The Effect of Heat Treatment Atmosphere on Hardening of Surface Region of H13 Tool Steel

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Abstract

The cost of an aluminium extrusion die accounts for 35-50% of the total extrusion cost, hence it is important to understand the kinetics of extrusion die heat treatment. The main objective of die heat treatment is to increase the surface hardness so the surface wear property can be enhanced, which extends the die service life. Before the die material is case hardened by processes such as nitriding, the material is first heat treated to certain hardness. Thus the aim of this investigation is to understand the kinetics of carbon diffusion during steel austenitzation because it is significant to steel hardness property.

H13 hot work tool steel, a well known material used as a die material for its superior mechanical and hardening properties, was used for the analysis of carbon diffusion during austenization. Samples made of H13 steel were subjected to four different atmospheric conditions: heat treatment without atmospheric control, heat treatment with stainless steel foil wrapping, pack carburization heat treatment and vacuum heat treatment. Three treatment time ranges were also applied for the carbon diffusion modelling. Some samples were further treated by gas nitriding to establish the effect of carbon content on the gas nitriding performance.

It was found that decarburization occurred when atmospheric control did not take place during the heat treatment process. Through the carbon diffusion analysis, at austenitizing temperature of 1020ºC, the equilibrium surface carbon content at 1020ºC was 0.157wt%, with activation energy of carbon in H13 steel of 20,200cal/mol, and carbon diffusivity at 1020ºC was $1.97 \times 10^{-8} cm^2/s$.

This study also proved that proper stainless steel foil wrapping on the heat treating material could restrict decarburization process, resulting in a constant hardness profile as vacuum heat treatment does. However the tempering characteristic between this two heat treatment methods are different to each other.

For the pack carburization heat treatment, it was noted that the samples suffered from decarburization at early stage of heat treatment as carbon monoxide level was not adequate for carburization process.

Results from the gas nitrided samples showed that the thickness and the hardness of the nitrided layer was independent to the carbon content in H13 steel. After 2 rounds of gas nitriding process, further nitriding seemed to have no significant effect on the hardness and thickness of the nitrided layer. Furthermore, the white layer was not observed in the nitrided samples which were heat treated without atmospheric control.

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Statement of Originality

"I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgment is made in the acknowledgments."

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Chapter 1 Introduction

Heat treatment is a process to alter the metallurgical and mechanical properties for specific purposes that involves heating and cooling of material. Heat treatment has a very long history, and one of the most famous applications would be the forging of the Katana, the Japanese sword. It is also known that such technique was adopted from Chinese and has been used by the Chinese since the Qin Dynasty around 2500 years ago (1).

This process is of interest for many fields of industries because through heat treatment, the mechanical properties of metals can be improved in various ways. In the world of aluminium extrusion industry, heat treatment of steel plays a major role on the determination of process efficiency and product quality. This is because the die, which is made of tool steel, must undergo a series of heat treatment processes to obtain the desired properties. Because an extrusion die covers around 35%-50% of the total manufacturing cost (2), it is essential to obtain thorough understanding on the effectiveness and the kinetics of die heat treatment, so precise process design can be achieved with a good quality control.

Until now, huge amount of research related to heat treatment of steel has been conducted so desired mechanical properties can be achieved with the improvement of heat treatment efficiency. This research project was conducted under the collaboration between Auckland University of Technology (AUT) and Heat Treatment Limited. The purpose of this research is to understand the kinetics of carbon diffusion during heat treatment under different atmospheric conditions, and the influence of carbon content on the effectiveness for the case hardening process, nitriding. Through this, the carbon diffusion at various hardening conditions can be made known. It can also be used to monitor the influence of carbon loss on the hardness profile of case hardened material and eventually improve the process design for die material hardening.

The following gives a brief introduction for each chapter:

- Chapter 1 covers an introduction and background information of the heat treatment hardening process, the theory of hardening process and an insight of mass transfer during austenitizing.

- Chapter 2 is a literature review summarizing previous researches related to the carbon diffusion in steel, microstructure of interest and the gas nitriding process. This chapter further develops the reason behind this investigation and its values.

- Chapter 3 shows the details of the conducted experiments such as materials and equipments, and the setting of the experiments.

- Chapter 4 summarizes all the experimental results in a logical order which will be discussed further on the subsequent chapter.

- Chapter 5 discusses and analyse the available results theoretically.

- Chapter 6 gives the conclusions of this finding and suggests what may be done for the process improvement.

1-1 Heat Treatment Limited

Heat Treatment Limited is a New Zealand company conducts various material heat treatment processes. The company's goal is to provide consistent, reliable and economical service to clients in accordance to their specific requirement. In order to do so, it requires effective quality management system which is able to provide the concept of reliability, quality assurance and continuous improvement.

The company plays an important role in New Zealand heat treating industry by being the first company in New Zealand to offer a full range of hardening such as vacuum heat treatment, controlled atmosphere heat treatment, air hardening, carburizing, carbonitriding and nitriding processes. Availability of many types of heat treatment process is crucial because each specific process has its own heat treatment characteristic which determines the material properties. Heat Treatment Limited also has its own fully equipped and up to date machine shop with an in-house laboratory. Heat Treatment Limited is able to maintain high quality service with professional advice to their clients.

One of the major businesses in Heat Treatment Limited is hardening of extrusion die. To ensure the heat treatment quality is reliable, Heat Treatment Limited introduced vacuum heat treatment for hardening process.

1-2 Die Material

Aluminium extrusion is a process for tube, rod, beam or wire type product by pressing the aluminium through the extrusion die. The process pre-heats the aluminium billet to a temperature around 500°C and the aluminium is pressed across the pre-shaped die at a temperature of 550°C - 620°C. The profile is then cooled to a lower temperature at the exit of the extrusion die. Extrusion is a high flow velocity and high production rate process with significant die temperature gradient on the tool surface under extremely high working pressure (~210MPa). The interaction between the die and surrounding plays a major role in initiation of soldering, micro-cracking, crack propagation and catastrophic failure, especially in high working temperature, which results in premature failure such as heat and gross cracking, erosive wear, solder and corrosion (3). To serve such working environment, the selection of material becomes crucial. The chosen material must be able to withstand high mechanical and thermal loading, and good resistance to wear and failure. Bjork et.al (4) states that the wear resistance of extrusion die plays a major role in terms of technological and economical aspect because it affects both the surface finish and dimension of the extrudate. Tool steel is the material widely used to serve such working environment. The followings would show the dominant properties of tool steel material for such application.

1-2.1 Tool Steel

Tool steel signifies a family of highly alloyed steels that can be hardened and tempered with guaranteed hardening characteristic to provide improved strength and wear resistance (5). The typical differences between tool steel and other carbon/ alloy steels are that tool steel has better hardenability and heat resistance, it is more resistible to thermal softening and contains higher alloying contents with wider range of alloying elements. Frequently additive alloying elements are tungsten, chromium, molybdenum and vanadium. Each alloying element serves a specific function for the improvement of mechanical or thermal properties, and for the improvement of processing efficiency. Six main categories of tool steels are available and they are classified based on their application. The most common methods used for the classification of tool steel are guidelines based on the "Society of Automotive Engineers" (SAE) and "American Iron and Steel Institute" (AISI). The following table shows details for each type of tool steel under AISI method:

Table 1 Characteristic of each Tool Steel Type

Type	AISI
High speed	M (molybdenu T (tungsten ba
Hot work	H1 to H19 (chromium base) ← H13 H20 to H39 (tungsten base) H40 to H59 (molybdenum base)
Cold work	D (high carbon, high chromium) A (medium alloy, air hardening) O (oil hardening)
Shock resisting	S
Mold steels	P1 to P19 (low c P20 to P39 (others)
Special purpose	L (low alloy) F (carbon-tungsten)
Water hardening	W

Among them, H13 steel which is under the category of hot work tool steel is the most widely used material for the construction of aluminium extrusion die.

1-2.2 Hot Work Tool Steel

To serve as die material for extrusion process, hot work tool steel is the best in such working environment. Such type of steel is identified by a suffix of H on the standard AISI designation. H13 (4Cr5MoSiV1) is a chromium type hot work tool steel with medium level of carbon content, used extensively for general hot work application, such as aluminium extrusion dies, forging dies, plastic and nonferrous injection molding cavities and all types of dies for hot work application that involves shock. This material is well known within the industry because of the specific characteristic below: (6-10)

- good resistance to deformation at high temperature,
- high hardenability and toughness
- high thermal fatigue resistance,
- good oxidation, heat, pressure, shock and abrasion resistance.

The chemical composition of such material is shown in Table 2 below.

Table 2 Table of the standard composition (wt%) of H13 steel (4Cr5MoSiV1)

Chemical Formula	*C*	*Cr*	*Mo*	*V*	*Si*	*Reference*
4Cr5MoSiV1	*0.32-0.45*	*4.75-5.50*	*1.10-1.75*	*0.80-1.20*	*0.80-1.20*	*(11)*

H13 is type of steel alloyed with certain amount of chromium as a replacement of iron to form carbide, which can prevent decarburization by fixing the carbon as carbides of low chemical potential (12). Research shows addition of 1% chromium results in 10.5MPa stronger than normal steel of the same carbon content with slight increase in toughness (13). Though the chromium content increases the decarburization resistance, significant decarburization can still be found on heat treated H13 steel if the heat treatment was not properly controlled (14).

The mechanical properties of H13 tool steel at annealed condition are not good enough to withstand the high stress and high friction environment because its hardness level is about 15Rc, which is significantly lower than the practically required hardness of ~49Rc. So in order for H13 tool steel to be applicable for such hot working environment, the material must undergo a series of hardening process to increase the material hardness, and also surface hardening, such as nitriding to improve the wear resistance.

1-3 Hardening Process

Heat treatment is a very important process to the manufacturing industry because mechanical property modifications during the heat treatment have significant influence on the performance of die material. Degarmo et al, (15) specified the criteria of a metallurgist/ engineering designer--such person should have enough understanding on how the specific metal reacts to any process involving heating and cooling. Nicholson (16) describes heat treatment as a collective name for control of metal structure and properties through heating and cooling the metal. There are many different ways to perform heat treatment hardening, such as pack carburization, gas carburization, vacuum heat treatment, induction heat treatment, salt bath etc. As for

Heat Treatment Limited, the die is austenized in a vacuum furnace. Heat treatment is a process consisting of four main stages: preheat cycle, austenite formation stage, quenching and tempering. The target of heat treatment hardening is to harden the material by changing the structure from austenite structure, which is large, shape-edged, coarse and irregular structure to martensite structure, which is fine grain structure of hardened carbide.

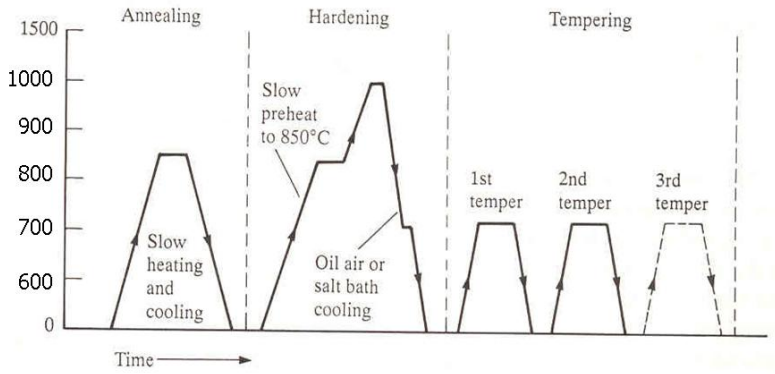


Figure 1-3-1 Heat Treatment Process Flow Diagram

Preheat cycle is an essential pre-process before heat treatment process. This process is important because it helps relieve the stresses and reorganise the grain structure. The main advantage of the preheat cycle is that it also reduces the opportunity of initiation of mechanical fatigue or cracking induced by thermal shock.

In Heat Treatment Limited, H13 extrusion dies are vacuum heat treated in Abar Vacuum Furnace at approximately 25micron (1micron = 0.0013332kPa). The preheating stage is a two step preheat, one hour at 650°C and one hour at 850°C.

1-3.1 Austenitizing Stage

After preheating, the material is heated to an austenite temperature, which is 995°C – 1040°C for H13 tool steel (17) to allow the carbides to dissolve into the austenite matrix until such a degree to give the hardening effect by transforming ferrite into austenite (18). It is a state of two phase structure containing both austenite and undissolved carbides. Si (11) suggests that the preferred austenite temperature is between 1000°C -1060°C, and 1020°C is the usual practical operating temperature because this ensures the carbon and alloying element to be homogenized within the austenite structure and the austenite grain size can reach level ASTM9. Brandes and Brook (19) also recommended 1020°C as the preferred austenitizing temperature. As for Heat Treatment Limited, the material is heated to 1040°C and is normally hold for 45 minutes.

This homogenization is the result of chemical diffusion. As the temperature is elevated to austenite temperature, pearlite is the first structure to be transformed into austenite state, then ferrite, a body centred cubic (BCC) crystal structure so called α-iron, experiences a polymorphic transformation to face centred cubic (FCC) structure so call austenite. (20)

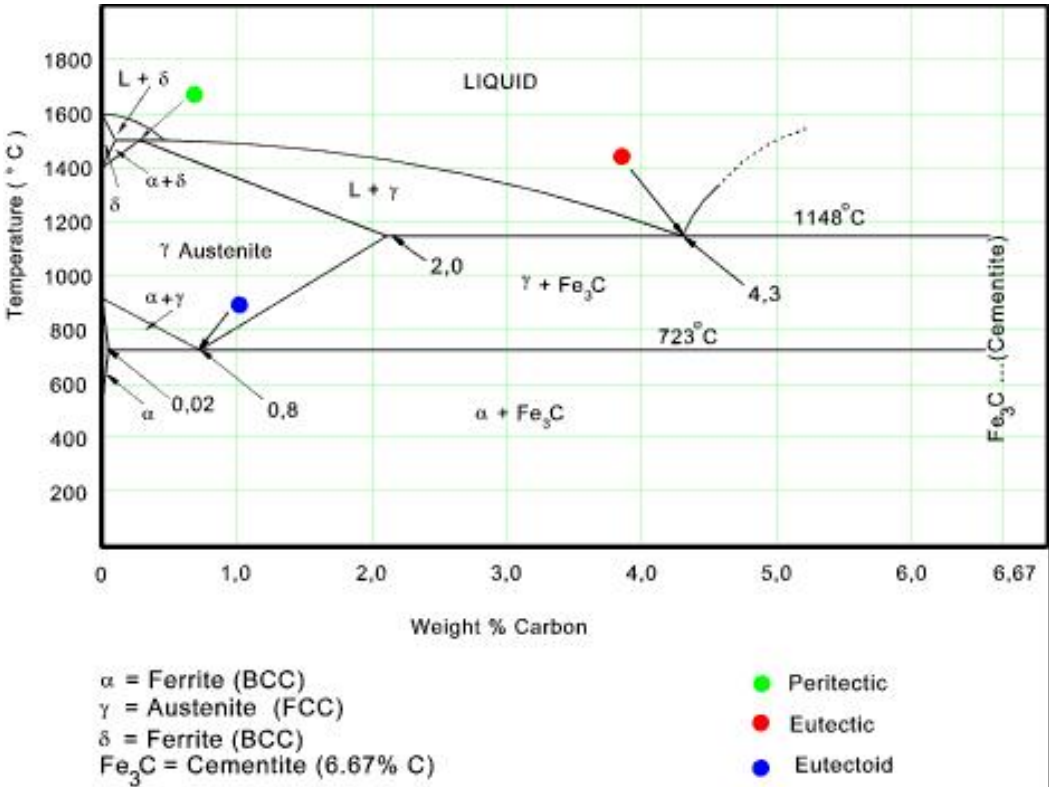


Figure 1-3-2 Carbon Steel Phase Diagram

Phase transformation of steel from austenite state to ferrite or cementite (Fe_3C) plays an important role in determining the mechanical properties of steel (21). It was found that the obtainable hardness for H13 steel increases with austenite temperature but austenization should not be conducted over 1100°C because grains will grow in a very high rate which could lower toughness (9).

At the austenite state, carbon and alloy elements in steel are homogenize by a two step process. The first step is the formation of austenite at the ferrite cementite grain boundary, and eventually the newly formed austenite consumes all ferrite and cementite and the austenite formation is terminated here. At the same time, carbide is also dissolved into austenite, and eventually increases the overall carbon content and stabilize the austenitize structure (22). By this stage, the content of carbon and alloy elements are not yet evenly distributed, carbon and alloy elements begin to

homogenize through diffusion. Due to the fact that alloying elements have bigger atomic radius than carbon, the alloying elements take much longer time to be homogenized. As austenitizing is running at a high temperature range, there are various surface reactions and chemical diffusion may happen at austenite state depending on the heat treatment condition.

1-3.2 Quenching

Once the austenizing is completed, the material is immediately quenched to low temperature by media such as water, oil or air. Water is the fastest medium for material to cool down. Oil has a lower cooling rate than water but is still used extensively because it has higher viscosity and promotes slightly safer heat treatment. Air is the cooling medium with lowest cooling rate which results in lower thermal shock that is the cause of thermal stress. Materials heat treated in Abar vacuum furnace at Heat Treatment Ltd is quenched with two bar pressure of N_2, which gives a minimum cooling rate of 30°C/minutes from 1040°C to 500°C. Quenching is a process to transform the austenite to martensite. This may not be a perfect transformation so the final structure may contain mixture of martensite and austenite structure (also named retained austenite) with a portion of carbide formation. The formation of martensite structure is improtant because it enhances the strength and hardness of steel for industrial uses, however at the expense of material toughness (23). Selection of quenching media depends on which microstructure is desirable and the cooling characteristic of the material. Graphs so called time temperature transformation diagram (TTT) and continuous cooling transformation diagram (CCT) can aid the process designer to design the quenching process for specific combination of microstructure.

1-3.3 Tempering

As quenching induces stress within structure that easily causes rupture, tempering which is a reheating process, is required immediately after quenching for stress releasing and also for retained austenite transformation. During tempering, carbon suppressed in the martensite matrix diffuses out and form fine carbides with iron, thus reduces the martensite hardness, increases its toughness by reducing the amount of microcracks in martensite structure, reduce the grain size and produces a refined microstructure (2, 22, 24, 25). Three distinct stages were identified in tempering process (24, 26):

- Stage 1 – The formation of transition carbide, epsilon carbide, and the lowering of martensite carbon content to about 0.25% carbon.

- Stage 2 – The retained austenite is transformed into ferrite and cementite.

- Stage 3 – The replacement of the transition carbide and low carbon martensite by cementite and ferrite.

For high alloy chromium, hot work tool steel and high speed steel, retained austenite can transform to either bainite or martensite depends on the tempering temperature and time (26). Bainite is mostly formed isothermally whereas martensite is formed during the quenching from tempering temperature. The newly formed martensite with the precipitation of fine dispersed carbide result a secondary hardening effect, and is categorised as the forth stage of the tempering process. Details of this effect can be found in Figure 1-3-3.

For H13 steel, 2-3 times of high temperature tempering process is usually required, and the practical tempering temperature is 450°C - 520°C (11). As industrial practice, Heat Treatment Ltd normally tempers the extrusion dies twice. 1st tempering is at 540°C, follow by 595°C, each of two hours. With the 1st tempering temperature, 2nd hardening may initiated within temperature range of 400°C and 550°C because special carbides would be ejected from martensite (22, 27). Tempering at temperature over 550°C can reduce material hardness remarkably (2, 27). The relationship between the tempering temperature and material hardness is shown in Figure 1-3-3.

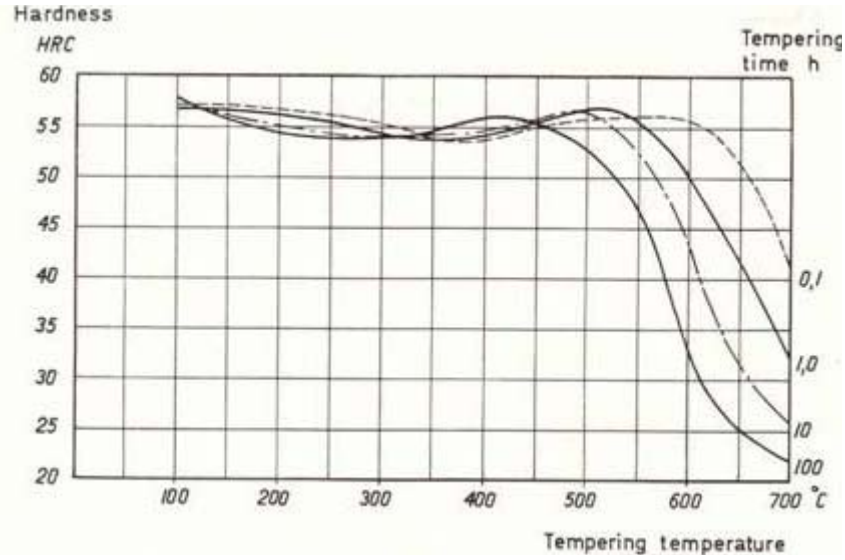


Figure 1-3-3 Relationship between H13 tool steel hardness and tempering temperature

As for die material, further case hardening such as nitriding is required to produce a harder die surface for wear resistance.

1-4 Nitriding

Bjork et al (4) state the main issue of extending the service life time of extrusion die is by delaying the removal of surface layer. Surface coating technology is always applied on H13 steel as extrusion die material because such a process induces better

wear and corrosion resistance to counter the consequence of exposure to severe mechanical, chemical and thermal conditions during the extrusion process. Nowadays, the most typical surface coating technology applied on extrusion die material is nitriding (4). Nitiding of steel should be conducted at atmosphere around 500ºC because this temperature gives the highest diffusion rate of nitrogen in steel (28). In an usual situation, the nitrated layer shall not be thicker than 0.3mm because it increases its brittleness and lowers the thermal fatigue resistance (11). There are many different types of nitriding process available, such as gas nitriding, plasma nitriding, ferritic nitrocarburizing, ion nitriding, etc. As for H13 tool steel, ion nitriding is not a promising nitriding process (28) because the compound layer formed on the surface often reduces the thermal fatigue resistance (29). For aluminium extrusion application, a deep nitrided case is not required, a case thickness of 0.25mm is sufficient (30).

1-5 Chemical Activity During the Heat Treatment Process

Heat treatment is a high temperature process, so it is understandable it promotes chemical reaction and also diffusion. Various reactions take place during the heat treatment process (31). Brandes and Brook (19) classified them into three main groups:

- Metal oxidation
- Carbon reaction to the surrounding, and
- Vapour gas reaction

Among those, the most significant chemical reaction is the activation and diffusion of carbon. If more carbon is introduced to steel, such process is named carburization. However, if carbon in steel escapes to the surrounding, it is called decarburization. On either process, surface reaction between steel material and surroundings introduce a carbon concentration gradient within the steel material. Such concentration gradient results in carbon diffusion from high concentration into low concentration and would not stop until an equilibrium state is reached, which is a constant carbon concentration profile. Hence with different atmosphere conditions, the process of carbon transfer during the austenization process can vary.

Carbon diffusion is an important phenomenon in heat treatment because variation of carbon content in steel can influence the mechanical properties of the treated steel. It is well known that there is an established relationship between the carbon content and martensite hardness (32-35). As carbon has a dominant effect on the mechanical properties of steel, it is important to understand the kinetics of carbon diffusion when steel is subjected to high temperature.

1-6 Summary

With detailed description on each stage of hardening process, there is no doubt that diffusion of carbon at austenization stage plays a major role on the mechanical properties of treated steel surface. As stated in Smithells Metal Reference Book (19), although the cost of the heat treatment process is only a minor portion of the total production cost, it is arguably the most important and crucial stage determining the die material quality. Hence, there is a need to gain further understanding on the following areas in order to improve the process efficiency:

- Effect/(s) of atmosphere condition during the heat treatment process to the quality of treated material,

- How does carbon react to atmosphere on material surface under various atmospheric conditions,

- What is the kinetics of carbon diffusion with respect to different heat treatment atmosphere condition,

- What the carbon diffusion governing parameters are,

- Effects of the carbon content of quenched material on the response of tempering,

- Influence of carbon content on the performance of nitriding.

Chapter 2 Literature Review

As described in the previous chapter, the degree of hardening obtained from hardening process is greatly influenced by the available carbon content in steel during quenching. The presence of carbon within the steel matrix is largely responsible to the obtainable mechanical properties, which makes the steel material a highly useful commodity of everyday life. It also affects both the minimum hardening temperature and the maximum achievable hardness (20). To establish a proper heat treatment atmosphere for steel heat treatment process, there is a need to understand the relationship between the atmosphere composition and the carbon content of steel during the austenization period (36). This chapter reviews the mechanism and kinetics of carbon during austenization, explores the controlling factors of carbon solid state diffusion and the major microstructure of tool steel.

2-1 Carbon Transfer during Austenization

Austenization of H13 steel is always conducted at temperature within 995°C -1040°C. At such high processing temperature, carbon may diffuse into or out from the material depending on the atmospheric condition and the processing temperature. This process

is crucial to steel mechanical properties because carbon content has direct relationship with the steel strength. Carburization and decarburization are carbon absorption/desorption process and diffusion process when steel is heated into austenite state and is in contact with an environment with difference on carbon partial pressure. It is comprised of two individual and simultaneous processes:

- Carbon surface activity, and,
- Carbon diffusion within the material.

