of carbon. The analysis of the results obtained should clearly specify the role of carbon in the treatment gas.

2. Grain boundaries, being the more likely paths for diffusion, might have some effect on the extent of penetration of nitrogen. Experiments with these steels, heat treated to have similar grain size would determine the effect of grain size.

REFERENCES

1. Fry, A., JISI, 125 (1932) 191.

2. Berghaus, B., German Patent DRP 668.639 (1932).

3. Berghaus, B., US Patent 3 018 409 (1956).

4. Edenhofer, B., Metals Australia, 9 (1974) 247-250.

5. Edenhofer, B., Hart. Tech. Mitt., 26 (1973) 165-172 .

6. Hudis, M., J. Appl. Phys., 44 (1973) 1489-1496.

7. Tibbetts, G.G., J. Appl. Phys., 45 (1974) 5072-5073.

8. Seybolt, A.U., Trans. Metall. Soc. AIME, 245 (1969) 769-778.

9. Takase, T., J. Japan Met. Mater 17 (1975) 19-25.

10. Butenko, O.I., Met. Sci. Heat. Treat., 10 (1969) 687-690.

11. Mullins, P.J., Iron-Age Metal work. Int., 6 (1974) 30-31.

12. Bewley, T.J., Metallurgia and Metal Forming, 41 (1974) 227-229.

13. Koller, K., Hart. Tech. Mitt., 26 (1971) 125.

14. Edenhofer, B., Heat Treat. Met., 2 (1974) 60.

15. Kurny, A.S.W., Ph.D. Thesis, Indian Institute of Science, Bangalore, (1981).

16. Cho, K.S. and Lee, C.O., J. Engg. Mat. & Tech. 102 (1980) 229-233.

17. Kurny, A.S.W., J. Inst. of Engineers, Bangladesh, Vol. 14, No. 3, July 1986.

18. Soccorsy, W.D., and Ebihara, W.T., Technical Report RE 70-156, US Army Weapons Command, June 1970

19. Jones, C.K., and Martins, S.W., Met. Prog. 85 (1964) 94-98.

20. Akhantev, V.P., Ivlev, V.I., and Kurbatov, V.P., Met. Sci. Heat. Treat., 1 (1977) 14.

21. Kurny, A.S.W., to be published.

22. Phillips, V.A., and Seybolt, A.U., Trans. Metall. Soc. AIME, 242 (1968) 2421.

23. Taylor, Al, Met. Prog., 117(1980) 142.

LIST OF FIGURES

LIST OF TABLES