2-1.1 Activity of Carbon on Surface

The most fundamental carburization process is a gaseous phase chemical reaction to introduce carbon onto material surface and diffuse into steel by heating up the steel material into austenite state which has higher carbon solubility. In material processing industry, various methods are available to conduct carburization. Each type of carburization method has its own intrinsic processing characteristic (26, 35).

Decarburization process is a vice versa process which happens when steel reacts to the oxygen, moist or dry oxygen in the atmosphere when it is heated at 600ºC or above where the driving force is the carbon chemical potential across the material and the atmosphere (5, 12). The most basic stoichiometric chemical reaction of carburization and decarburization is shown as follow:

$$CO_2(g) + C \leftrightarrow 2CO(g) \qquad (1)$$

This chemical reaction is reversible, and the chemical equilibrium constant (K) can be defined as (24, 37):

$$\log K = -\frac{8918}{T} + 9.1148 \quad (2)$$

where, T is temperature in Kelvin. With known partial pressure of carbon dioxide and carbon monoxide, the equilibrium weight percent of carbon on steel at given processing temperature can be predicted as follow (24, 37):

$$wt.\%C = \frac{1}{Kf_c}\frac{P_{CO}{}^2}{P_{CO_2}} \quad (3)$$

where P_{CO} and P_{CO_2} are partial pressure of its subscripts, f_c is activity coefficient of carbon. According to equation 3, the equilibrium surface carbon content is governed by the operating temperature since K is function of temperature, the partial pressure of both carbon dioxide and carbon monoxide. f_c for Fe-Cr-C alloy system can be calculated using this equation:

$$\log f_c = \frac{2300}{T} - 2.24 + (\frac{179}{T})(wt\%C) - (\frac{102}{T} - 0.033)(wt\%Cr) \quad (4)$$

With equation 2 and equation 3, Harvey (37) established an equation to estimate the heat treating atmosphere for small alloying constituents Fe-Cr-C steel system.

$$\log\frac{P_{co}{}^2}{P_{co_2}} = \log(wt\%C) + \frac{179}{T}(wt\%C) - (\frac{102}{T} - 0.033)(wt\%Cr) - \frac{6618}{T} + 6.875 \quad (5)$$

where P_{CO} and P_{CO_2} are partial pressure of its subscripts, and T is temperature in Kelvin.

Equation 1 shows that in carburization (right to left) reaction, gas carbon monoxide in the atmosphere decomposes on steel surface into nascent carbon and carbon dioxide. This results in higher carbon concentration on the surface, and a concentration gradient of carbon between the surface and the core of material is produced. Based on the diffusion theory which will be described afterward, the carbon decomposed on metal surface diffuses inward into the metal core until an equilibrium is reached, while the by-product carbon dioxide further react with carbonaceous material (if there is any) to generate fresh carbon monoxide (26).

Decarburization (left to right) is a reverse process of equation 1 operating in opposite order of carburization. Carbon in steel reacts with oxygen in the air to form carbon dioxide which further reacts with carbon in steel and forms carbon monoxide. The formed carbon dioxide and carbon monoxide escape to the ambient atmosphere through the pores and cracks in the scale. Arian (10) confirms that the alloying elements are lost with the carbon atom during the decarburization process, this effect makes the tool quality after the heat treatment process is somehow lower than the original expectation. Decarburized tool steel is comparably soft and its surface properties are not much better than ordinary 1020 steel.

2-1.2 Oxidation at Austenite State

Decarburization is accompanied by the formation of oxidation layer which is a solid, firm, porous layer that does not change the shape and the inner part of the material (38). Due to the fact oxidation at the metal surface corresponds to the decarburization process, to be more specific, decarburization does not complete until an equilibrium condition is reached at the surface oxide scale-metal interface. Unfortunately, the equilibrium carbon content at this interface is still not yet known. The surface oxide

scale has relatively low carbon solubility ($6x10^{-4}$wt% at 800ºC) and is composed of mostly wustite (FeO), with some magnetite (Fe_3O_4) and hematite (Fe_2O_3) (39). The outermost layer is composed of magnetite and hematite when the temperature is under 570ºC. Above this temperature, wustite forms underneath the magnetite layer (14). Some scientists (40-42) also pointed out that the formation of carbon diffusion barrier, chromium oxide, Cr_2O_3 is unavoidable during heat treatment. Such observation implies that the decarburization rate of H13 steel during the hardening process retards with the heat treatment time. Min et al (14) found that the thickness of the oxidation film formed during H13 oxidation increases with the processing time and temperature. This is because hematite formed over the magnetite layer during the oxidation process is reduced due to the low diffusion speed of metal ion and oxygen in hematite phase. Different oxidation mechanisms were noticed under different oxidation atmosphere (14). The following table shows the Gibbs free energy of the major oxide found during the heat treatment process.

Table 3 Free energies of formation in kJ/mol of common oxide in heat treatment process (19).

Compound	$-\Delta G_{300}$ *27ºC*	$-\Delta G_{500}$ *227ºC*	$-\Delta G_{1000}$ *727ºC*	$-\Delta G_{1500}$ *1227ºC*
$Fe_{0.95}O$	*241.2*	*228.6*	*197.2*	*165.8*
Fe_3O_4	*1015.3*	*950.0*	*780.8*	-
Fe_2O_3	-	*695.0*	*556.8*	-
Cr_2O_3	*1051.3*	*991.0*	*861.6*	*731.0*

2-1.3 Carbon Diffusion

As carbon in steel reacts with the surrounding species, there is a change in terms of carbon concentration. So carbon diffusion is initiated because of the input of concentration gradient by surface activity. The following diagrams picture the carburization and decarburization process. Open circles are oxygen atoms and solid circles represent carbon atoms.

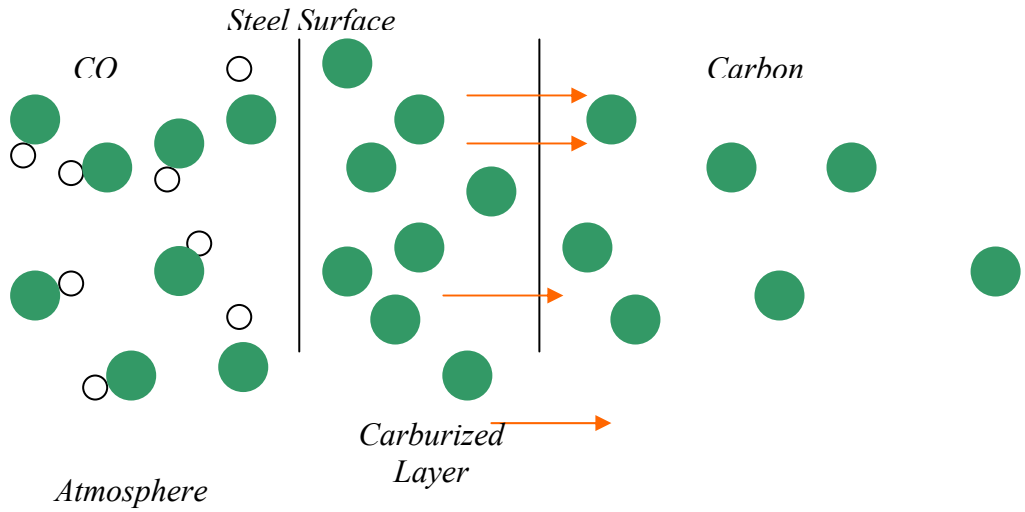


Figure 2-1-1 Diagram of Carburization Process

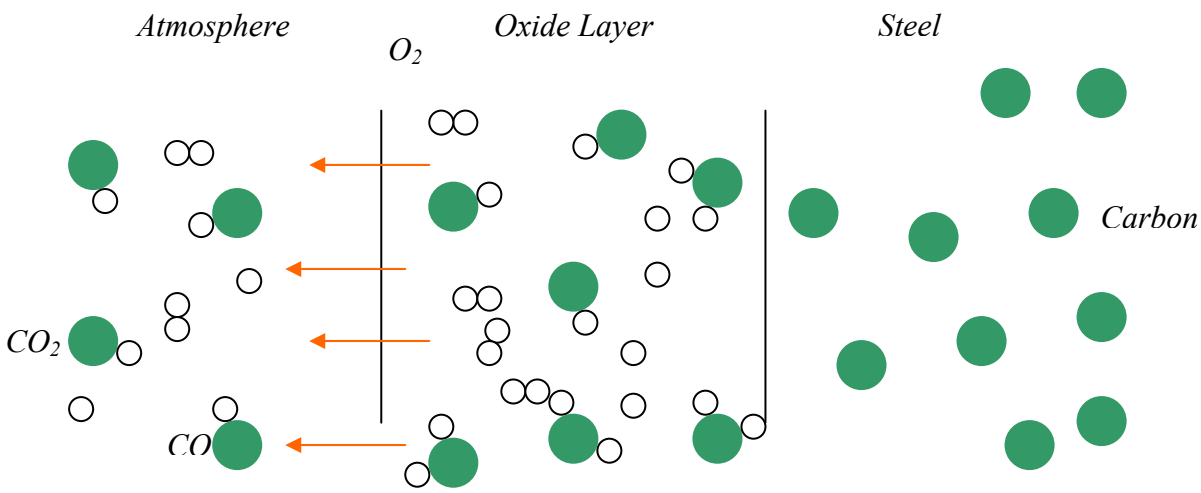


Figure 2-1-2 Diagram of Decarburization Process

From the two diagrams in Figure 2-1-2, it can be seen that two simultaneous processes are both active during the carburization or decarburization reaction: the carbon reactivity at steel-atmosphere interface, and the diffusion of carbon within the steel material. Samuels (39) and Terry et al. (39, 42) states that initially the carbon diffusion rate is the governing factor of carburization process, but after certain period of time, the carbon diffusion rate becomes higher than the carbon absorption rate due to the large concentration gradient. This results in the absorption rate to be the controlling factor of the carburize process.

In either carburization or decarburization, carbon moves from high concentration region into low concentration region. This statement does not mean carbon is only moving in one direction. In reality, carbon travels to any direction simultaneously but in average, a net diffusion flux of carbon diffuses to lower concentration region from high concentration region. For such diffusion process, Fick's Law can be used to describe:

$$J = -D\frac{\partial C}{\partial x} \tag{6}$$

where J is the diffusion flux per unit cross-section area per time, D is the diffusion coefficient, and δC/δx is the concentration gradient. The diffusivity of an element can be determined by Arrhenius reaction equation:

$$D = D_0 \exp(-\frac{E}{RT}) \tag{7}$$

In above equation, D is the diffusion coefficient, D_0 is the pre-exponential factor (cm^2/s), E is the activation energy for diffusion (J/mol), R= 8.314J/(molK) and T is the absolute temperature in Kelvin. Equation 6 and equation 7 show that the diffusion flux is governed by the concentration gradient of the diffusing species at any phase, diffusion temperature and the area perpendicular to the diffusion direction. Carbon diffusivity is relatively lower in tool steel than in other steel because it contains many carbide forming elements (Cr, Mo and V) and the presence of Si also reduces the degree of carbon diffusivity (41). This results in a comparatively thin concentrated carburized layer (41). Kucera et al (43) observed that the diffusion rate increases with increasing temperature, it can also be influenced by chemical composition, and the

depth of decarburized layer is increased with time. The following shows examples of the average diffusivity and activate energy of some common diffusing elements.

Table 4 Table of D_0 and Q of different diffusing element. (26)

Diffusing element	*Diffusing through*	*D_0 cm^2/s*	*E cal/mol*
Carbon	*α- iron*	*0.0079*	*18100*
Carbon	*γ- iron*	*0.21*	*33800*
Nickel	*γ- iron*	*0.5*	*66000*
Manganese	*γ- iron*	*0.35*	*67000*
Chromium	*α- iron*	*30000*	*82000*
Chromium	*γ- iron*	*18000*	*97000*

The values shown in Table 4 are only for general guidance purpose and the figures are different to each steel type. As described earlier, the carburization/decarburization process can be modelled by means of diffusion process. Unfortunately, Fick's first law is not applicable to this situation because the diffusion flux is changing with time since the concentration gradient is as a function of time. So there is a need for the application of Fick's second law, a second derivative model used to describe the time transient diffusion process. Fick's second law is shown as

$$\frac{\partial C_x}{\partial t} = -\frac{\partial}{\partial x}[-D\frac{\partial C_x}{\partial x}] = D\frac{\partial^2 C_x}{\partial x^2} \tag{8}$$

where C_x is the concentration at distance x from a reference point, and t is time.

The average carbon diffusivity (cm^2/s) for most steel can be approximated by (44):

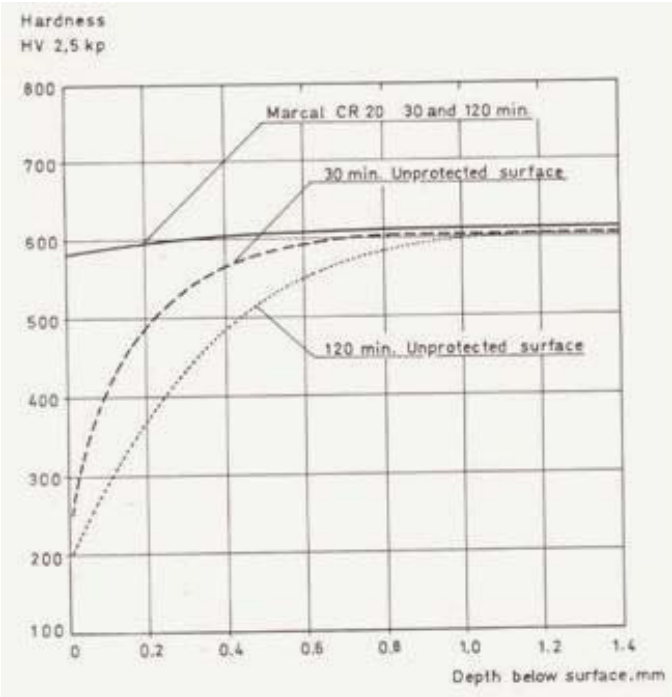
$$D_c^{\gamma} = 0.12 \times \exp(\frac{-16000}{T}) \tag{9}$$

where T is temperature in Kelvin. It must be noticed that the D_0 value in this equation is different than the value provided from Table 4. It is reasonable because the value

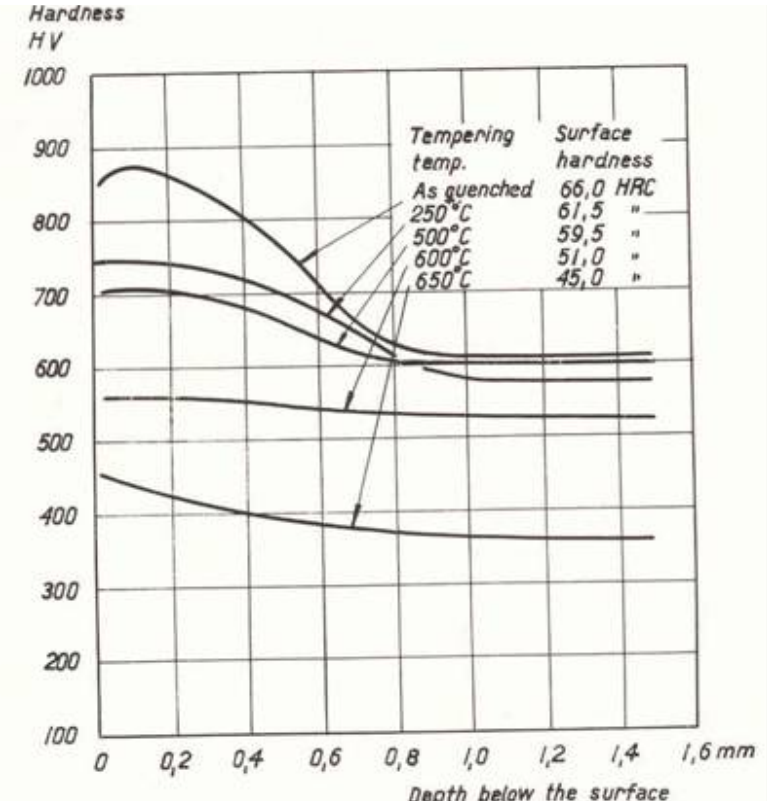
given in table 4 is for pure steel only, while equation 9 is applied for general steel which has other alloying elements diffused into it. With the following boundary condition: at time = 0, surface concentration is equal to the surrounding concentration, and considering the material is infinitely long, the concentration on the other side (away from surface) is equal to initial concentration, so Van-Ostrand-Dewey solution to the Fick's second law diffusion equation is defined as follow:

$$\frac{C_x - C_s}{C_o - C_s} = erf\left(\frac{X}{2\sqrt{Dt}}\right) \tag{10}$$

If carburization occurs during the heat treatment, carbon is absorbed from the working environment resulting in a higher carbon content at the specimen surface than the initial condition, then carbon diffuses into core region by the driving force of concentration gradient, so a decreasing carbon concentration-depth curve, carburizing curve, can be obtained after the heat treatment process. However, for decarburization process, carbon in steel escapes from metal surface to the surrounding, resulting in a lower carbon content than the initial one and carbon will now diffuse from the inner core to the surface because the inner core has higher carbon concentration. In this case an increasing carbon concentration-depth curve will be resulted. The following figures show the carburization and decarburization characteristic curves.



(a)



(b)

Figure 2-1-3 Characteristic curve for (a) decarburization and (b) carburization (26)

As shown later of this section, there is a significant relationship between the martensite hardness and carbon content. Thus, through hardness test, it is possible to

estimate the carbon content, and to monitor the kinetic of carbon diffusion during the hardening process.

2-2 Hardness

Hardness is a material property to give indication of material strength and resistance to wearing and scratching. Unlike tensile test, hardness measurement does not damage the test pieces so it is the preferable technique in the industry for the indication of material strength. Many types of hardness test are available to scale the material hardness, and the most commonly used testing method for steel materials is Rockwell hardness test. However, due to the indentation size, hardness profile from surface to core has to be done with Vickers test. The indentation of Vickers test at a relative low loads, is able to maintain shape less than 0.5mm on the diagonal. So it can be used to describe the material hardness profile.

Microstructure has a great influence on material hardness. So it is important to know what kind of microstructure would form after the hardening process.

2-3 Microstructure

Metal microstructure exhibits various mechanical properties and is governed by the number of phases presents in the alloy, the proportion of each individual phase and its distribution (21). These phase features are characterised by the presence of alloying elements, its concentration, and the heat treatment temperature, the heat treatment time and the cooling rate.

2-3.1 Ferrite

Ferrite, after ferrum, the Latin word for iron, (20) is a body centered cubic (BCC) structure of iron with tiny amount of soluble carbon. The maximum amount of soluble carbon in ferrite is 0.022% by weight content at temperature of 727ºC. Although ferrite can only house relatively small concentration of carbon, such addition can influence ferrite mechanical properties significantly. Ferrite is a relatively soft ductile microstructure with hardness of about 100 HV and can be magnetized at temperature below 768ºC (21). Although this is not a desire structure for die material, it contributes other form of microstructure.

2-3.2 Carbides

Carbide forms if the carbon content of steel is over the carbon solubility, the excessive carbon would form carbide with iron instead of dissolving into the ferrite matrix. Plain carbon steel typically has a carbon solubility of 0.022%. Unlike ferrite, it is a very hard and brittle intermetallic compound. At recommended heat treatment temperature, there is evidence shows formation of carbides precipitate at grain boundary in H13 steel is unavoidable. This precipitation reduces material toughness (10, 45, 46). Tekmen et al. (47) suggest the present of particles at grain boundary reduces the phase boundary area, thus reduces the material strength. Okuno (48) confirms the toughness value reduces in H13 is in good correlation with increasing density of fine carbide in the metal matrix and the fraction of retained carbides. West et al. (40) also explain the high amount of carbide formation at ground boundary and in the grain would severely affect the material fatigue property. During the tempering stage, carbon may diffuse out from the martensite structure to produce fine carbide, which can increase the material toughness (2).

2-3.3 Austenite

As steel being heated up to austenite temperature, a new phase called austenite (γ) is resulted. Austenite is a non-magnetic face centered cubic (FCC) structure which has considerably high carbon solubility in compare with ferrite. This solid solution is stable at ambient temperature only with high concentration of elements such as nickel and manganese is presence (39). Austenization is an important process for microstructure reformation. As shown from Table 4, carbon can diffuse better in austenite than in ferrite. It is expected the carbon diffusion kinetics is the most significant during the austenitizing stage.

During austenitization, the austenite grains grow with normal growth process so minimum grain boundary area can be achieved. Two factors are governing this thermodynamic tendency—the maximum temperature and the austenitic grain growth characteristics of the particular steel (39).

2-3.4 Pearlite

Pearlite is the lamellae structure of ferrite and cementite, a structure which plate cementite is lying between the ferrite plates. Two forms of pearlite, fine pearlite and coarse pearlite can form depending on the cooling rate from the austenite state. Fine pearlite forms at relative high cooling rate such as air cooling, while coarse pearlite forms if the material is cooled slowly such as furnace cooling.

2-3.5 Bainite

Bainite is a very fine microstructure formed in alloyed steel which the cooling rate is higher than the transformation of pearlite. It is also composed of both ferrite and cementite but have different structure than pearlite. In bainite, the cementite is

presented as filaments within the ferrite matrix. Although bainite is stronger and more ductile than pearlite, the amount of bainite in H13 die material must be minimised to achieve optimum impact toughness and dimensional stability. Bainite formation is determined by the cooling rate within the temperature range 950ºC - 750ºC and the formation completion is depending on the cooling rate between the temperature range of 320ºC and 270ºC (45).

2-3.6 Martensite

Martensite, a body centered tetragonal (BCT) structure, is a non-equilibrium structure of supersaturated solid solution formed as a result of diffusionless shear transformation of austenite (21). This microstructure only forms when the cooling rate is high enough to prevent any ferrite and cementite formation through carbon diffusion, and has carbon content same as its austenite state that can be as high as 2wt% (21, 24, 35). Through the instant transformation form γ into α, the carbon atoms remain in the limited space within the α-iron matrix which causes the lattice expands, and the resulting state of stress increases the hardness of the steel (26).

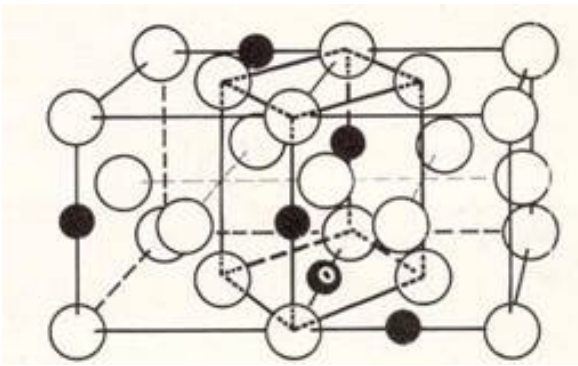


Figure 2-3-1 Simple model for the martensite (α) structure (26).

Due to the fact that the volume of the martensite increases with increasing carbon content, the hardness of martensite is proportional to the carbon content, (26) which can also be shown from the following diagram.

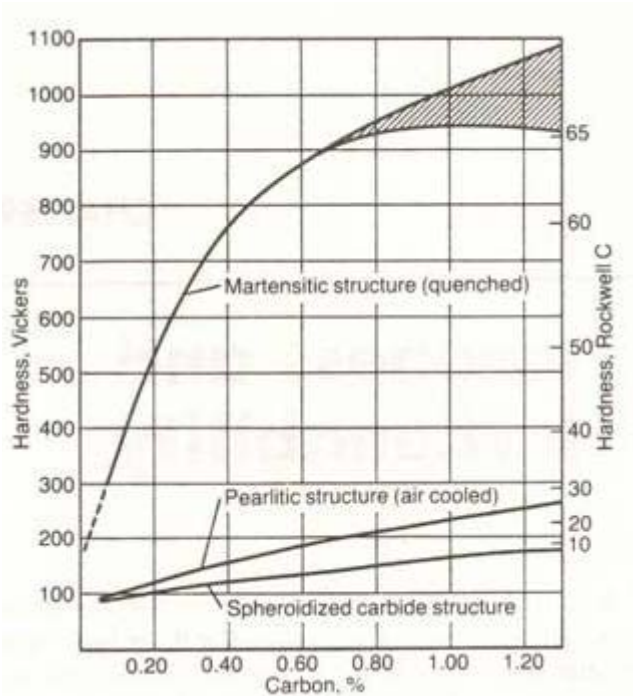


Figure 2-3-2 Hardness as a function of carbon concentration for plain carbon martensitic, tempered martensitic. Cross hatched area shows effect of retained austenite (24).

Two types of martensite structure can form in steel alloy depending on the carbon content. For carbon content of 0.6wt% or lower, which H13 tool steel is under this category, the formed martensite has a laths appearance. Lath martensite is formed side by side and are aligned parallel to each other which are grouped as a larger structure entity called block. For steel alloy with carbon content more than 0.6wt%, lenticular (plate) martensite is formed. Krauss (25) summarised that plate martensite associate with significant amount of retained austenite with a concernable amount of microcrack, which may be responsible for negative mechanical property change.

Formation of martensite is purely temperature dependence and is not related to time as pearlite or bainite formation does (20, 26, 35, 49). Martensite formation is nucleated at the boundary of austenite structure as soon as the temperature of martensite formation is reached (44). Recent research also found that the carbon content in an alloy has a significant influence on both the starting martensite transformation temperature and the volume fraction of retained austenite (49). The finding by Ferguson et al. (49) shows as carbon content goes up, the starting martensite transformation temperature drops with increasing retained austenite content.

2-3.7 Retained Austenite

Retained austenite is a structure that is unable to transform into martensite during quenching after commencing martensite transformation (21, 39). It is especially significant for high carbon steel. Also as the treatment temperature increases, a higher amount of retain austenite result (24, 26). Perhaps due to a higher temperature, more carbon is diffused into austenite, which results in a higher amount of retain austenite. Higher alloy content also results a higher amount of retained austenite (24, 26). Figure 2-3-3 shows the relationship between the amount of retained austenite and the austenite carbon content.

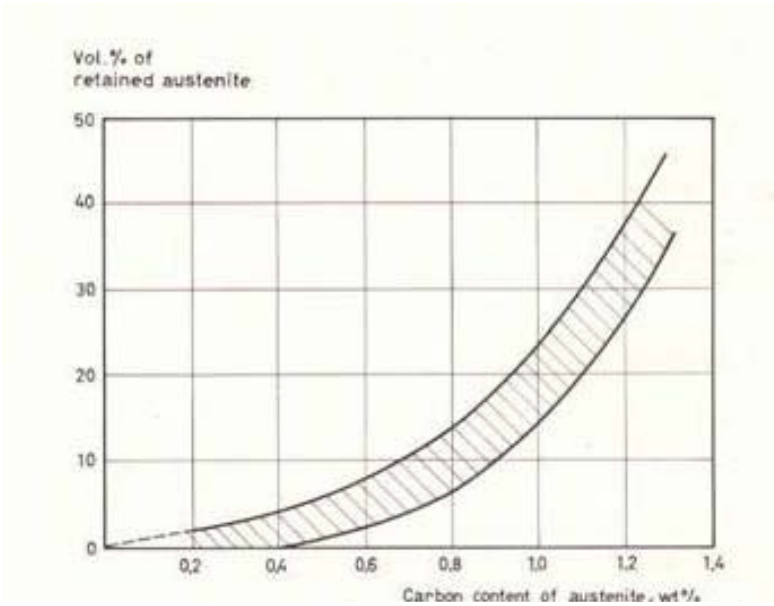


Figure 2-3-3 Variation in the amount of retained austenite with austenitic carbon content on hardening (26)

The presence of retained austensite has a considerable effect on material hardness. The influence is especially significant for steel with more than 0.7% carbon (24). This can be seen in Figure 2-3-2.

To predict the amount of retained austenite within the martensite structure of pure iron-carbon alloy or plain carbon steel, Koistinen et al (50) has developed the following equation, which the quenching temperature (T_q) must lie within $M_s > T_q > -80°C$:

$$V_\gamma = e^{\left[-1.10\times10^{-2}(M_s - T_q)\right]} \qquad M_s \rangle T_q \rangle -80^o C \tag{11}$$

where V_γ is the volume fraction retained austenite, M_s is the starting temperature of martensite formation, and T_q is the quenching temperature. The volume fraction of martensite is (35):

$$V_m = 1 - V_\gamma \tag{12}$$

The amount of retained austenite content in quenched steel can be measured accurately by X-ray diffraction technique (44).

When the retained austenite is heated to temperature over 350°C and is hold at that temperature long enough, it can be transformed to a duplex structure containing both ferrite and carbide. The transformation commences at the surface of the martensite structure only after the transition carbide is well established (24), and slowly progresses, by migration of a relatively smooth interface into the austenite (39).

2-3.8 Tempered Martensite

For structural application, martensite is too brittle to serve as die material. Thus, it must be tempered to obtain tempered martensite with better toughness. The strength of tempered martensite decreases with tempering time due to the growth of carbide particles (21, 47, 48). The tempered martensite contains various structure such as carbide, ferrite, and low carbon content martensite depends on the tempering conditions(24, 26, 39). This is because the growth of carbide particles reduces the phase boundary area per unit volume which makes the material weaker and softer. Carbon diffusion during the tempering process plays a major role in determining the carbide growth rate, so the tempering temperature and the time of tempering process must be designated carefully.

2-4 TTT and CCT Diagrams

If the heat treatment process is an ideal equilibrium process, desire structure can be obtained with ease. Unfortunately, the process is nonequilibrium in reality,

insignificant variations in cooling can also produce major variations in structure and properties (15).

Isothermal Diagram (IT), also known as time temperature transformation diagram (TTT) is a powerful tool for engineer to determine phases present after the heat treatment process. The information shown in TTT diagram is obtained through the observation of microstructure produced by “instantaneously” quench the heat treating thin specimen of particular steel from uniform chemistry austenite state, to an austenite non stable temperature and hold it for variable period of time (51).

However, TTT is only application in the case of isothermal situation, its use for heat treatment process is limited. Thus, continuous cooling transformation diagram (CCT) is constructed to allow technician to predict as the cooling rate varies.

As the temperature drops below the austenite stable temperature, the face centred austenite is willing to transform to body centred ferrite and carbon rich cementite. Such transition rate is governed by two major thermodynamic factors: the driving force and the atom diffusivity, which are both closely related to the cooling temperature and time. Figure 2-4-1 shows the CCT diagram of H13 material. (46)

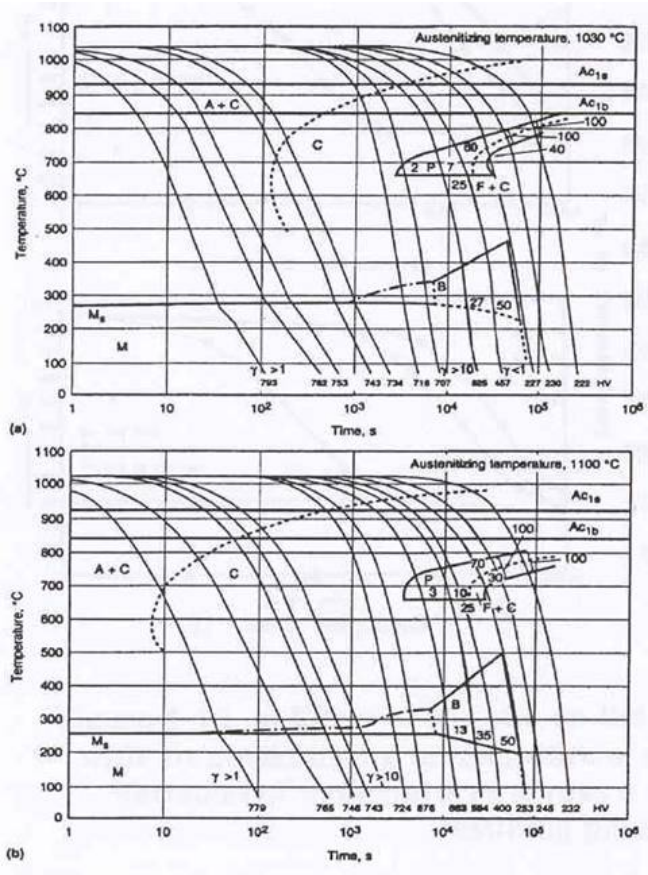


Figure 2-4-1 H13 CCT diagram (a) at austenitizing temperature 1030°C (b) at austenitizing temperature 1100°C.

2-5 Research Objectives

Realistic carbon diffusion model for the carbon profile is important. As mentioned previously, carbon can either diffuses out or into steel matrix depending on the working environment. If decarburization occurs, the hardness on the surface of the treated material is going to be lower than expected. However, if carburization take place, the treated material would be hardened. Many researches have been conducted related to the carburization process (32-35), however, understanding of decarburization during heat treatment is still limited, especially for H13 tool steel. Although Arain (10) has conducted investigation on the difference between open atmosphere heat treatment and vacuum heat treatment, his focus was mainly on H13

toughness behaviour. The kinetics of carbon diffusion within material H13 tool steel is still not yet clear.

As Heat Treatment Limited is the only company in New Zealand using vacuum furnace to conduct hardening process. This is worth to investigate the advantages and disadvantages in both economical and practical use of vacuum furnace in comparison to heat treatment without atmospheric control. It is necessary to determine the difference in hardness profile between the vacuum treated H13 steel and the decarburized H13 steel which can be obtained after the nitriding process.

Thus, the main objective of this research is to investigate how the surrounding condition during heat treatment process influences the steel hardness profile. And conduct a study on the carbon diffusion kinetic when the material is subjected to different atmospheric condition during austenitizing stage. Samples of specific size of H13 steel would be subjected to heat treatment process with different duration time and under different atmospheric conditions. Hardness profile of each sample would then be constructed and analysed. It is also of interest to investigate the difference in effectiveness of gas nitriding process on samples heat treated without atmospheric control and heat treated with atmospheric control. The heat treated samples would further be subjected to nitriding case hardening process with hardness profile being measured and compared. In summary, the aims of this research are to:

- Establish the effect of different atmosphere conditions on the carbon profile in as quenched state after H13 has been austenized at relative high temperature.

- Investigate the kinetics of carbon diffusion in H13 steel during heat treatment under different atmospheric conditions.

- Model such carbon diffusion process based on previous defined model – the Van-Ostrand-Dewey solution, and to determine the carbon activation energy and carbon diffusivity at 1020°C.

- Study the influence of carbon content on the effectiveness of nitriding case hardening.

Chapter 3 Experiment Procedures

Experiments were designed to investigate how the carbon profile changing when H13 steel is subjected to heat treatment under various atmosphere conditions. Since in this research the kinetics of carbon diffusion during the hardening process was also considered, experiments with different treatment duration and different quenching method were conducted. Further more, after the hardening process, the specimen underwent further processes for case hardening by gas nitriding. This chapter will describe the procedure of these experiments.

3-1 Experiment Plan

To investigate the carbon concentration change within the H13 steel matrix during heat treatment process, and how each processing parameter influences the resulted hardness profile, the following experiments were conducted.

Heat treatment processes of four different atmospheric conditions were applied in this investigation. Each atmospheric condition shall show distinct characteristic in terms

of carbon diffusion and exchange at the steel surface during the hardening process. The four heat treatment atmospheric conditions are:

- Heat treatment without atmospheric control,
- Heat treatment with stainless steel foil wrapping,
- Pack carburizing heat treatment, and
- Vacuum heat treatment

Further treatment was also conducted to investigate the effect of carbon content on the efficiency of the nitriding case hardening process. Hence, after quenching, samples were subjected to two tempering processes followed by gas nitriding. Between each process, a sample was collected for analysis. Table 5 is the summary of the experiment plan.

Table 5 Experiment Summary

Heat Treatment Stage Experimental Planning												
Treatment Condition	*Heat Treatment without Atmospheric Control*			*Heat Treatment with Stainless Steel Foil Wrapping*			*Vacuum Heat Treatment*			*Pack Carburization Heat Treatment*		
Sample Size	*7x10x60 (mm^3)*			*7x10x60 (mm^3)*			*7x10x60 (mm^3)*			*7x10x60 (mm^3)*		
Pre-heat Temperature (ºC)	*815*			*815*			*850*			*815*		
Austinitizing Temperature(ºC)	*1020*			*1020*			*1040*			*1020*		
Treatment Duration (hour)	*1*	*3*	*5*	*1*	*3*	*5*	*1*	*1.5*	*2*	*1*	*3*	*5*
Cooling Medium	*Fan Cooling Water Quench*			*Fan Cooling Water Quench*			*Vacuum Furnace Quenching*			*Fan Cooling Water Quench*		
1st Sample Collection												
1st Tempering at Temperature of 540ºC for 4 hours												
2nd Sample Collection												
2nd Tempering at Temperature of 595ºC for 4 hours												
3rd Sample Collection												
1st Gas Nitriding at Temperature of 530ºC for6.5 hours										*No Gas Nitriding Treatment*		
4th Sample Collection												
2nd Gas Nitriding at Temperature of 530ºC for 6.5 hours												
5th Sample Collection												
3rd Gas Nitriding at Temperature of 530ºC for 6.5 hours												
6th Sample Collection												

3-2 Specimen Preparation

Specimens with size of about 20x10x60mm^3 were cut from a H13 circular log shown below, which was provided by EXCO Limited under annealed condition, with initial hardness of ~12HRC.

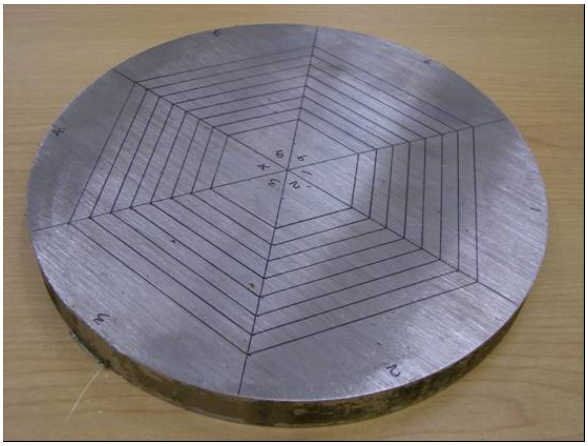


Figure 3-2-1 Picture of a circular section cut from H13 circular log

The circular log was divided into six equal sections and four of them were used for this research. Each section was dedicated to one heat treatment atmosphere condition:

- heat treatment without atmospheric control,
- heat treatment with stainless steel foil wrapping,
- pack carburization heat treatment, and
- vacuum heat treatment.

The following diagram shows the position of each specimen taken out from each section.

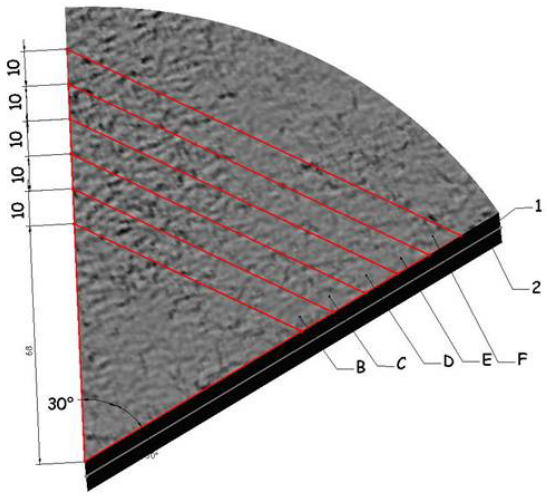


Figure 3-2-2 Sample Cut Overview

Strips with thickness of 10mm were machined from each section as shown above and is named alphabetically. Sample of size 7x10x60mm^3 was then sectioned from the metal strip and divided into two parts as numbered in Figure 3-2-2. The letters shown in Figure 3-2-2 refers to the time duration of heat treatment, the numbers 1 and 2 on the diagram indicate the material was treated by different cooling method. There was only one cooling method for vacuum heat treatment experiments (vacuum furnace cooling). All specimens were then surface machined with the milling machine and the new specimen dimensions were measured. All specimens shall have a rectangular shape as shown in Figure 3-2-3:

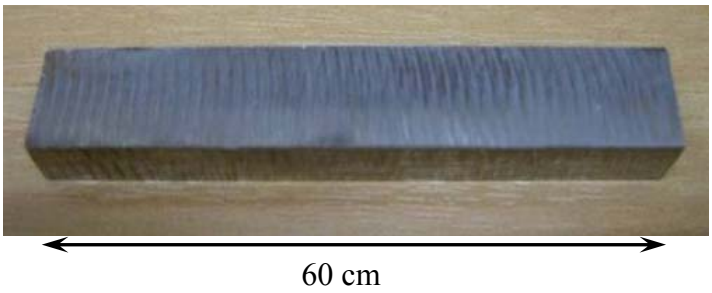


Figure 3-2-3 Specimen for Heat Treatment Experiments

This is done to ensure similar surface finish as in industrial practice and to produce fairly flat surface for carbon diffusion modelling. The chemical composition of the H13 material is shown on Table 6:

Table 6 Chemical composition of H13 tool steel used in this research

Chemical Formula	*C*	*Cr*	*Mo*	*V*	*Si*	*Mn*	*Fe*
4Cr5MoSiV1	*0.41*	*5.03*	*1.24*	*0.88*	*0.97*	*0.38*	*Remaining*

3-3 Hardening Processes

This section describes how each of the four heat treatments was performed.

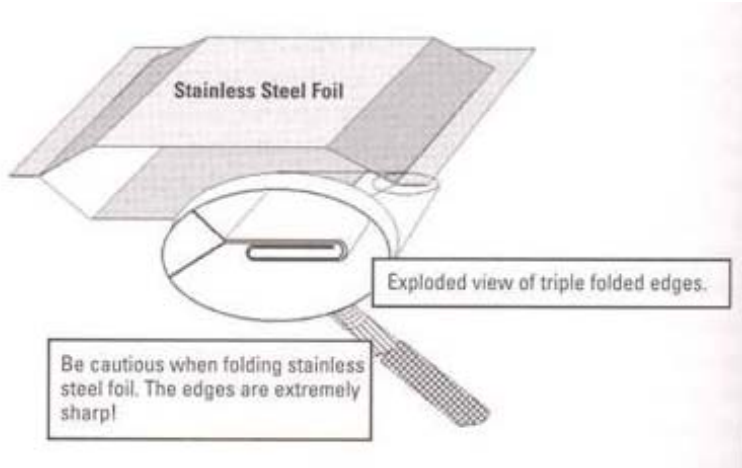
3-3.1 Heat Treatment without Atmospheric Control

Heat treatment without atmospheric control means that the specimen was subjected to heat treatment in a muffle furnace, at austenitizing temperature of 1020ºC for a specified time period. The samples were positioned at the centre region of the muffle furnace and were in direct contact with the surrounding atmosphere. For this atmospheric condition, carbon in steel could freely react with the ambient atmosphere. An electrical heated open atmosphere furnace (muffle furnace) was used for all heat treatment processes except vacuum heat treatment process. Data logger with a thermocouple was used for all heat treatment processes conducted at AUT to monitor and ensure the right treatment temperature was maintained during heat treatment.

3-3.2 Heat Treatment with Stainless Steel Foil Wrapping

Heat treatment with stainless steel foil wrapping represents that the specimens were fully wrapped with a piece of stainless steel foil, to reduce the rate of chemical

diffusion between the specimen and the furnace atmosphere. This method is commonly used in industry and the suggested wrapping procedures can be found in Bryson (18). For this research, each sample was first wrapped with the long side (the length) double folded, then double folded inwardly from the other two ends (the widths). The following is an example of the wrapping method:



(a)

(b)

Figure 3-3-1 Picture of Stainless Steel Foil Wrapping (a) suggesting method (18), (b) practical method

This experiment setting aimed to minimise the continuous carbon reaction and oxidation between the sample and the ambient atmosphere by the existence of stainless steel foil. The stainless steel foil acts as a barrier to restrict the carbon reaction between the specimen and the surroundings.

3-3.3 Pack Carburization

Pack carburization heat treatment is the carburization process chosen for this study. In pack carburization, a steel box holding a specimen was fully packed with charcoal with case hardening crystal, barium salt, chemical formula of $Ba(ClO_3)_2$, was heated to an elevated temperature (1020 ºC) so the specimen was cooked under carburized atmosphere. The specimen was located at the central of the steel box and was fully covered by barium salt, so each specimen surface was in contact with same carburized atmosphere condition. An example of pack carburization experiment before the sample is covered up with barium salt is given in Figure 3-3-2.

Figure 3-3-2 Photograph showing location of sample in the box holding sample for pack carburization

3-3.4 Vacuum Heat Treatment

Samples were sent to Heat Treatment Limited located at Mount Roskill in Auckland, New Zealand, for vacuum heat treatment. The vacuum treatment was conducted in an Abar vacuum furnace at approximate 25 microns and preheated at temperature of 650ºC and 850ºC. Each preheating stage takes 1 hour. Then it is heated up to 1040ºC and held for either 60, 90 or 120 minutes, and finally cooled to room temperature in a

rate of 30ºC per minutes. The photograph below shows the muffle furnace and the Abar vacuum furnace used for this research.

(a) (b)

Figure 3-3-3 Furnaces used for heat treatment hardening experiments (a) Muffle Furnace, (b) Vacuum Furnace

3-4 Quenching of Material

Once the austenitizing time is reached, the specimen must be rapidly cooled from austenite state to room temperature to form martensite. Two different cooling methods were applied on experiments conducted at AUT. They were fan cooling and water quench. For fan cooling, specimens were taken out from the furnace and were cooled in front of a running fan. The specimens were kept rotating so the cooling rate would be even on all surface. Water quench was conducted by taking out the specimens from furnace and put it into a pool of water, and kept stirring in water for 2 minutes. Due to practical difficulties, specimens heat treated in vacuum treatment could only be cooled in vacuum furnace, so there was no fan cooling and water

quench data for vacuum heat treated samples. The cooling rate of vacuum furnace cooling has a minimum rate of 30ºC/minute and the specimens were cooled with 2bar of nitrogen gas.

3-5 Sample Collection

After the cooling, specimen dimensions were measured again to look for size changes during processing, then a small sample with size of about 7x10x10mm^3 was cut from each quenched specimen for hardness test and metallographic analysis. Figure 3-5-1 is an example of the sample obtained from a test specimen.

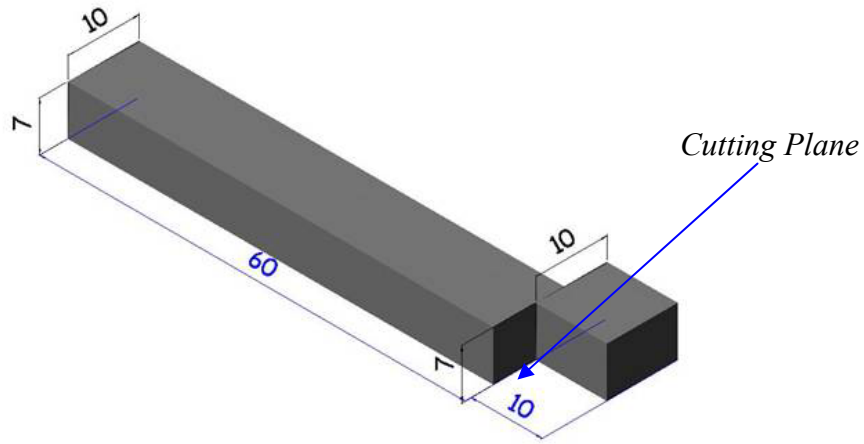


Figure 3-5-1 Example of sample cutting plane

3-6 Tempering and Nitriding

The remaining part of the specimens were then subjected to two tempering processes which were held at temperature of 540ºC and 595ºC respectively in a vacuum furnace for four hours. Since the dynamics of the carbon content on the efficiency of case hardening by gas nitriding is also concentration in this research, the last part of the remaining treated samples were cut into three different pieces and subjected to once, twice or thrice times of case hardening process. Samples from pack carburization

experiment were not subjected to case hardening process because this is not an usual practice in industry. The gas nitriding process was conducted at 530ºC under controlled atmosphere for 6.5 hours.

3-7 Sample Surface Preparation

All samples were subjected to a series of surface preparation process before any metallographic analysis. Firstly, the treated samples were mounted using a moulding unit as shown in Figure 3-7-1 for ease of polishing, with the cut face facing downward which was the polishing side. The cut face must be the polishing side because this is the face enables the exposure of the hardness details hence to describe the carbon content variation and efficiency of case hardening process.

Figure 3-7-1 Hot Mounting Unit

These samples were surface polished by a rotary grinder with 100, 320, 500, 1000, 2400 grit grinding papers, followed by material polishing disk with 6 µm and 1µm diamond paste and microhardness test would be conducted on each sample.

Photograph for the polishing tool can be found in Figure 3-7-2. The polished surface should appear as shinny as a mirror.

(a)

(b)

Figure 3-7-2 Polishing Tool (a) Rotary Grinder, (b) Universal Polisher

3-8 Microhardness Test

The microhardness test method used for this research is Vicker's Hardness Test and the load applied was 300gf. Hardness measurements were conducted from the sample edge to the centre of samples, which was approximately 5000µm from the edge using

the Vicker's microhardness machine shown in Figure 3-8-1. The hardness measurements were measured in step of 50µm until 1000µm, with one extra measurement at 20µm. For region between 1000µm and 5000µm, the measurements are measured in step of 250µm.

Figure 3-8-1 Vicker's Microhardness Machine

After microhardness tests, the samples would be subjected to surface polishing again and were etched with Nital solution, 3% HNO_3 in ethanol. The polished surface was washed with alcohol and dried with warm air immediately after etching, to expose the microstructure details. Metallographic pictures would be taken for the measurement of the depth of the carburization/ decarburization layer or the case hardening layer, and for the microstructure examination. All results are presented on the following chapter.

Chapter 4 Experimental Results

This chapter presents all the results of hardness profile from each experiment in a logical format. Hardness profiles of all heat treatment stages, including as quenched state, 1st tempered state, 2nd tempered state, and all of the three nitrided states are shown. The micrograph of as quenched state will also be included. It must be noted that although the microhardness tests were conducted with Vicker's measurement, during the process of analysis, the data was converted into Rockwell (HRC) scale. It is because Rockwell scale is the common scale used in steel industry.

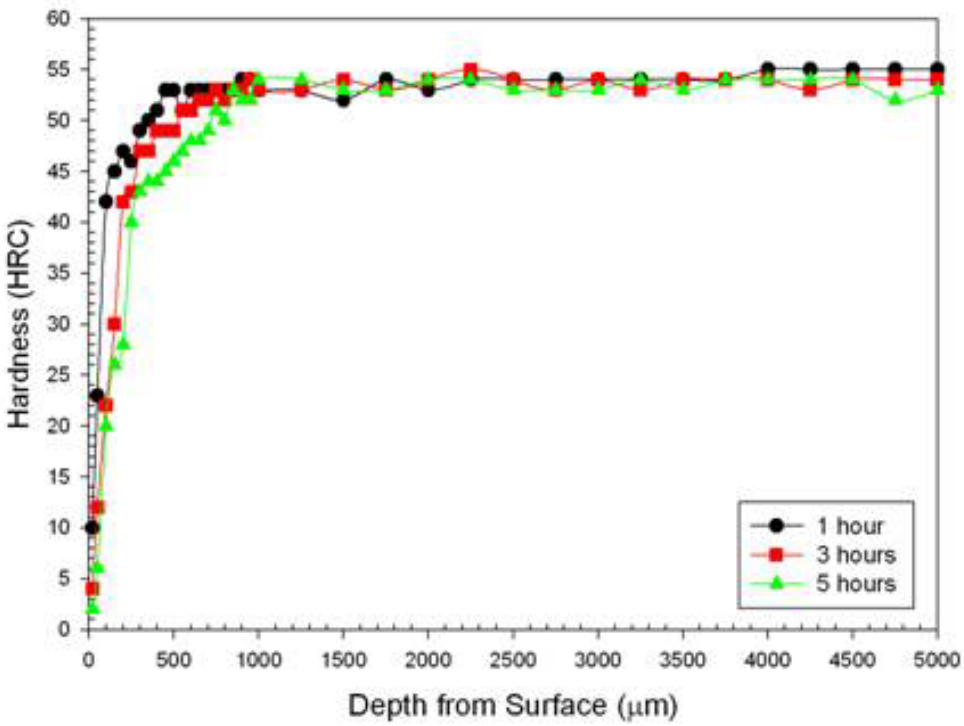
4-1 Heat Treatment without Atmospheric Control

4-1.1 Microhardness Result

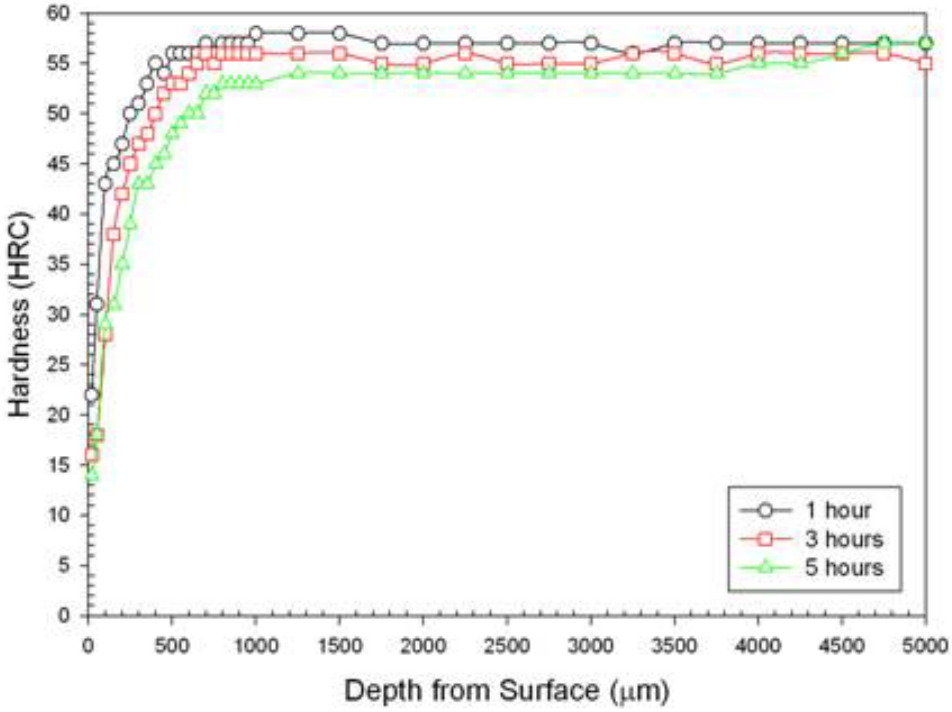
The process of heat treatment without atmospheric control means that the test specimens were heat treated at temperature of 1020°C under the uncontrolled atmospheric condition for various treatment duration. The treatment times were 1 hour, 3 hours and 5 hours and the test specimens were cooled by either fan cooling or water quenching. The following graphs, Figure 4-1-1, show the hardness profile for all samples heat treated without atmospheric control. The symbols circle, square and

triangle signify 1 hour treatment, 3 hours treatments and 5 hours treatments, respectively. The curves with solid symbols are treatment cooled with fan cooling, while curves with open symbols are treatment cooled by water quenching.

Hardness decrease can be found towards the surface region of all samples heat treated without any atmospheric control. The hardness profiles of all samples heat treated without atmospheric show similar characteristics. The hardness at region 100μm underneath the surface increases progressively, then the hardness slowly increases toward the constant state.



(a)



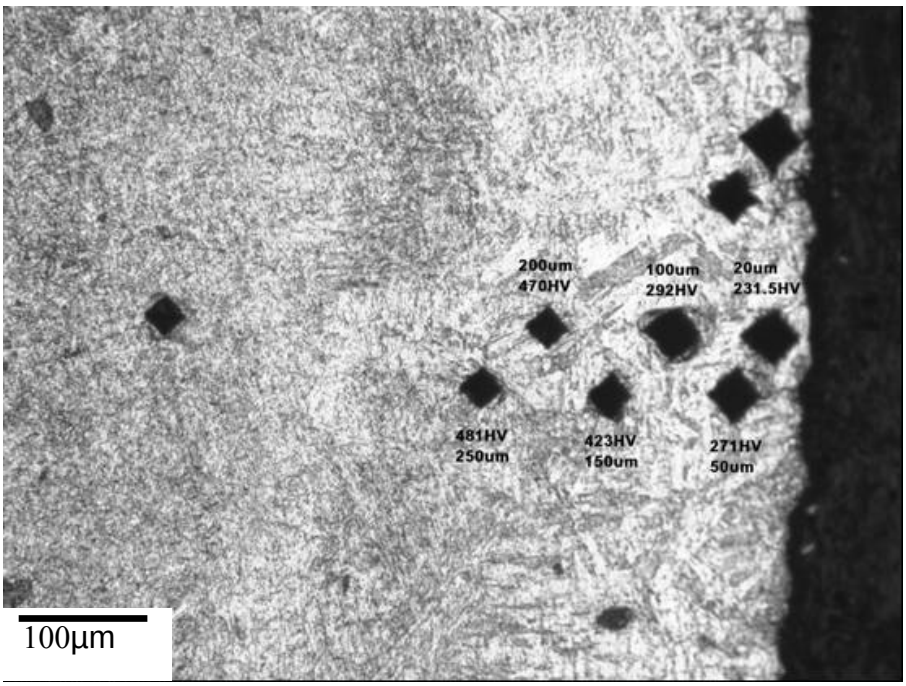
(b)

Figure 4-1-1 Hardness profile of samples heat treated at 1020°C in an uncontrolled atmosphere for 1, 3 and 5 hours followed by (a) fan cooling, and (b) water quench.

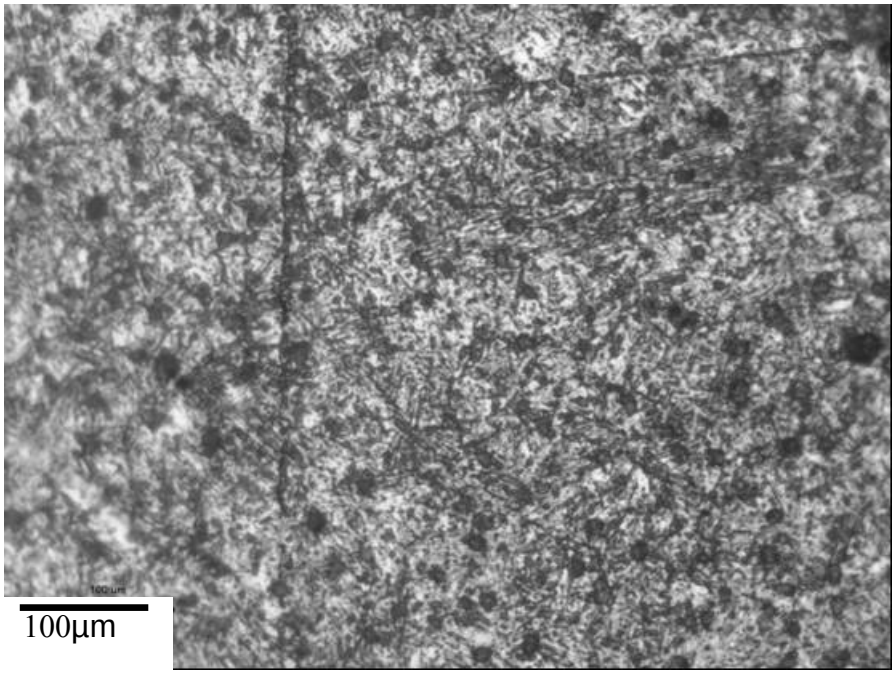
From the graphs shown, in Figure 4-1-1 it can be seen that there is an influence on of the cooling method the material core hardness. The graph shows that samples cooled by water generally have higher hardness values (54-57HRC) than samples cooled by fan air (53-54HRC). The decarburized layer is found to be thicker as treatment time increases. Another notable difference is that the surface hardness (20μm below sample surface), fan cooling samples were lower than those of the water quenched samples. Fan cooling samples had a surface hardness of 2-10 HRC while water quenched samples had a surface hardness of 14-22HRC.

Figure 4-1-2a and b show that there are differences in microstructure between the surface region and the core region after the sample was heat treated with uncontrolled atmosphere. It can be seen from the micrographs that the hardness increases from the surface toward the core, and the microstructure changes with respect to the depth from

the surface. The structure close to the surface was mainly ferrite and martensite begins to appear at the inner part of the sample (Figure 4-1-2b).

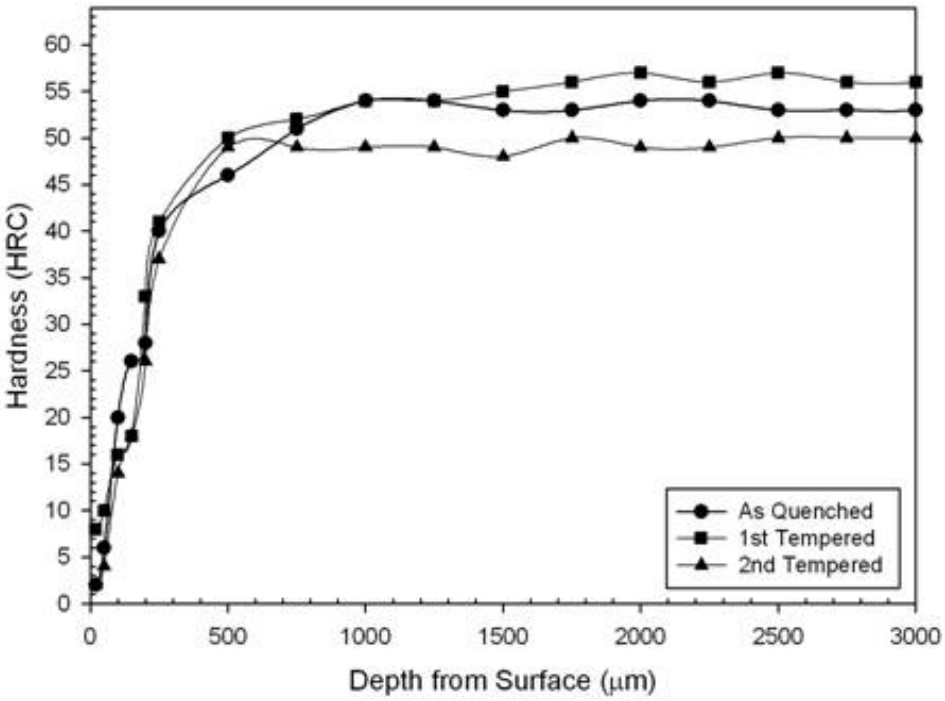


(a)

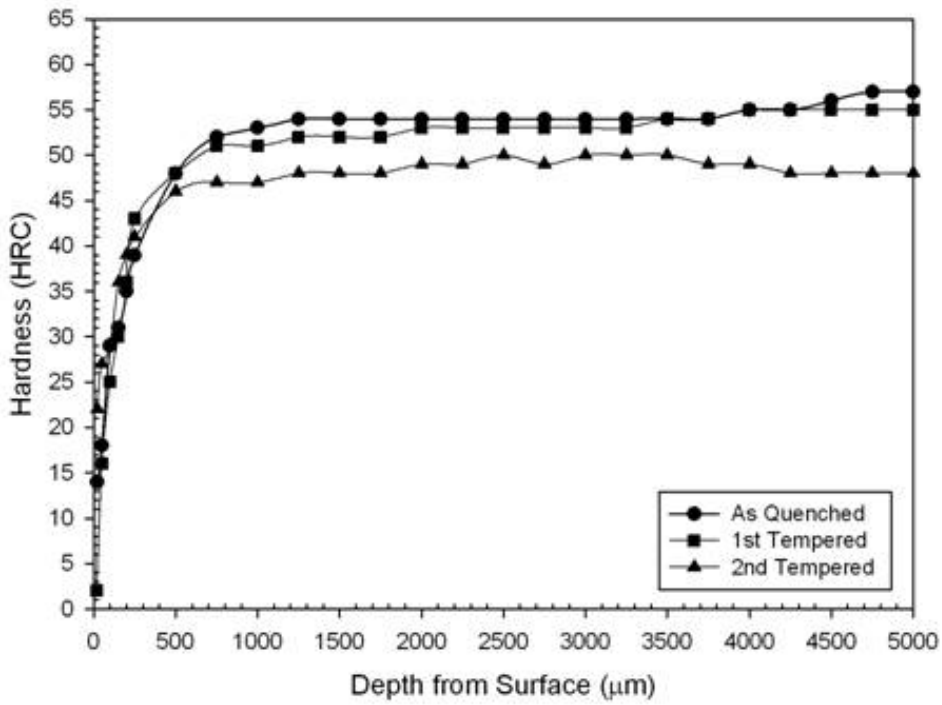


(b)

Figure 4-1-2 Micrograph at as quenched state of sample heat treated at 1020°C in an uncontrolled atmosphere for 5 hours on the(a) surface region with microhardness indention, (b) core region



(a)



(b)

Figure 4-1-3 Comparison of hardness profile of sample heat treated without atmospheric control at 1020 °C for 5 hours in the as quenched, 1st tempered and 2nd tempered conditions (a) fan cooling, (b) water quench

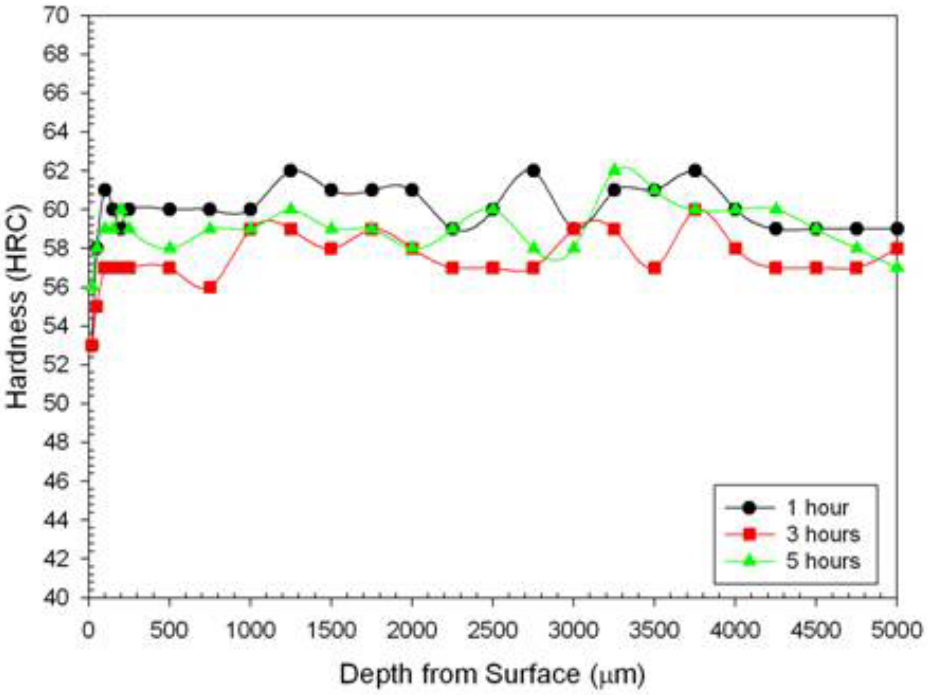
For the tempering characteristic, the results shown are as follows. Since each treatment duration gives similar characteristic trend, only the result of treatment for five hours are shown in Figure 4-1-3.

The graphs show that fan cooling specimens had hardness increase after the 1st tempering stage while water quenched specimens do not show any hardness increase. However, after the 2nd tempering stage, hardness of both fan cooled samples and water quenched samples dropped to around 46 to 48 HRC. Note that the tempering process does not appear to have any effect on the decarburising zone.

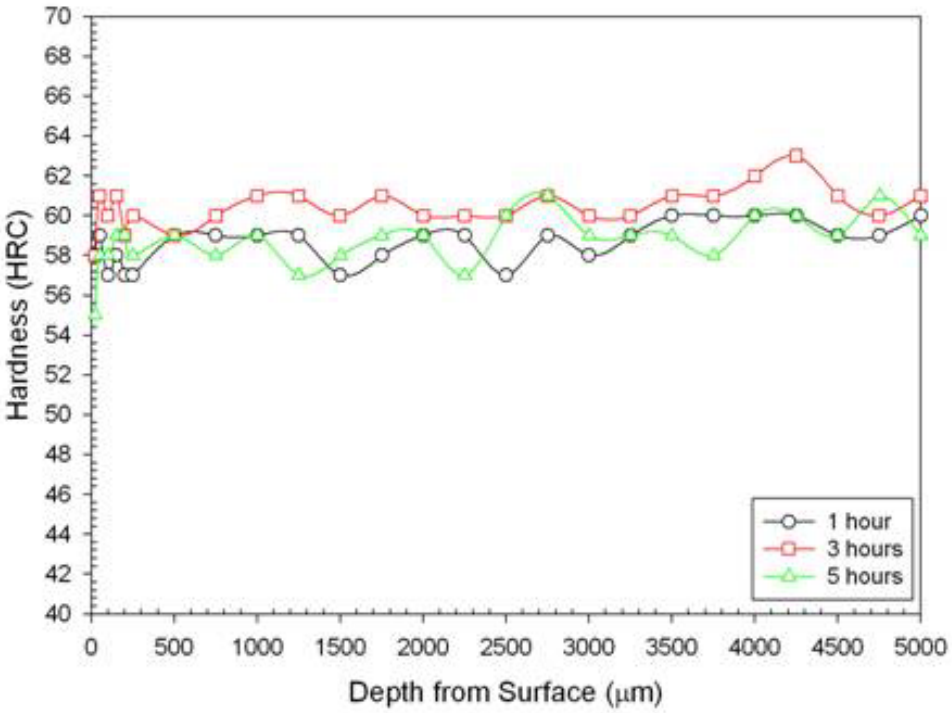
4-2 Heat Treatment with Stainless Steel Foil Wrapping

4-2.1 Microhardness Result

Heat treatment with stainless steel foil wrapping is a method of heat treatment that prevents the heat treated specimen from coming into contact with the surrounding atmosphere. A sheet of stainless steel foil is wrapped around the material in a special way. The whole piece would then be placed in a furnace and heat treated to a temperature of 1020°C for either 1 hour, 3 hours and 5 hours. The cooling methods of fan cooling and water quenching were then applied.



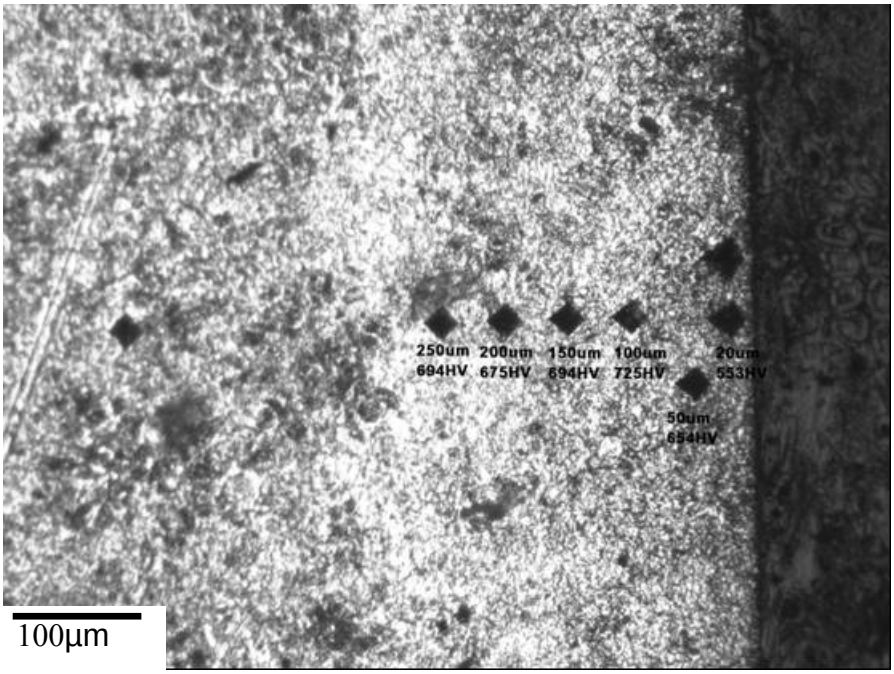
(a)



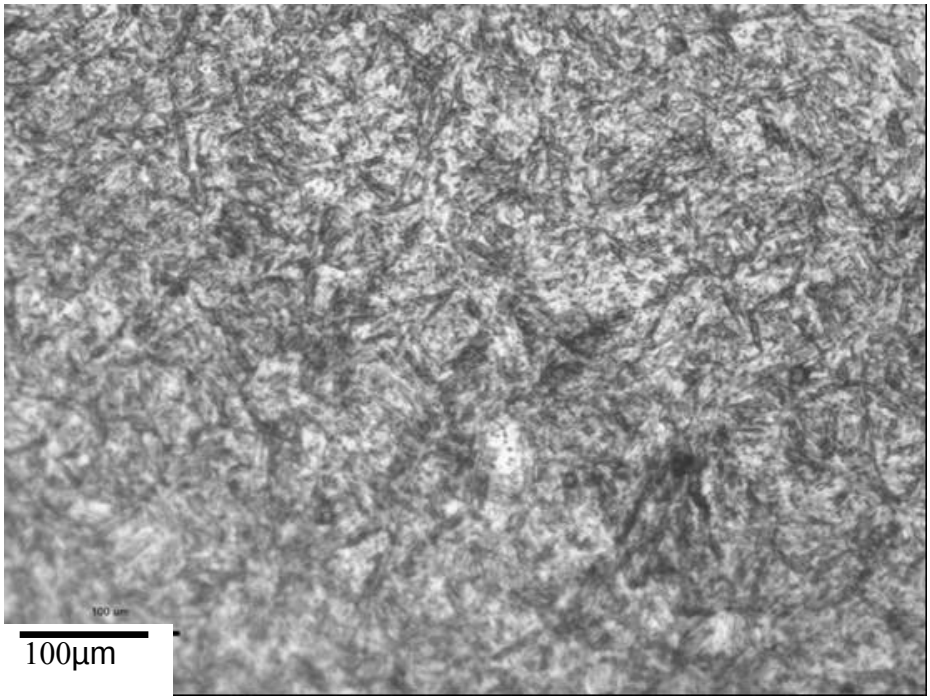
(b)

Figure 4-2-1 Hardness profile of samples heat treated at 1020°C with stainless steel foil wrapping for 1, 3 and 5 hours followed by: (a) fan cooling, (b) water quench.

The hardness profile as shown in Figure 4-2-1 of all the samples heat treated with stainless steel foil wrapping shows a distinct characteristic. Such heat treatment method gives a reasonably constant hardness profile throughout. Although there are variations in terms of hardness, the variations are only 1-2 scale points from the average value, which is acceptable in the industry. The treatment time did not seem to have any direct influence on hardness profile characteristic. The results also show that a slightly drop in hardness can be found around 20μm from the surface.



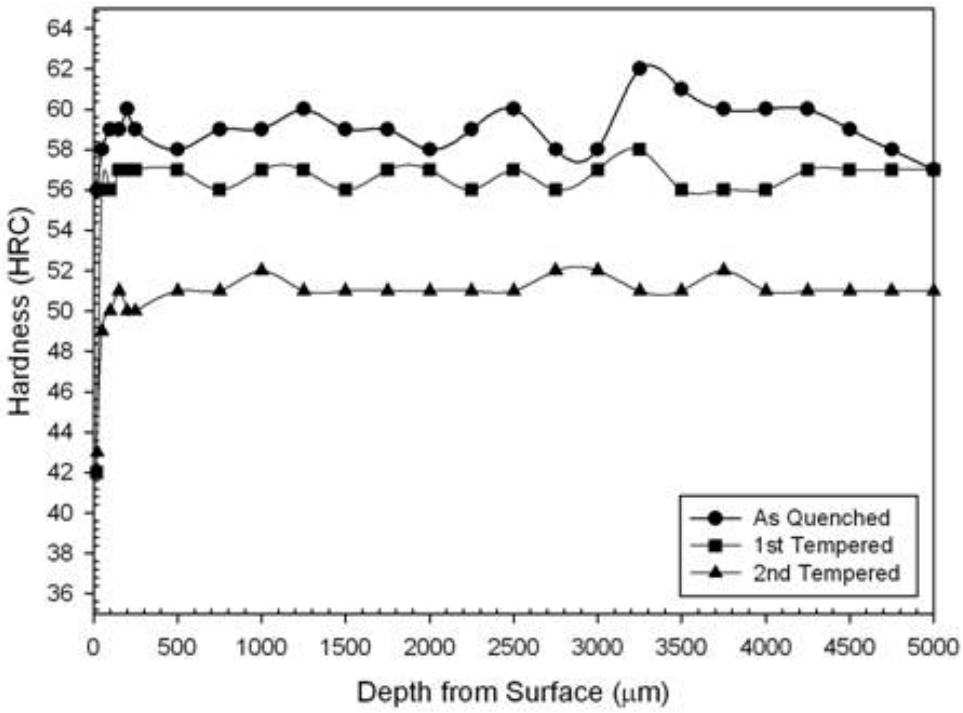
(a)



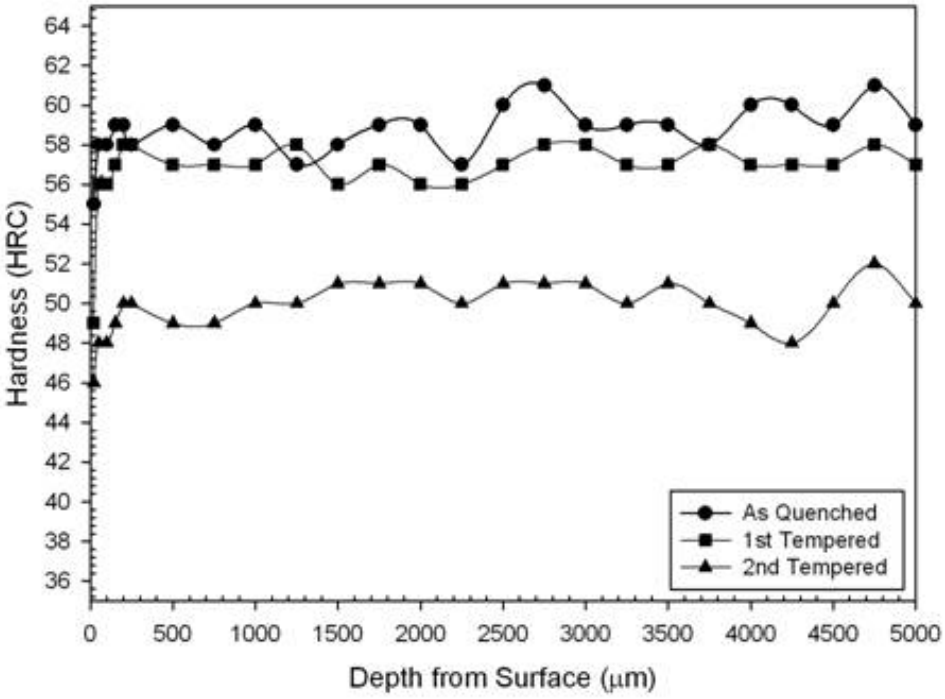
(b)

Figure 4-2-2 Micrograph at as quenched state of sample wrapped with stainless steel foil and heat treated at 1020°C for 1 hour (a) surface region, with microhardness indention (b) core region

The above two micrographs show that the sample contains martensite structure from the surface to the core region. Figure 4-2-2a also shows that the surface hardness remains constant throughout the surface region except for the measurement at 20µm underneath the surface.



(a)



(b)

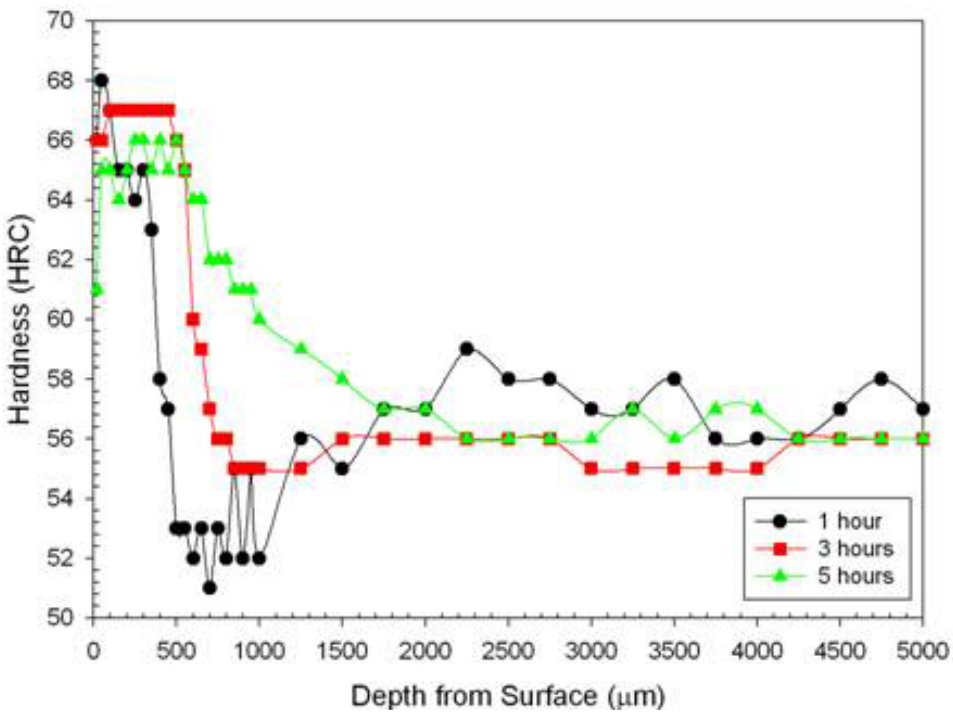
Figure 4-2-3 Comparison of hardness profile of samples heat treated with stainless steel foil wrapping at 1020 °C for 5 hours in the as quenched, 1st tempered and 2nd tempered conditions (a) fan cooling, (b) water quench

The hardness result of the tempered samples are presented in Figure 4-2-3. The graphs show that the 1st tempering process decreases the hardness of the as quenched samples from an average of 59HRC to 57HRC, while the 2nd tempering process further decreases the hardness to around 48-50HRC.

4-3 Pack Carburized Heat Treatment

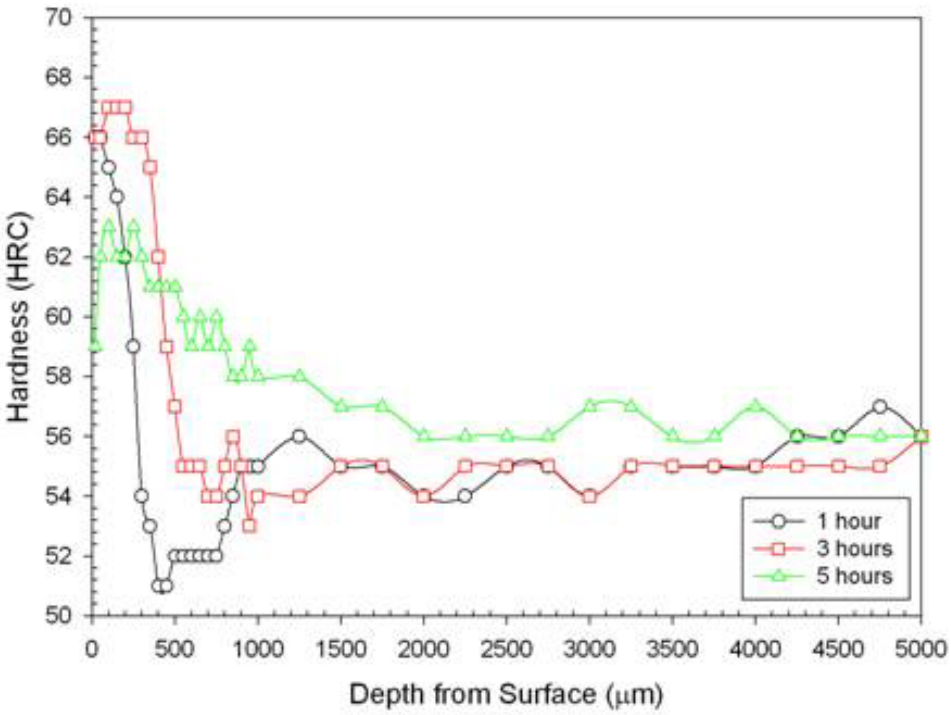
4-3.1 Microhardness Result

Pack carburized heat treatment is a heat treatment process whereby the specimens were placed into a pack of charcoal at 1020°C for a period of treatment. The three treatment duration periods are the same as the previous two atmospheric conditions: 1 hour, 3 hours and 5 hours. Two types of cooling method were used as previous experiments: fan cooling and water quenching.



(a)

Figure 4-3-1 Hardness profile of samples of pack carburization heat treated at 1020°C for 1, 3 and 5 hours followed by: (a) fan cooling, (b) water quench.



(b)

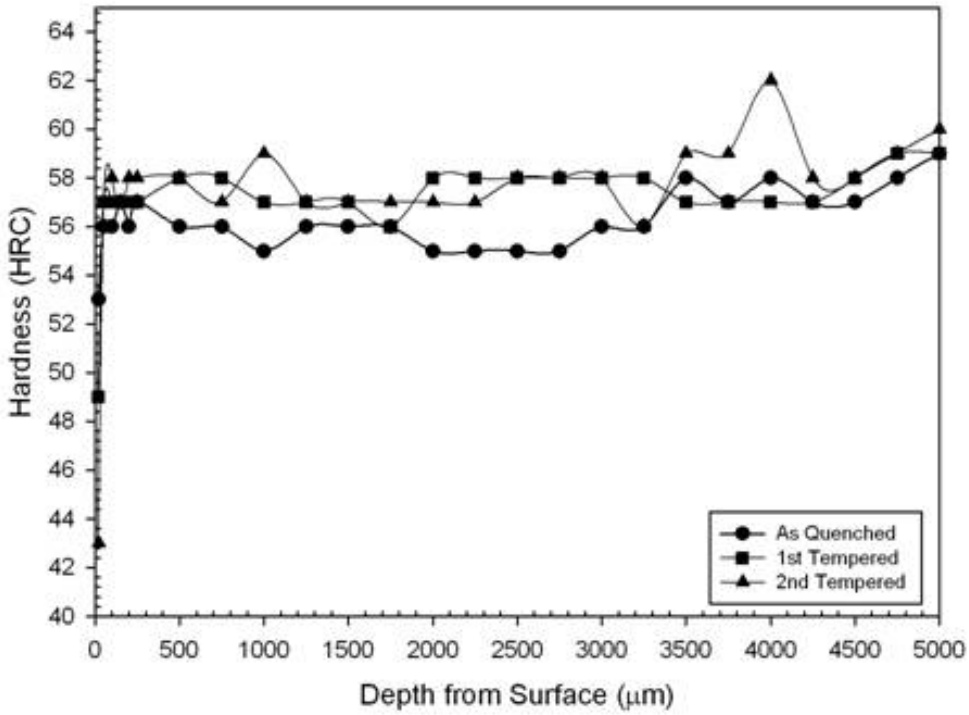
Figure 4-3-1 cont.

From the results shown in Figure 4-3-1, all the samples experienced a hardening effect on the surface. Beyond the carburized layer, the hardness of all pack carburized samples were approximately the same. It must be noticed that the hardness at region 500μm-1000μm was comparably lower than its core hardness for samples heat treated for 1 hour. This difference does not show in samples heat treated for 3 hours and samples heat treated for 5 hours.

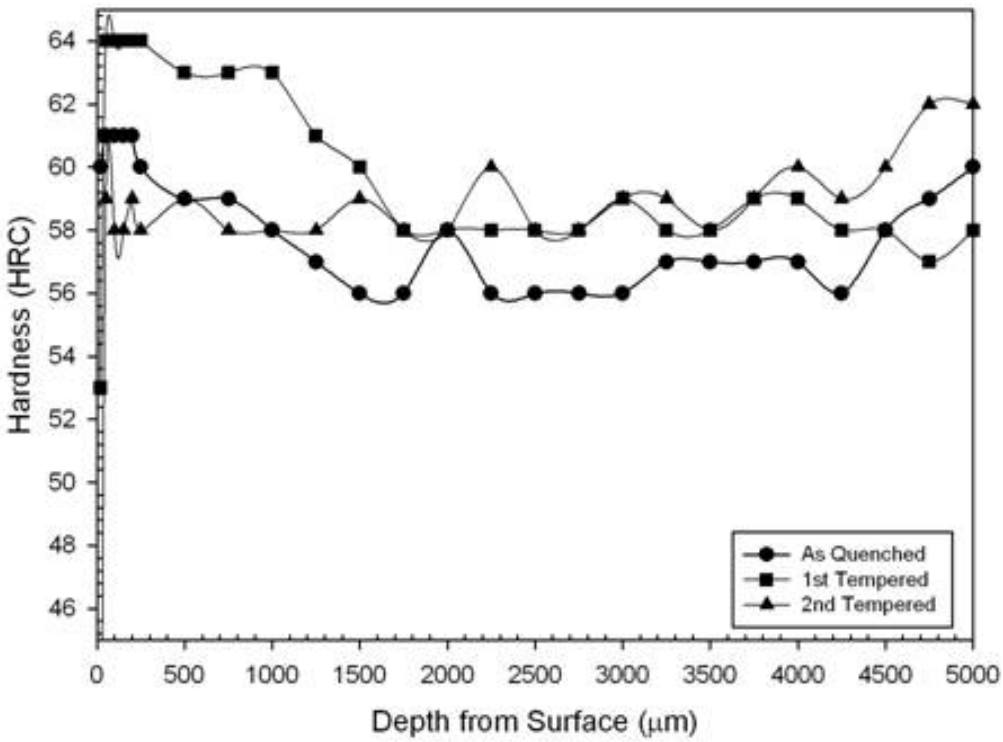
By studying the hardness profile of the surface region up to 500μm from the edges, it can be seen that as the treatment time becomes longer, the surface hardness increases respectively. The graphs also show that samples cooled by water in fact have lower surface hardness than samples cooled by fan cooling.

The 1st tempered and 2nd tempered hardening characteristic for pack carburized heat treatment is shown in Figure 4-3-2.

Hardness increase can be found in the carburized samples cooled by fan cooling after the 1st tempering stage. The improvement in hardness after the 1st tempering process is especially significant at the central region of the sample. It was increased from 56HRC to 58HRC. The 2nd tempering stage does not show any effect on hardness change.



(a)



(b)

Figure 4-3-2 Comparison of hardness profile of samples pack carburized heat treated at 1020 °C for 5 hours in the as quenched, 1st tempered and 2nd tempered conditions (a) fan cooling, (b) water quench

However, if the carburized samples were cooled by water quench, after the 1st tempering stage, secondary hardening effect can be found throughout the samples and is especially dominant at the surface region. An increase in hardness can be found at region 1000μm underneath the surface. After the 2nd tempering process, the hardness profile became constant with hardness at around 59HRC, the similar hardness as the core hardness of the 1st tempered condition.

4-4 Vacuum Heat Treatment

4-4.1 Microhardness Result

Samples from the vacuum heat treatment experiments were obtained by holding the samples in a vacuum furnace at 1040°C for 1 hour, 1.5 hours and 2 hours followed by vacuum furnace cooling under 2 bar pressure of N_2 at a rate of 30°C/minute. The

treatment durations and the cooling method were different from other experiments because of the limitations of practical difficulties.

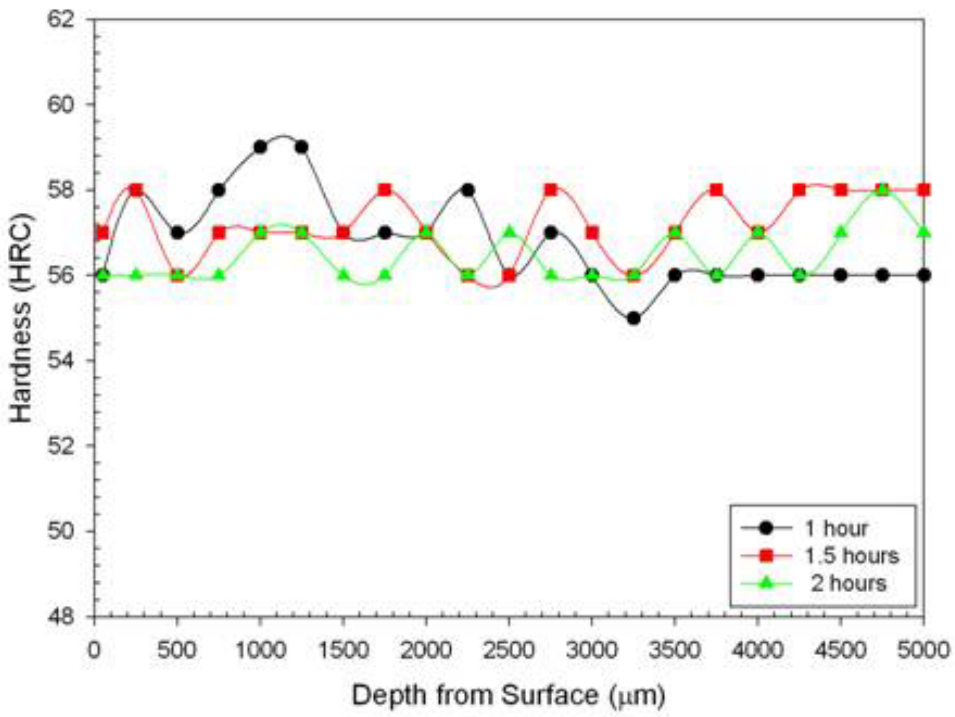
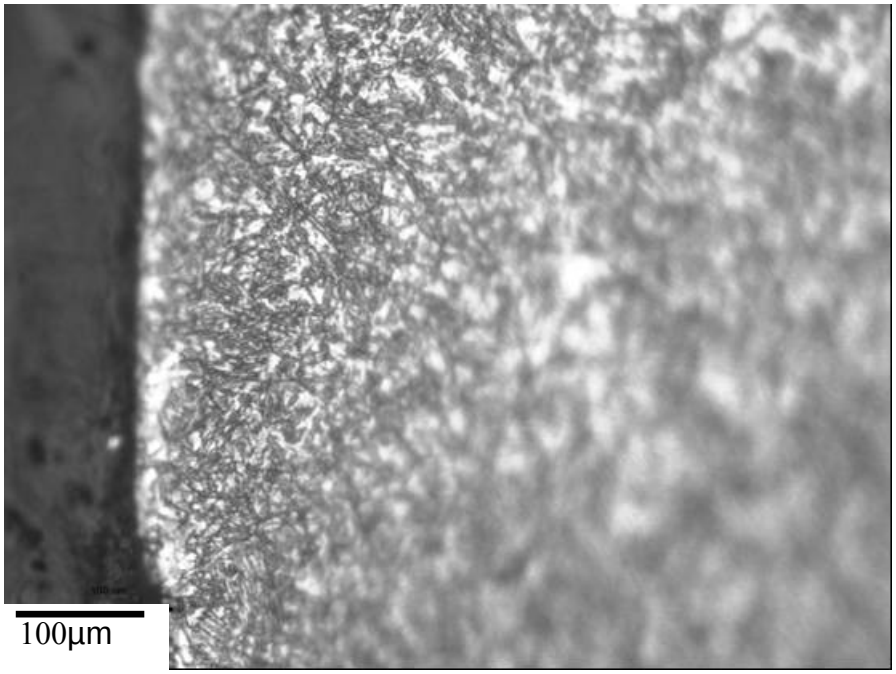


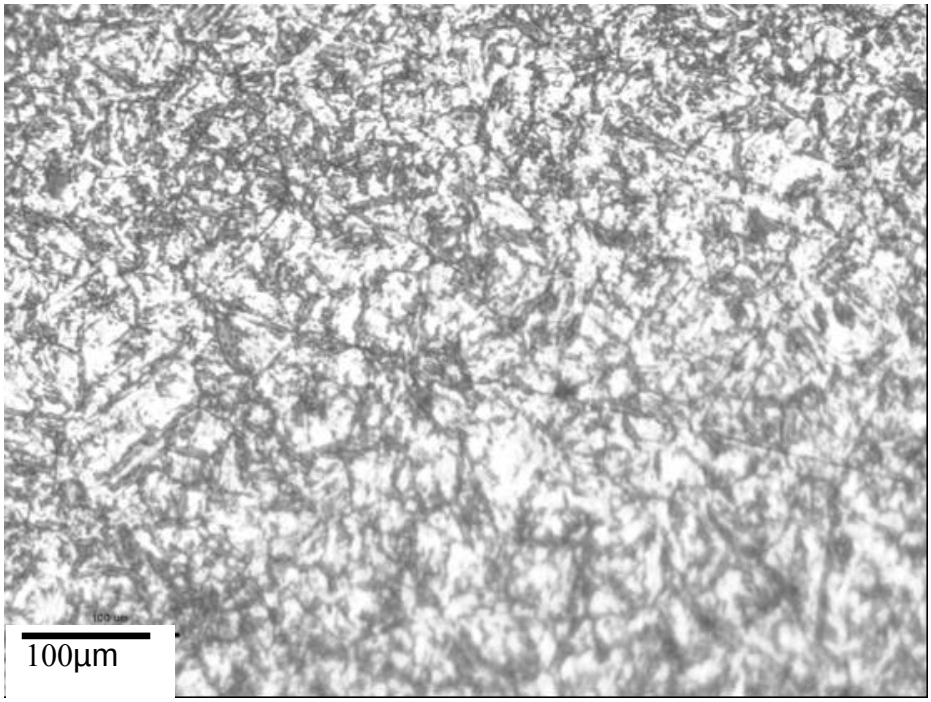
Figure 4-4-1 Hardness profile of samples vacuum heat treated at 1, 1.5 and 2 hours followed by vacuum cooling

As shown in Figure 4-4-1, there is no indication suggesting that the time of heat treatment has significant effect on the hardness of the as quenched samples. All as quenched samples have a similar hardness level. The hardness profile of each sample is reasonably constant. No decarburization layer or carburization layer is found. The hardness varies one or two scale points at around 57HRC. There is only a slight indication, if any, that if the treatment duration increases, the level of hardness variation is lower.

The micrographs in Figure 4-4-2 show that martensite is formed on most of the area including the surface region and the core region.



(a)



(b)

Figure 4-4-2 Micrograph at as quenched state of sample heat treated at 1040°C with vacuum furnace for 1.5 hours (a) surface region, (b) core region

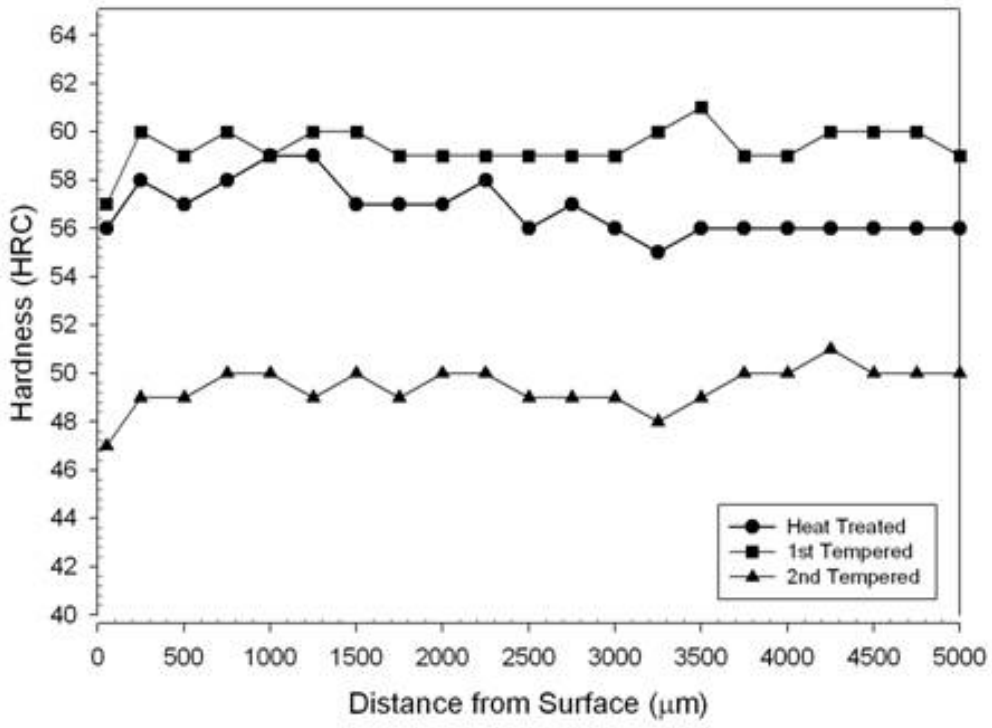


Figure 4-4-3 Comparison of hardness profile of samples heat treated in vacuum furnace at 1040°C for 1 hour in the as quenched, 1st tempered and 2nd tempered conditions

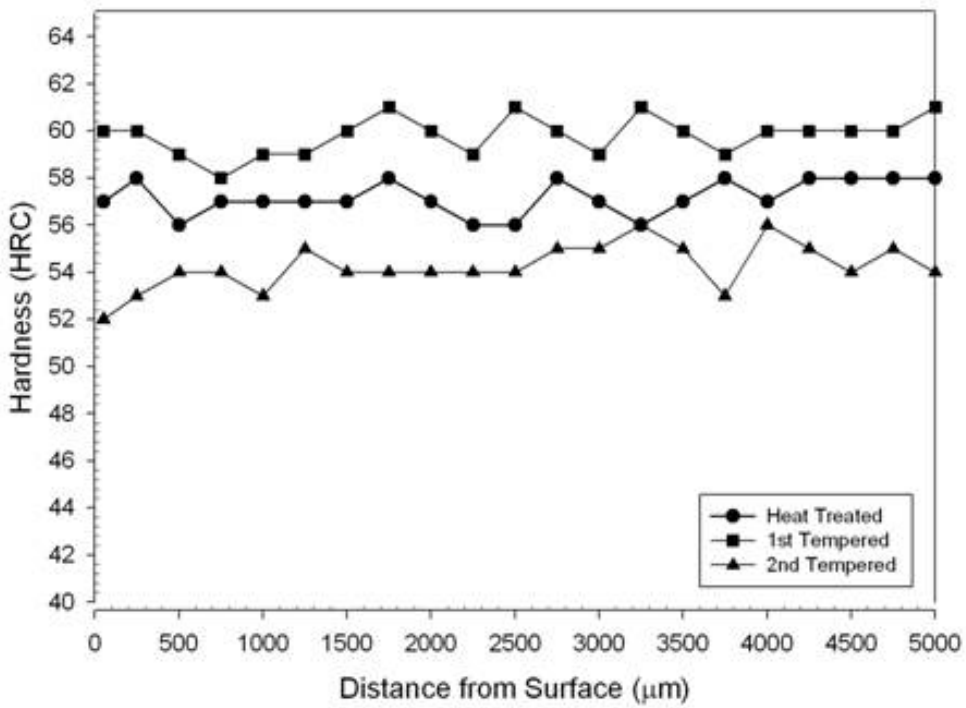


Figure 4-4-4 Comparison of hardness profile of samples heat treated in vacuum furnace at 1040°C for 1.5 hours in the as quenched, 1st tempered and 2nd tempered conditions

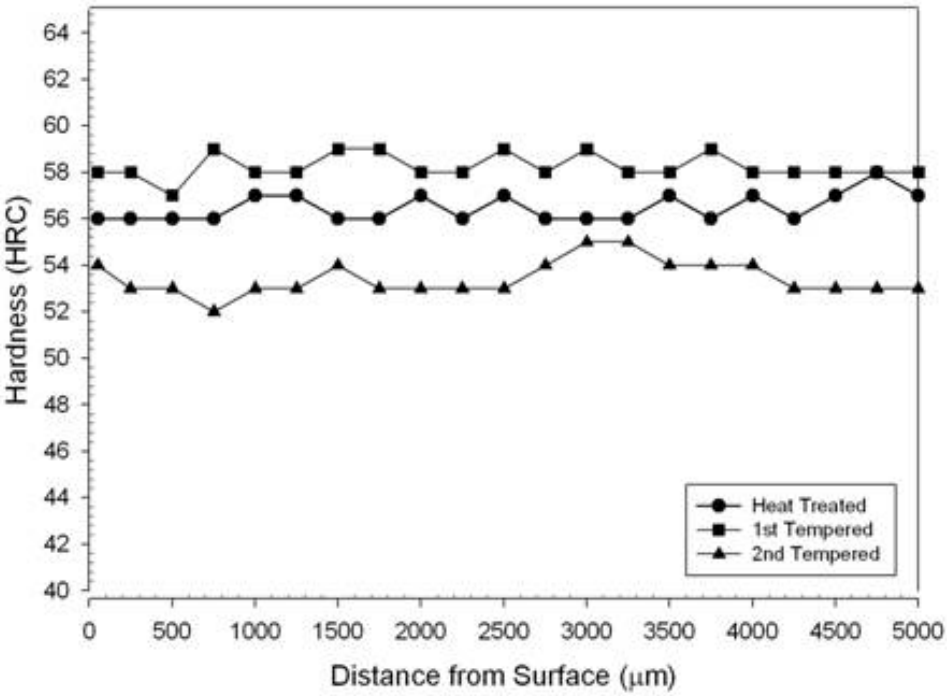


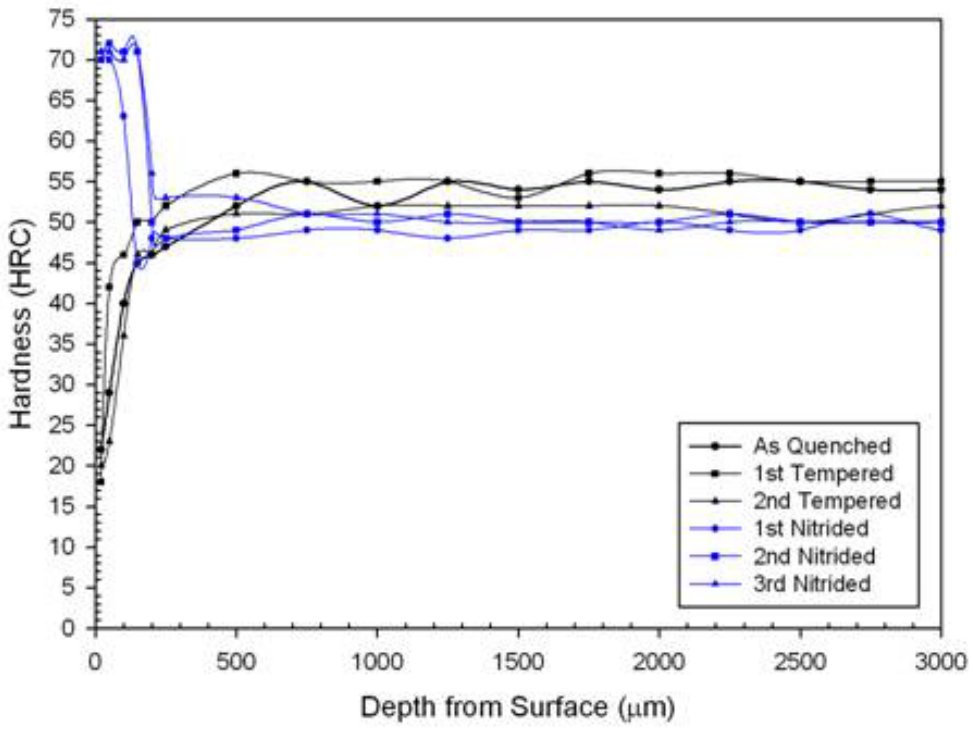
Figure 4-4-5 Comparison of hardness profile of samples heat treated in vacuum furnace at 1040°C for 2 hours in the as quenched, 1st tempered and 2nd tempered conditions

The hardness results obtained from the 1st tempered and 2nd tempered samples are analysed and are presented in Figure 4-4-5. At first, all three graphs express similar characteristics. After the 1st temper, the material hardness increased, then it decreased below the as quenched hardness after the 2nd tempered process. Comparing the three graphs, it can be concluded that the hardness variation between the 1st tempered stage and 2nd tempered stage becomes narrower as treatment time increases.

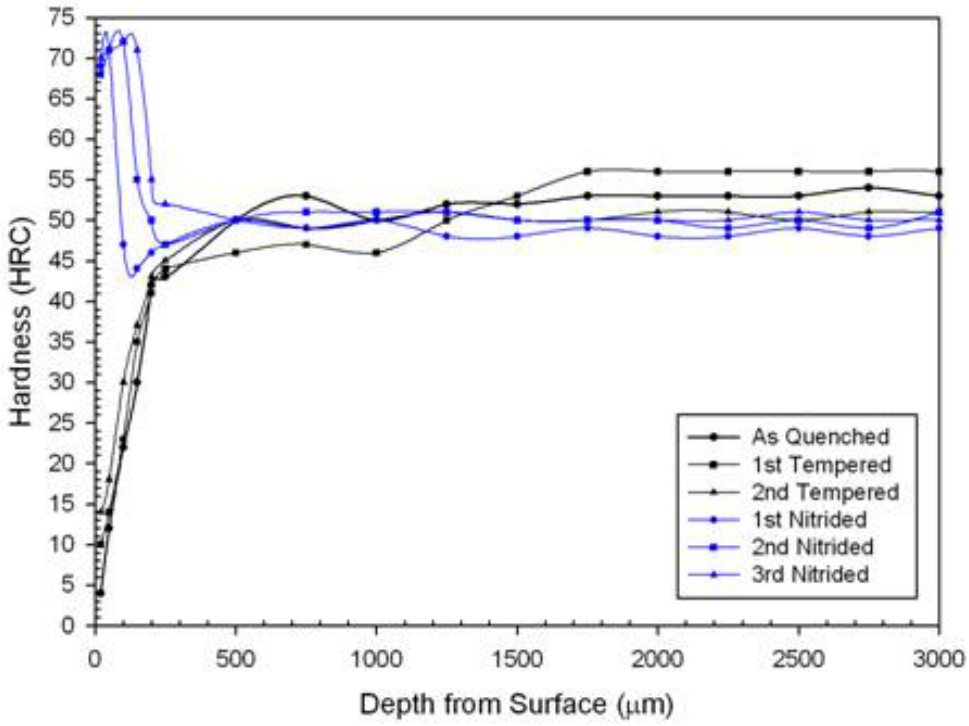
4-5 Nitriding Case Hardening Results

For each heat treating condition, the samples were further hardened by gas nitriding process. The blue lines are hardness profile results of the nitrided samples and the black lines are hardness profile results from as quenched state, 1st tempered state and 2nd tempered state. The hardness profiles of each heat treated sample are shown according to their hardening process atmospheric condition.

4-5.1 Heat Treatment without Atmospheric Control

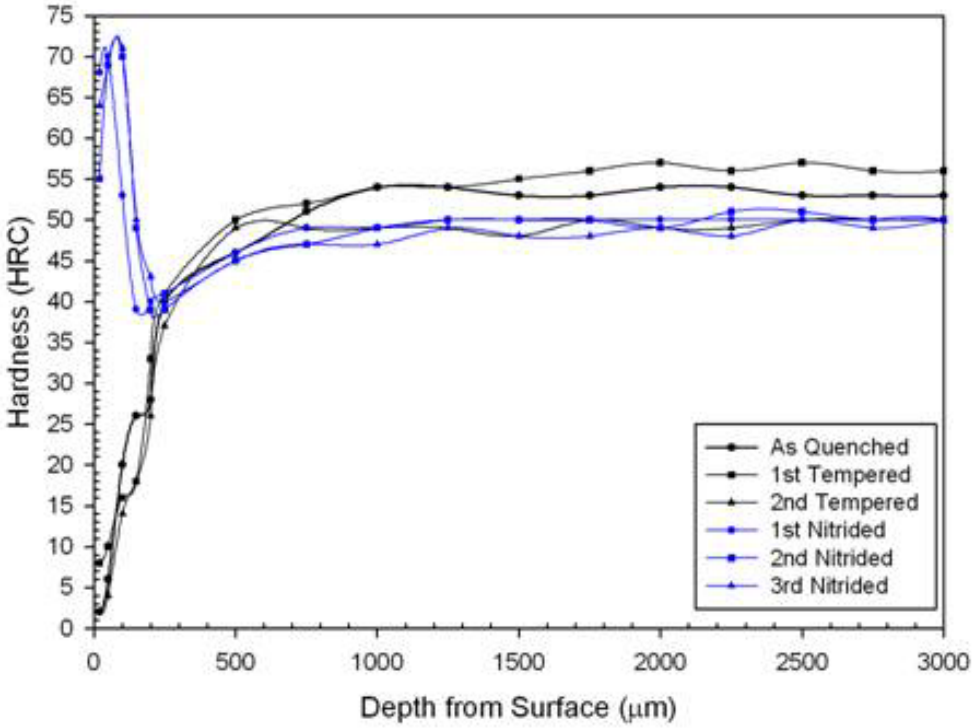


(a)



(b)

Figure 4-5-1 Hardness profile of gas nitrided sample heat treated without atmospheric control at 1020°C followed by fan cooling (a) 1 hour heat treatment, (b) 3 hours heat treatment, (c) 5 hours heat treatment

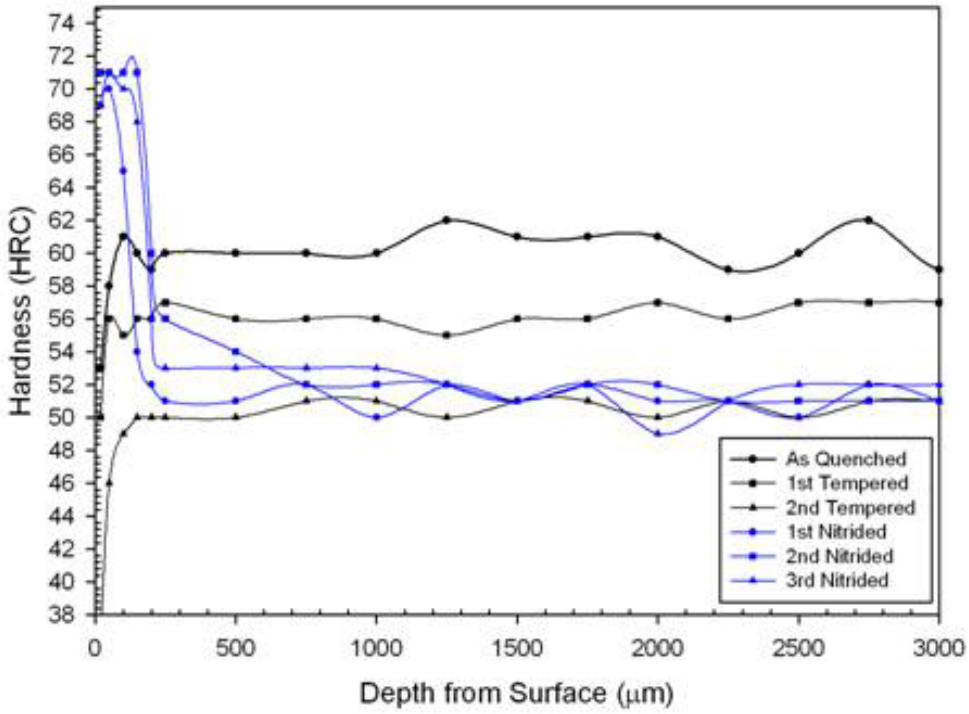


(c)

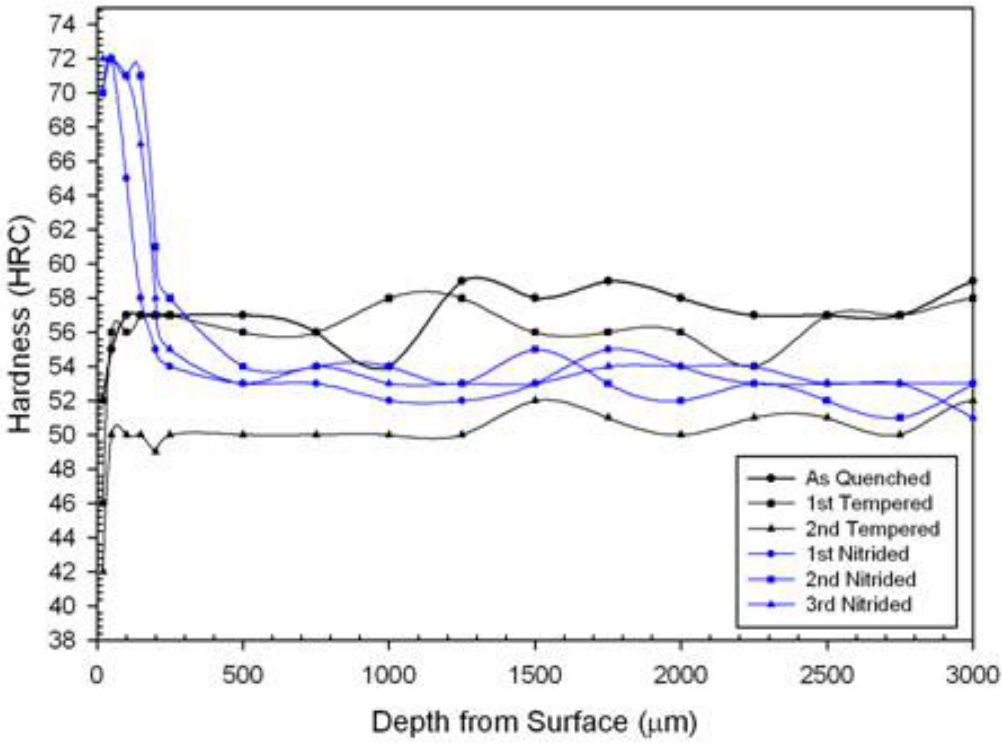
Figure 4-5-1 cont.

The graphs from Figure 4-5-1 show that even if with a decarburized layer, the nitriding process can still increase the surface hardness significantly up to a certain depth from the surface. The peak hardness is somewhere at 70-73HRC. Results indicate that except for the 3rd nitriding process, both the 1st nitriding and 2nd nitriding processes result in hardness improvements after the nitriding process. With increasing heat treatment duration, the surface hardness (20μm underneath the surface) became lower respectively. However, the surface hardness was increased with the number of times of nitriding process. As presented in Figure 4-5-1c, the surface hardness was increased from 55HRC to 71HRC after two times of extra nitriding process.

4-5.2 Heat Treatment with Stainless Steel Foil Wrapping

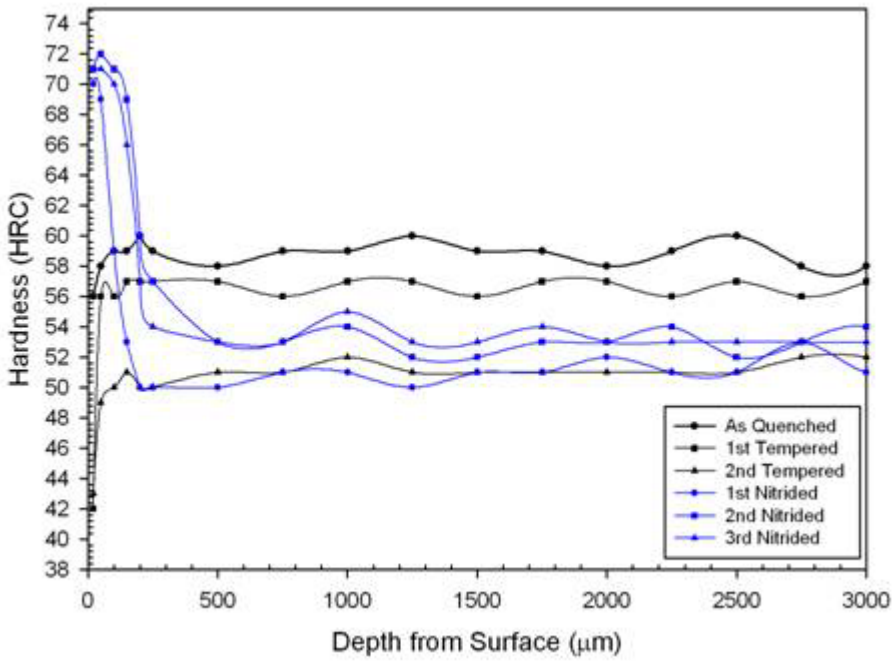


(a)



(b)

Figure 4-5-2 Hardness profile of gas nitrided sample heat treated Stainless Steel Foil Wrapping at 1020°C followed by fan cooling (a) 1 hour heat treatment, (b) 3 hours heat treatment, (c) 5 hours heat treatment

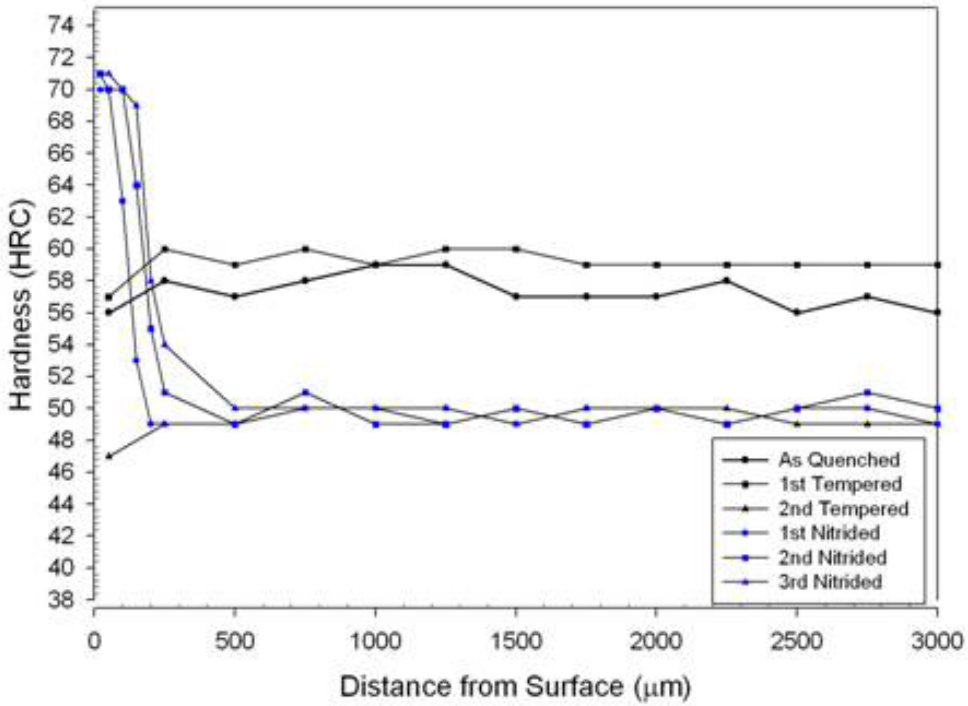


(c)

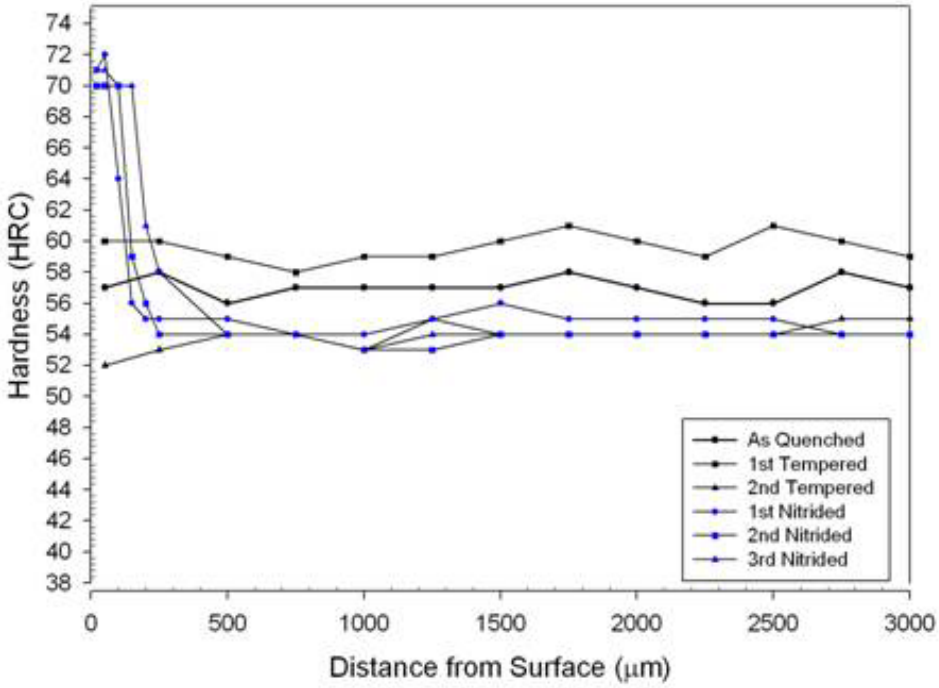
Figure 4-5-2 cont.

It can be seen that after the nitriding process, the hardness at region 500μm from the surface increased dramatically. All results show that there is an improvement on surface hardness after the nitriding process except the 3rd nitriding. Compared to the hardness profile of the 2nd nitriding process, there is no indication of significant improvement in terms of hardness property for the 3rd nitriding process. Except for the results of the 3 hours heat treatment, the core hardness of nitrided samples is approximately the same as the hardness of the 2nd tempered samples.

4-5.3 Vacuum Heat Treatment

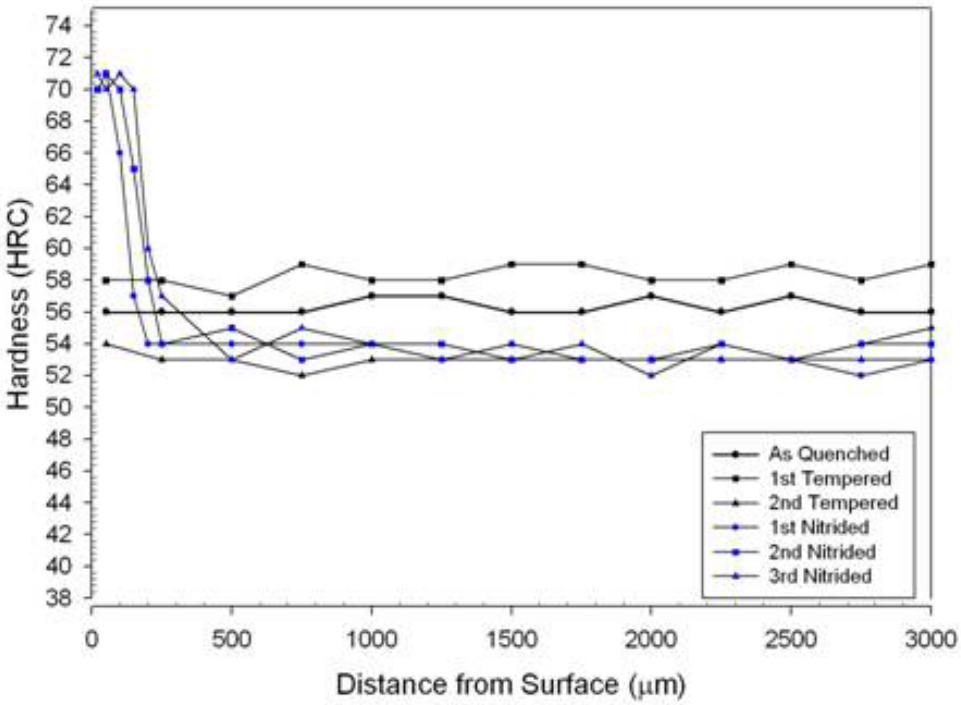


(a)



(b)

Figure 4-5-3 Hardness profile of gas nitrided sample heat treated with vacuum furnace at 1040°C followed by fan cooling for (a) 1 hour heat treatment, (b) 1.5 hours heat treatment, (c) 2 hours heat treatment



(c)

Figure 4-5-3 cont.

The three graphs in Figure 4-5-3, showed an increase in hardness on the surface region after gas nitriding. The hardened surface layer became thicker as gas nitriding process was conducted longer. However, if the graphs are studied closely, they show that the hardened layer difference in thickness between 3rd nitrided and 2nd nitrided samples is smaller than the difference in thickness between 2nd nitrided and 1st nitrided samples. Results also show that the hardness below the hardened layer remains the same level as the hardness at 2nd tempered condition.

Chapter 5 Analysis and Discussion

As expected from literature research, results from the previous chapter clearly show that the austenizing atmosphere condition has a dominant effect on the hardness profile of the hardened material. The carbon profile characteristic basically can be divided into three main groups:

- Decarburization,
- Constant hardness profile, and
- Carburization.

Discussion about the nitriding characteristic with respect to the heat treatment method will be conducted in the last part of this chapter.

Carbon diffusion can proceed at any time and at any temperature. Thus, carbon may escape to the surrounding from the material at temperatures above 500°C after the formation of iron oxide. However, the carbon diffusion effect during the preheating stage can be neglected. It is because figures from Table 4 show that carbon diffusion

rate in ferrite and cementite is negligible in comparison with the carbon diffusion rate in austenite. Thus, it is reasonable to picture the carbons kinetic during austenitization without considering the carbon diffusion during the preheating stage.

One of the aims of this investigation is to monitor carbon diffusion indirectly by studying the martensitic hardness profile of the quenched material. It is known if the cooling rate is not sufficiently high, bainite or pearlite may form during the quenching step. This can reduce the accuracy of the conversion between martensite hardness and material carbon content. However, Babu et al. (46) confirms full martensite structure can be achieved if the material is cooled to 300°C within 1000 seconds. Since most of the treated samples were quenched to room temperature within 1000 seconds due to the small sample size, it can be assumed full martensitic structure was produced. Since the presence of retained austenite does not have a significant contribution to martensite hardness unless the carbon content is over 0.7wt% (24), the carbon content at as quenched state can be estimated indirectly by measuring the martensite hardness.

5-1 Decarburization

Hardness profile of samples heat treated without atmospheric control have revealed the formation of a decarburized layer. From the results shown in Section 4-1, there is no indication that the treatment time has affected on the equivalent hardness at the core after the as quenched stage, but it does influence the thickness of the decarburized layer. Through the software SigmaPlot, the following model can be constructed based on the data from Figure 4-1-1:

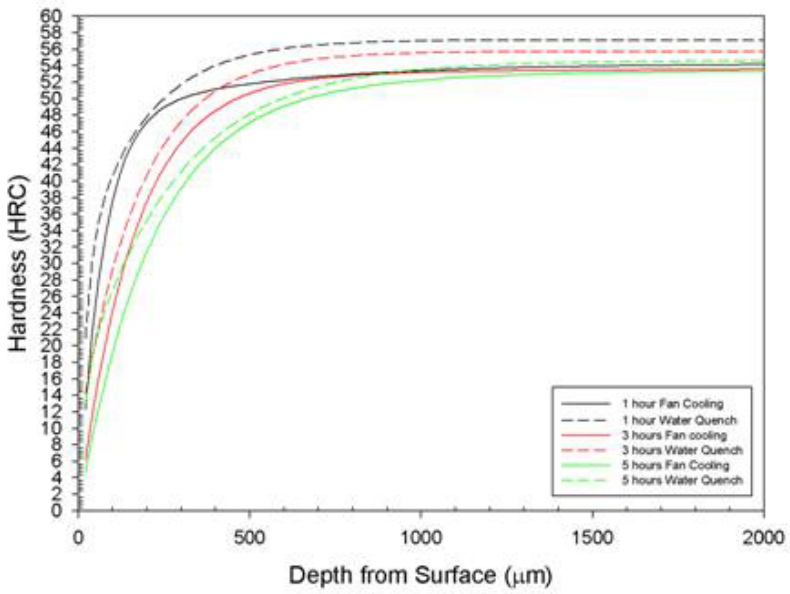


Figure 5-1-1 Regression model for heat treatment without atmospheric control

Compared to the following graph (Figure 5-1-2) provided by Pickering (52), the quenched hardness at core region obtained from this investigation (Figure 5-1-1) matches the predicted value. This indicates that the experiment was conducted similar to industrial practice.

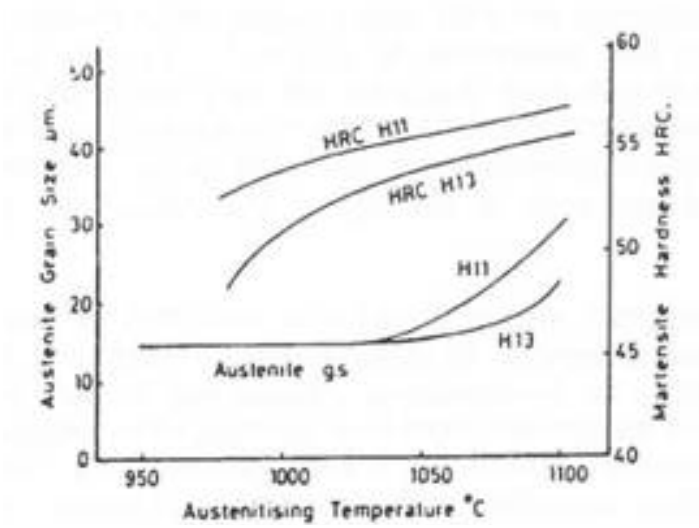


Figure 5-1-2 Effect of austenitzing temperatures on as quenched hardness (52)

The steel is said to be decarburized if the carbon content is lost and becomes lower than the initial carbon content. The distance measured from the point of drop in carbon content until the point reaching the initial carbon content is termed the total depth of decarburization. However it is difficult to determine due to the asymptotic manner and is practically insignificant in the industry. Thus, the effective depth of decarburization is used. It is defined as surface distance at ~0.9 of initial carbon content (39, 53).

For this investigation, the carbon content profile is difficult to define without the use of special equipment. Instead, -2 HRC of the core hardness was used as a guide to determine the effective decarburization depth. If the average core hardness is 56HRC, the effective decarburization depth would be the point where the hardness reaches 54HRC. This guide was used because +/- 2HRC is an acceptable value in the heat treatment industry. Through that, the relationship between treatment time and the decarburization layer thickness can be constructed. This is presented in Figure 5-1-3.

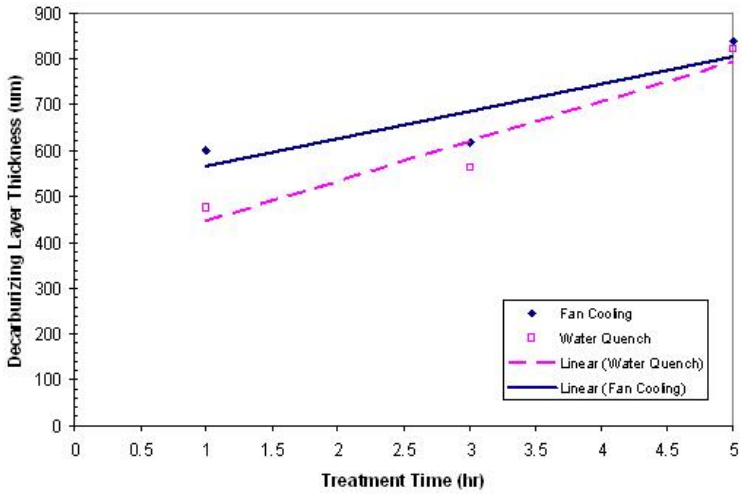


Figure 5-1-3 Graph of decarburization layer thickness

In comparison with the Thelning's (26) decarburization result shown in Figure 2-1-3a, the result of this investigation closely matches his model. Two hours of uncontrolled atmosphere heat treatment process gives a decarburization layer thickness of ~0.550mm.

Figure 5-1-3 shows the linearization does not cross the origin of the graph. This is because the rate of decarburization is governed by two simultaneous processes mentioned in Chapter 2: the surface activity and the diffusion of carbon. Thus, the diffusion of carbon during austenization is discussed here.

Using the Van-Ostrand-Dewey solution (equation 10) given in Chapter 2, the carbon profile can be modelled as:

$$C_x = C_s + erf\left(\frac{X}{2\sqrt{Dt}}\right) \times (C_0 + C_s) \qquad (13)$$

Unfortunately, the carbon diffusivity in H13 steel is not yet well published. None of the publications were able to provide such a value (10, 14, 17, 44-46), so there is a need to determine the figure using the experiment result. In this investigation, the carbon diffusivity is assumed to be independent of carbon concentration. Thus, by combining equation 7 with equation 13, it is transformed and gives the following:

$$C_x = C_s + erf\left(\frac{X}{2\sqrt{[D_0 \exp(-\frac{E}{RT})]t}}\right) \times (C_0 + C_s) \qquad (14)$$

Through the application of the carbon profile equation (equation 14) and setting D_0 as 0.12 (given in Equation 9), the initial carbon content as 0.4, the temperature as 1293K

and t as 3600sec, 7200sec and 18000sec for 1 hour treatment, 3 hours treatment and 5 hours treatment respectively, a theoretical carbon content profile at as quenched state after heat treatment without atmosphere control at 1020°C can be constructed. Through this equation, it was found that the carbon activation energy is 20200cal/mol, which gives the carbon diffusivity in H13 steel to be somewhere around 1.97×10^{-8} cm^2/s at temperature of 1020°C by equation 7. And the equilibrium surface carbon content is around 0.14wt%. Figure 5-1-4 shows the comparison between the theoretical loss of the carbon content and the as quenched hardness profile result of those samples heat treated without atmospheric control.

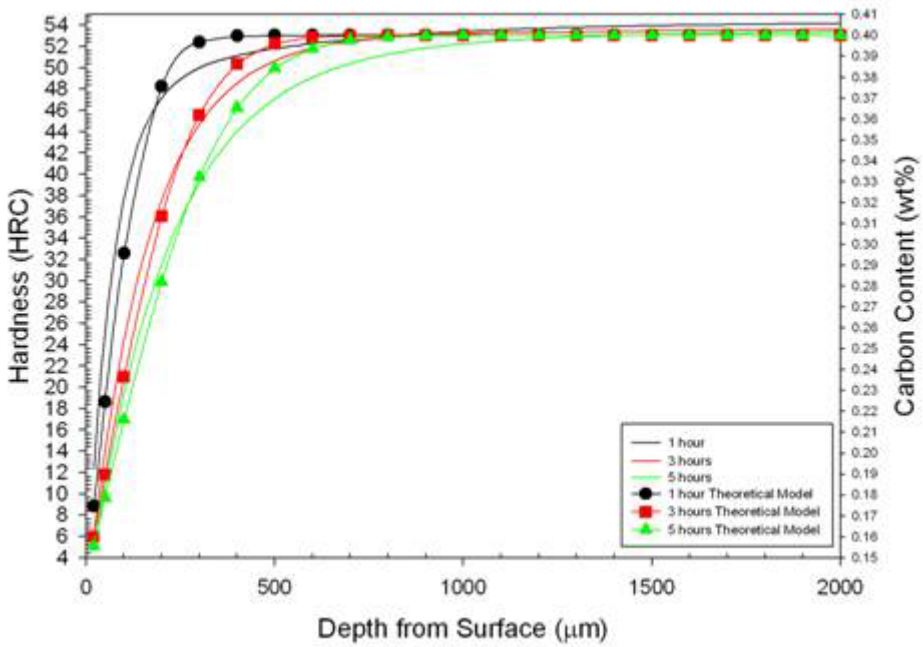


Figure 5-1-4 Comparison between the experimental value of heat treatment without atmospheric control at 1020°C followed by fan cooling and theoretical model

Although equation 14 cannot perfectly match the experimental value, it describes the decarburization kinetic reasonably well. By assuming full martensite structure was obtained, a relationship between H13 martensite hardness and carbon content as Figure 2-3-2 can also be constructed.

This shall be a reliable model because through equation 2, 3 and 4, the equilibrium carbon content on the metal surface can be calculated as follow:

$$\log f_c = \frac{2300}{T} - 2.24 + (\frac{179}{T})(wt\%C) - (\frac{102}{T} - 0.033)(wt\%Cr)$$
$$\log f_c = \frac{2300}{1293} - 2.24 + (\frac{179}{1293})(0.4) - (\frac{102}{1293} - 0.033)(5)$$
$$\log f_c = -0.63525$$
$$f_c = 0.23161$$

And,

$$\log K = -\frac{8918}{T} + 9.1148$$
$$\log K = -\frac{8918}{1293} + 9.1148$$
$$K = 165.3719$$

Also the partial pressure P_{CO} and P_{CO_2} at the operation temperature can be defined using the carburization/decarburization reaction equilibrium diagram as follow:

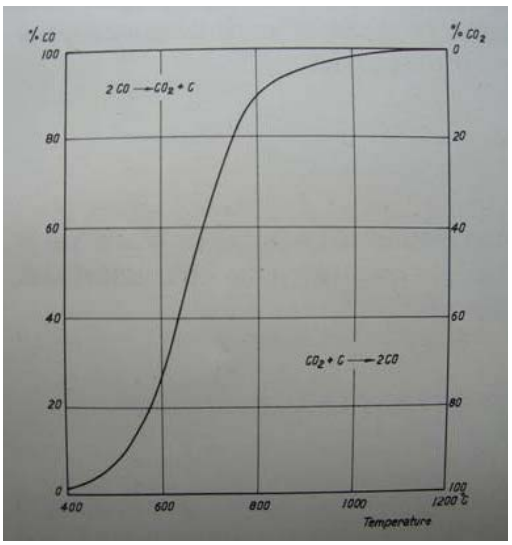


Figure 5-1-5 Equilibrium diagram for carburization/decarburization reaction at pressure of one atmosphere (26)

where the %CO and % CO_2 at 1020ºC are found to be 98% and 2% respectively (Figure 5-1-5).

The equilibrium weight carbon content on surface can be found using equation 3. The chemical equation (equation 1) given in section 2-1.3 is used for carburization process, as for decarburization process, it will be transformed into

$$wt.\%C = \frac{1}{Kf_c}\frac{P_{CO_2}{}^2}{P_{CO}} \tag{15}$$

So the equilibrium weight carbon content on surface is:

$$wt.\%C = \frac{1}{Kf_c}\frac{P_{CO_2}{}^2}{P_{CO}}$$
$$wt\%C = \frac{1}{(165.3719)(0.23161)}\frac{(101.325.x0.02)^2}{(101.325x0.98)}$$
$$wt\%C = 0.157$$

This surface weight percent of carbon is compare to that shown in Figure 5-1-4. This proofs the relationship shown in Figure 5-1-4 between the carbon content and the martensite hardness of H13 steel is valid.

Furthermore, by reading the experimental result in Figure 5-1-4 carefully, it was found that the decarburized layer thickness between one hour hardening and three hours hardening is wider than the decarburized layer thickness between three hours treatment and five hours treatment. It can be explained as the result of the oxide formation of chromium oxide, Cr_2O_3 (40, 42). The formation of chromium oxide layer acts as a carbon diffusion barrier which slows down the kinetic of carbon diffusion.

5-2 Constant Hardness Profile

Results from Figure 4-3-1 and Figure 4-4-1 have shown that both vacuum heat treatment and heat treatment with stainless steel foil wrapping produce a reasonably constant hardness profile on the as quenched samples. This suggests that the carbon neither diffuses into or out from metal matrix during austenitization. This is understandable for treatment in vacuum furnace because carburization cannot be initiated due to the absence of carbon monoxide. Neither can decarburization proceed because oxide layer cannot be formed in vacuum condition. For heat treatment with stainless steel foil wrapping, without continuous supply of carbon dioxide and based on the equilibrium diagram on Figure 5-1-5, it is believed that the samples were in decarburization during austenitization. This can be supported by the drop in hardness at 20μm underneath the samples surface. However, with the negligible amount of carbon dioxide inside the wrapping, the decarburization process reaches equilibrium after a short period of time.

Although both vacuum heat treatment and heat treatment with stainless steel foil wrapping are able to prevent the decarburizaiton process, they perform different tempering characteristic to each other. In vacuum heat treatment process, secondary hardening can be found after the 1st temper stage as predicted from Figure 1-3-3. Figure 1-3-3 shows that between the tempering temperature of 500ºC and 550ºC, a secondary hardening effect was found. This secondary hardening effect is the 4th stage of the tempering process. From the micrograph shown, it can be seen that the sample after 1st tempering process is filled with martensite.

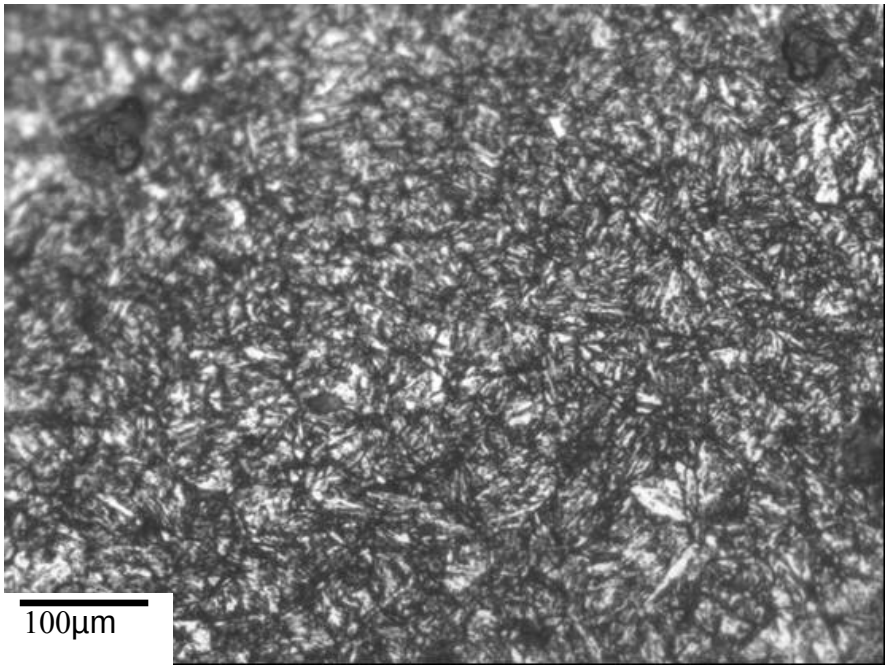


Figure 5-2-1 Micrograph of samples after 1st tempering heat treated in vacuum furnace

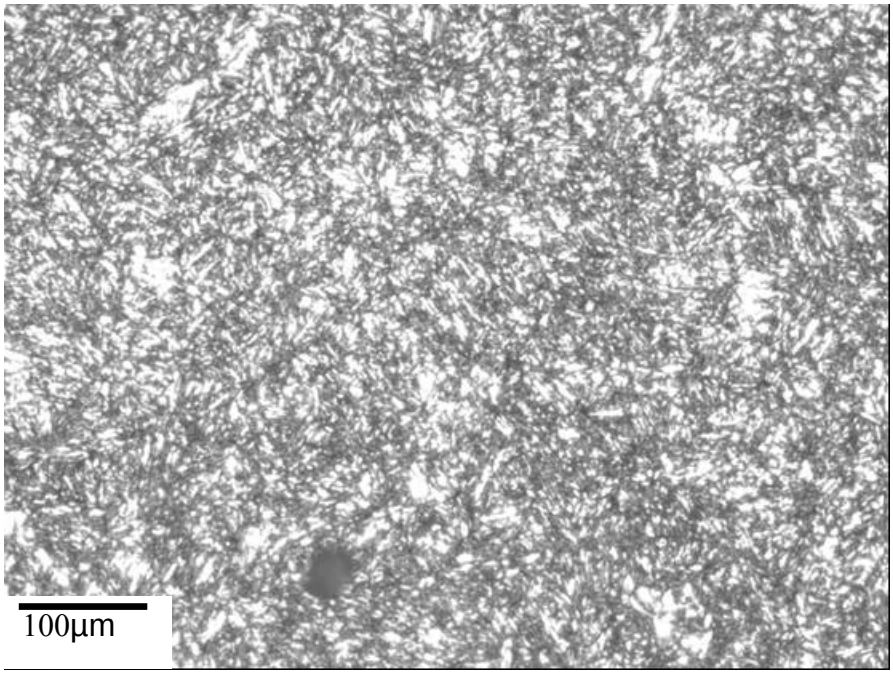


Figure 5-2-2 Micrograph of samples after 1st tempering heat treated in muffle furnace with stainless steel foil wrapping

However, the stage four tempering process is not that significant in samples heat treated with stainless steel foil wrapping. For the heat treatment with stainless steel

foil wrapping, the results show the hardness decreased after the 1st tempering stage even though martensite structure was found in the tempered samples (Figure 4-2-3).

Moreover, samples heat treated in vacuum furnace also show special characteristic in hardness after the 2nd tempering process. This can be seen from Figure 4-4-3 to Figure 4-4-5. The results show that with longer treatment time in vacuum treatment process, the hardness after 2nd tempering increases respectively. However, such characteristic cannot be found for samples heat treated with stainless steel foil wrapping. This can be explained by the increasing amount of transition carbide and martensite formed during the tempering stage. With longer austenization time, more carbon is dissolved into the metal matrix which causes a higher amount of retained austenite after quenching (24, 26). Thus, more martensite and carbide are formed in tempering process which causes an increase of hardness.

5-3 Carburization

A slight decrease in hardness can be found at region 200 μm underneath the surface from the graphs presented in Figure 4-3-1. This is not an unusual phenomena because Li et al research also obtained similar result (41). The drop in hardness at the surface region of the carburized samples is claimed to be the result of the presence of retain austenite. This may happen to some carburized alloys with high surface carbon content, or when the cooling rate is fast (54). As expected, the carburized layer thickens with heat treatment time. In order to determine the thickness of the carburized layer, a similar method as described in section 5-1 was used. The effective thickness of the carburized layer was determined as the point where the hardness dropped to +2HRC of core hardness. The results are presented in Figure 5-3-1.

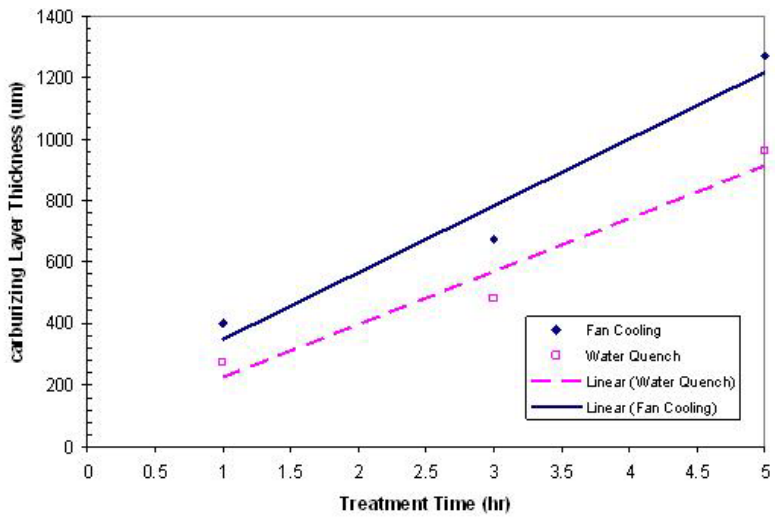


Figure 5-3-1 Graph of carburized layer thickness

For samples carburized for 1 hour, it is notable that the hardness at region 400-1000μm underneath the surface is lower than the core hardness. That may be because during the beginning of the pack carburization process, the atmosphere surrounding the test specimen was not yet saturated with carbon dioxide. Thus, until that time, the samples suffered from decarburization instead. Since decarburization was initiated at the early stage of the carburization process, the result is not sufficient for carbon diffusion analysis of the carburization process.

Although samples pack carburized for 5 hours have thicker carburized layer, its surface hardness is slightly lower and is especially significant in samples cooled by water quenching. This may be because with longer treatment time, the carbon content of the material built up which increase the amount of retained austenite (26). As shown in Figure 2-3-2, retained austenite tends to decrease martensite hardness when the carbon content in plain steel in over 0.7%. Research conducted by Krauss (25) also pointed out that in carburized steel, retained austenite and microcracks are absent at the core region of the material, but increasing toward the surface.

Unlike results of other heat treatment conditions, the pack carburized samples cooled by water quenching have lower hardness than pack carburized samples cooled by fan cooling under the same austenizing conditions. The explanation is not yet known but may due to the thermal cracks produced by fast cooling due to sudden thermal shock and large thermal gradient (21, 46, 55), or the tendency of high alloy carburized steel retaining an undue amount of austenite with a high cooling rate (54). This may also be the reason why after the 1st tempered stage, the hardness of the carburized sample cooled by water quenching was improved significantly. Through the tempering process, the microstructure was refined and the microcracks were reduced, along with smaller grain size was produced (2, 22, 24, 25).

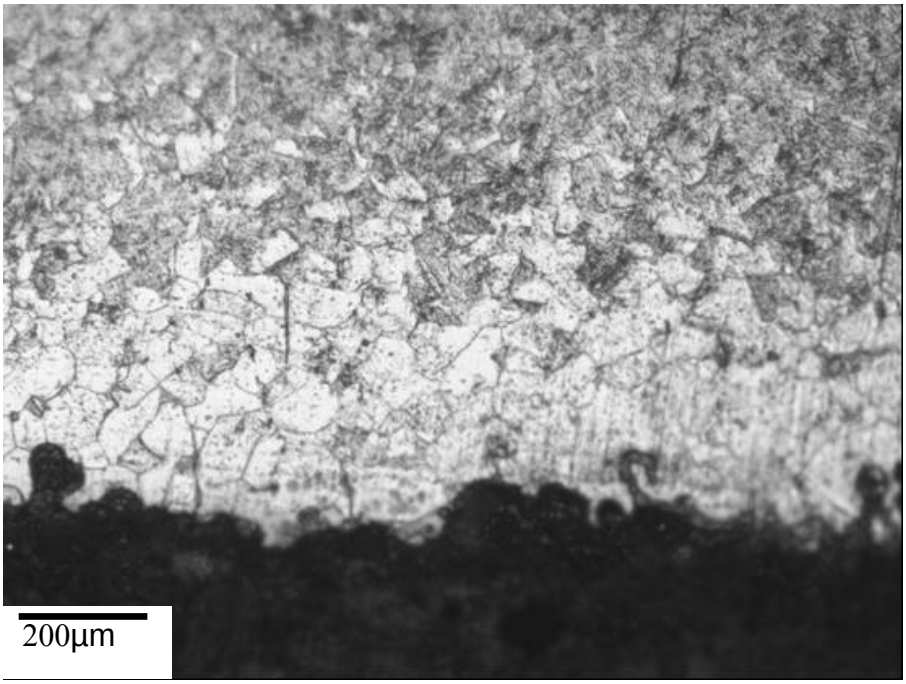
5-4 Gas Nitriding

All heat treated samples were further processed with the gas nitriding process. With the same gas nitriding condition, the result in section 4-5 shows that all samples have similar case hardening characteristic.

All samples present peak hardness within 70-73HRC. However, a significant hardness decrease was found on the surface (20μm underneath the surface) for samples heat treated without atmospheric control. Slightly drop in surface hardness can also be found in samples heat treated with stainless steel foil wrapping. From the above observations, this suggests that the performance of gas nitriding process is independent of the initial carbon content if it is not too low in value.

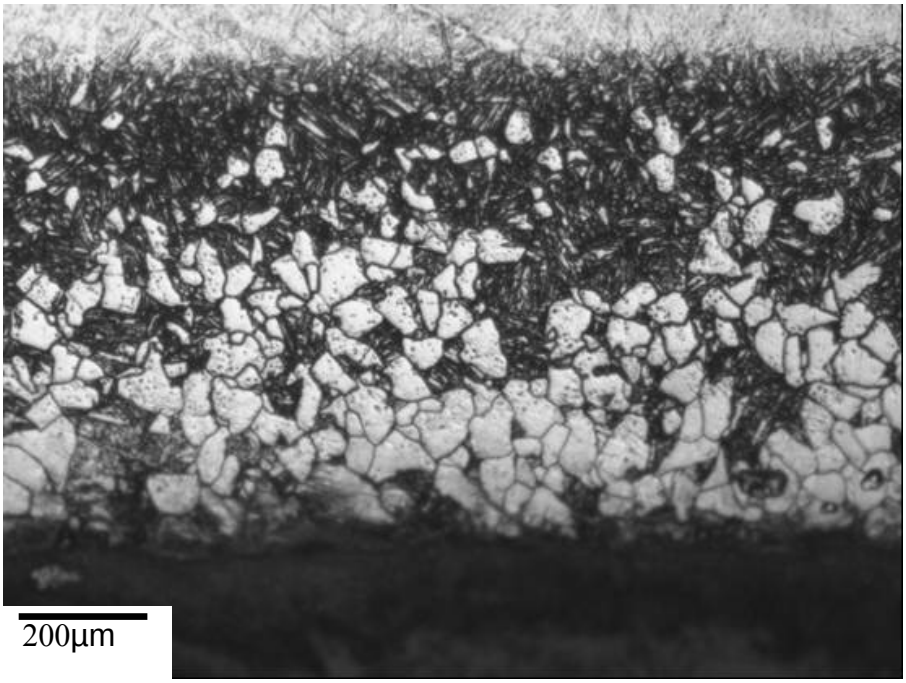
Moreover, a similar thickness of hardened layer was produced no matter which austenitizing atmospheric condition the sample experienced. All samples have a hardened case thickness of ~0.15mm after the 1st nitriding process. The hardened

case thickness was then increased to ~0.25mm after the 2nd nitriding process. However, the 3rd nitriding process does not provide any significant hardened case thickness improvement for all samples. For each individual heat treatment method, if the hardness profiles of nitrided samples are compared with the hardness profile of its 2nd tempered state, the hardness profile beyond the nitrided layer is similar to each other. These results indicate that the gas nitriding process does not alter the microstructure beyond within the nitrided region. This can be supported by the micrographs shown in Figure 5-4-1. These micrographs show the comparison between as quench state and nitrided state for samples heat treated without atmosphere control.



(a)

Figure 5-4-1 Micrograph of sample heat treated at 1020°C in an uncontrolled atmosphere for 5 hours (a) as quenched state, (b) 3rd nitrided state



(b)

Figure 5-4-1 cont.

The micrographs show that the gas nitriding process introduces the hardened layer within the decarburized layer by letting nitrogen to diffuse into the core region and alter the surface composition (30, 56), however the compound layer cannot be found on the surface. The results from section heading 4-5 suggest that the gas nitriding itself does not have any direct influence on the hardness profile of the inner part of the samples. It is because beyond the nitrided zone, the hardness profile closely matches the hardness profile of the respective 2nd tempered condition. From this, it shows the advantage of using vacuum furnace over the muffle furnace. It is because if the nitrided layer does not cover the decarburizing zone, there is a significant hardness drop below the nitrided layer, which can result mechanical failure. This is a realistic case especially for the heat treatment of aluminium extrusion die. It is because the recommended thickness of the nitriding layer is not more than ~0.25mm (30). However the present experiments show that even one hour of heat treatment without

atmospheric control gives a decarburization layer thickness of ~0.5mm. Thus there is always a considerable depth of decarburisation layer underneath the nitrided layer. It must also be noted that the thickness of the nitrided layer is not directly proportional to the number of times of the gas nitriding process being conducted. After the 2nd time of gas nitriding process, further case hardening process does not seem to give any hardness improvement.

Chapter 6 Conclusion and Recommendations

6-1 Conclusion

In the study of carbon diffusion in H13 steel during austenitization, a series of heat treatment experiments had been conducted under different atmospheric conditions and lengths of treatment. Four austenitzation atmospheric conditions were studied and they were: heat treatment without atmospheric control, heat treatment with stainless steel foil wrapping, pack carburization heat treatment and vacuum heat treatment.

The carbon movement during austenitization of H13 tool steel in the surface region totally depends on the surrounding atmospheric condition. At austenitizing temperature of 1020ºC, without continuous supply of carbon dioxide, carbon in steel tend to react with carbon dioxide in the layer of iron oxide and escape to the atmosphere. This is the decarburization process and is shown by the heat treatment without atmospheric control experiments. However the decarburization process can be restricted by either limiting the supply of carbon dioxide, or austeniting the

material in a vacuum environment. With stainless steel foil wrapping, samples were able to maintain its carbon content during the heat treatment process and produce a fairly constant hardness profile similar to that of the samples heat treated in vacuum furnace.

On the other hand, if carbon monoxide is supplied continuously with partial pressure the equilibrium state of the treatment temperature, carburization process will be initiated. This was the case of pack carburization experiment. Carbon monoxide was supplied continuously from the surrounding charoal, this caused increased carbon decomposition on the sample surface, consequently an increase of hardness. Although each heat treatment condition resulted in a different hardness profile to the others, it did not affect the results for gas nitriding. All samples subjected to the nitriding process produced similar thicknesses of hardened case layer with average hardness of 70~72HRC if the initial carbon content is not too low in value. Therefore, in conclusion,

- Heat treatment without atmospheric control resulted in a lower hardness on the surface since the material were subjected to decarburization effect. Although the thickness of the decarburization layer increased with processing time, decarburization rate decreased by formation of chromium oxide, Cr_2O_3 (40, 42).

- Stainless steel foil wrapping around the sample can restrict the decarburization process by shielding the sample in contact from the surrounding.

- Heat treatment in a vacuum furnace can prevent the materials from decarburization and decarburization.

- Pack carburization heat treatment resulted in a carburization effect on the material. However, it was observed that a short period of time was required to build up the carbon monoxide level. Before this was achieved, decarburization was most likely in control.

- Carbon diffusion in H13 steel during decarburization was examined and the following figures was determined based on Van-Ostrand-Dewey solution: equilibrium surface carbon content at 1020ºC was 0.157wt%, activation energy of carbon in H13 steel was 20200cal/mol, and carbon diffusivity at 1020ºC was $1.97 \times 10^{-8} cm^2/s$.

- The efficiency of gas nitriding process was independent to the carbon content if the initial carbon content is not too low in value. However, gas nitriding process of more than two rounds did not seem to give any significant effect in surface hardness and the thickness of the hardened case layer.

6-2 Recommendations

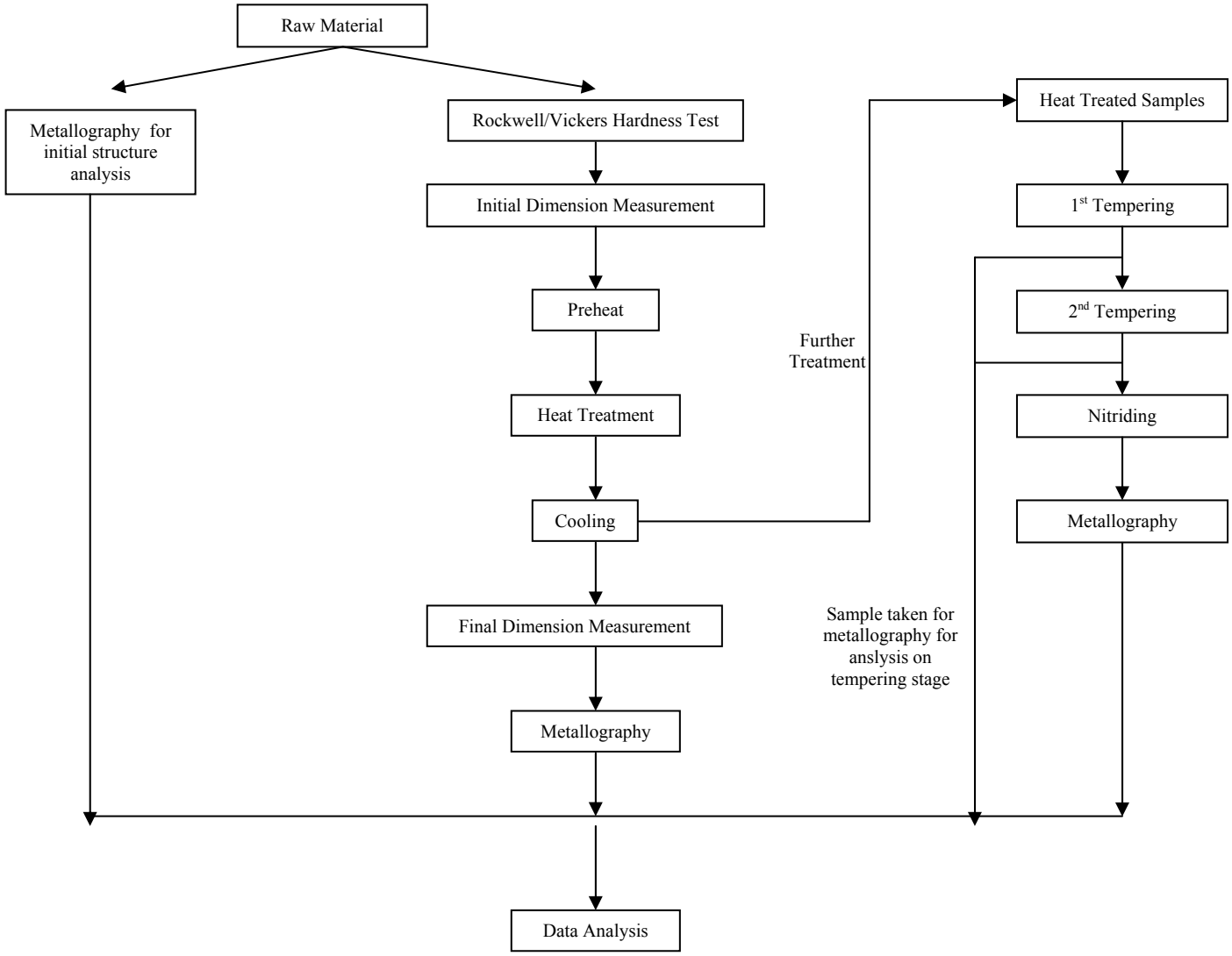
- The impact of the oxide layer and the carbon surface activity on the decarburization rate should be investigated for the improvement of aluminium extrusion die heat treatment.

- The decarburization effect at early stage of pack carburization heat treatment was observed. If further study on the carburization kinetic is required, it is recommended to extend the treatment time of the experiment so the decarburization effect can be neglected.

- The difference of H13 tempering characteristic between heat treatment with stainless steel foil wrapping and vacuum heat treatment should be study further. This is beneficial for selection of economical heat treatment method for aluminium extrusion die.

- It is also recommended to investigate the reason of the absence of compound layer of the nitrided samples which were heat treated without atmospheric control.

Appendix A. Experiment Procedure



Appendix B. Microhardness Result

- Heat Treatment without Atmospheric Control

As Quenched

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(µm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	10.00	22.00	4.00	16.00	2.00	14.00
50	23.00	31.00	12.00	18.00	6.00	18.00
100	42.00	43.00	22.00	28.00	20.00	29.00
150	45.00	45.00	30.00	38.00	26.00	31.00
200	47.00	47.00	42.00	42.00	28.00	35.00
250	46.00	50.00	43.00	45.00	40.00	39.00
300	49.00	51.00	47.00	47.00	43.00	43.00
350	50.00	53.00	47.00	48.00	44.00	43.00
400	51.00	55.00	49.00	50.00	44.00	45.00
450	53.00	54.00	49.00	52.00	45.00	46.00
500	53.00	56.00	49.00	53.00	46.00	48.00
550	51.00	56.00	51.00	53.00	47.00	49.00
600	53.00	56.00	51.00	54.00	48.00	50.00
650	53.00	56.00	52.00	55.00	48.00	50.00
700	53.00	57.00	52.00	56.00	49.00	52.00
750	53.00	56.00	53.00	55.00	51.00	52.00
800	53.00	57.00	52.00	56.00	50.00	53.00
850	53.00	57.00	53.00	56.00	53.00	53.00
900	54.00	57.00	53.00	56.00	52.00	53.00
950	54.00	57.00	54.00	56.00	52.00	53.00
1000	53.00	58.00	53.00	56.00	54.00	53.00
1250	53.00	58.00	53.00	56.00	54.00	54.00
1500	52.00	58.00	54.00	56.00	53.00	54.00
1750	54.00	57.00	53.00	55.00	53.00	54.00
2000	53.00	57.00	54.00	55.00	54.00	54.00
2250	54.00	57.00	55.00	56.00	54.00	54.00
2500	54.00	57.00	54.00	55.00	53.00	54.00
2750	54.00	57.00	53.00	55.00	53.00	54.00
3000	54.00	57.00	54.00	55.00	53.00	54.00
3250	54.00	56.00	53.00	56.00	54.00	54.00
3500	54.00	57.00	54.00	56.00	53.00	54.00
3750	54.00	57.00	54.00	55.00	54.00	54.00
4000	55.00	57.00	54.00	56.00	54.00	55.00
4250	55.00	57.00	53.00	56.00	54.00	55.00
4500	55.00	57.00	54.00	56.00	54.00	56.00
4750	55.00	57.00	54.00	56.00	52.00	57.00
5000	55.00	57.00	54.00	55.00	53.00	57.00

1st Tempered

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	18.00	23.00	10.00	12.00	8.00	2.00
50	42.00	36.00	14.00	21.00	10.00	16.00
100	46.00	45.00	23.00	32.00	16.00	25.00
150	50.00	48.00	35.00	40.00	18.00	30.00
200	50.00	51.00	41.00	46.00	33.00	36.00
250	52.00	52.00	44.00	48.00	41.00	43.00
500	56.00	55.00	46.00	52.00	50.00	48.00
750	55.00	55.00	47.00	54.00	52.00	51.00
1000	55.00	54.00	46.00	53.00	54.00	51.00
1250	55.00	56.00	50.00	54.00	54.00	52.00
1500	53.00	55.00	53.00	53.00	55.00	52.00
1750	56.00	55.00	56.00	54.00	56.00	52.00
2000	56.00	54.00	56.00	53.00	57.00	53.00
2250	56.00	53.00	56.00	54.00	56.00	53.00
2500	55.00	53.00	56.00	54.00	57.00	53.00
2750	55.00	55.00	56.00	54.00	56.00	53.00
3000	55.00	54.00	56.00	54.00	56.00	53.00
3250	55.00	54.00	55.00	54.00	57.00	53.00
3500	56.00	55.00	56.00	54.00	57.00	54.00
3750	56.00	55.00	56.00	55.00	58.00	54.00
4000	56.00	54.00	55.00	54.00	57.00	55.00
4250	54.00	56.00	55.00	55.00	56.00	55.00
4500	55.00	55.00	57.00	55.00	56.00	55.00
4750	56.00	55.00	56.00	54.00	56.00	55.00
5000	56.00	54.00	56.00	54.00	56.00	55.00

2nd Tempered

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	20.00	22.00	14.00	20.00	2.00	22.00
50	23.00	31.00	18.00	20.00	4.00	27.00
100	36.00	42.00	30.00	29.00	14.00	29.00
150	46.00	44.00	37.00	38.00	18.00	36.00
200	46.00	46.00	43.00	42.00	26.00	39.00
250	49.00	47.00	45.00	43.00	37.00	41.00
500	51.00	46.00	50.00	47.00	49.00	46.00
750	51.00	50.00	49.00	49.00	49.00	47.00
1000	52.00	50.00	50.00	49.00	49.00	47.00
1250	52.00	50.00	51.00	49.00	49.00	48.00
1500	52.00	51.00	50.00	49.00	48.00	48.00
1750	52.00	51.00	50.00	48.00	50.00	48.00
2000	52.00	50.00	51.00	49.00	49.00	49.00
2250	51.00	49.00	51.00	49.00	49.00	49.00
2500	50.00	50.00	50.00	50.00	50.00	50.00
2750	51.00	50.00	51.00	48.00	50.00	49.00
3000	52.00	50.00	51.00	49.00	50.00	50.00
3250	52.00	50.00	52.00	48.00	50.00	50.00
3500	51.00	49.00	52.00	50.00	50.00	50.00
3750	52.00	49.00	51.00	49.00	50.00	49.00
4000	52.00	51.00	52.00	49.00	50.00	49.00
4250	51.00	50.00	50.00	48.00	50.00	48.00
4500	51.00	51.00	51.00	49.00	50.00	48.00
4750	52.00	51.00	52.00	48.00	50.00	48.00
5000	51.00	50.00	52.00	49.00	50.00	48.00

1st Nitrided

Temperature	1020	1020	1020	1020	1020	1020
Duration	1	1	3	3	5	5
Quenching	Fan Cooling	Water Quench	Fan Cooling	Water Quench	Fan Cooling	Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	70	69	69	69	68	55
50	70	71	71	70	70	71
100	63	40	47	48	53	53
150	45	48	44	41	39	35
200	48	47	46	44	40	36
250	48	48	47	46	41	39
500	48	50	50	50	46	45
750	49	51	49	48	49	46
1000	49	52	50	48	49	48
1250	48	52	48	48	50	48
1500	49	51	48	48	50	48
1750	49	51	49	49	50	49
2000	50	51	48	49	50	49
2250	49	52	48	49	50	49
2500	49	51	49	49	50	49
2750	51	52	48	49	50	50
3000	49	52	49	50	50	48

2nd Nitrided

20	70	71	68	68	55	64
50	72	71	71	71	69	69
100	71	70	72	72	70	70
150	71	63	55	49	49	40
200	50	46	50	47	39	37
250	48	48	47	46	39	37
500	49	51	50	49	45	42
750	51	51	51	50	47	44
1000	50	50	51	50	49	45
1250	51	52	51	50	50	45
1500	50	51	50	50	50	46
1750	50	50	50	51	50	48
2000	50	51	50	51	49	47
2250	51	51	49	51	51	48
2500	50	51	50	51	51	47
2750	50	51	49	51	50	48
3000	50	49	51	50	50	47

3rd Nitrided

20	71	72	70	69	64	71
50	71	72	71	71	69	71
100	70	71	72	70	71	71
150	71	65	71	71	50	48
200	56	57	55	48	43	37
250	53	54	52	48	40	38
500	53	51	50	48	45	42
750	51	50	49	49	47	44
1000	51	50	50	49	47	44
1250	50	49	51	50	49	45
1500	50	49	50	50	48	47
1750	50	50	50	50	48	47
2000	49	50	50	50	49	47
2250	50	50	50	50	48	47
2500	50	50	51	50	50	47
2750	50	50	50	50	49	49
3000	50	49	50	49	50	48

- Heat Treatment with Stainless Steel Foil Wrapping

As Quenched

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(µm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	53.00	58.00	53.00	58.00	56.00	55.00
50	58.00	59.00	55.00	61.00	58.00	58.00
100	61.00	57.00	57.00	60.00	59.00	58.00
150	60.00	58.00	57.00	61.00	59.00	59.00
200	59.00	57.00	57.00	59.00	60.00	59.00
250	60.00	57.00	57.00	60.00	59.00	58.00
500	60.00	59.00	57.00	59.00	58.00	59.00
750	60.00	59.00	56.00	60.00	59.00	58.00
1000	60.00	59.00	59.00	61.00	59.00	59.00
1250	62.00	59.00	59.00	61.00	60.00	57.00
1500	61.00	57.00	58.00	60.00	59.00	58.00
1750	61.00	58.00	59.00	61.00	59.00	59.00
2000	61.00	59.00	58.00	60.00	58.00	59.00
2250	59.00	59.00	57.00	60.00	59.00	57.00
2500	60.00	57.00	57.00	60.00	60.00	60.00
2750	62.00	59.00	57.00	61.00	58.00	61.00
3000	59.00	58.00	59.00	60.00	58.00	59.00
3250	61.00	59.00	59.00	60.00	62.00	59.00
3500	61.00	60.00	57.00	61.00	61.00	59.00
3750	62.00	60.00	60.00	61.00	60.00	58.00
4000	60.00	60.00	58.00	62.00	60.00	60.00
4250	59.00	60.00	57.00	63.00	60.00	60.00
4500	59.00	59.00	57.00	61.00	59.00	59.00
4750	59.00	59.00	57.00	60.00	58.00	61.00
5000	59.00	60.00	58.00	61.00	57.00	59.00

1st Tempered

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	50.00	49.00	46.00	47.00	42.00	49.00
50	56.00	56.00	56.00	54.00	56.00	56.00
100	55.00	57.00	56.00	54.00	56.00	56.00
150	56.00	57.00	57.00	54.00	57.00	57.00
200	56.00	57.00	57.00	56.00	57.00	58.00
250	57.00	56.00	57.00	55.00	57.00	58.00
500	56.00	57.00	56.00	55.00	57.00	57.00
750	56.00	58.00	56.00	55.00	56.00	57.00
1000	56.00	57.00	58.00	56.00	57.00	57.00
1250	55.00	56.00	58.00	56.00	57.00	58.00
1500	56.00	57.00	56.00	58.00	56.00	56.00
1750	56.00	56.00	56.00	56.00	57.00	57.00
2000	57.00	58.00	56.00	57.00	57.00	56.00
2250	56.00	56.00	54.00	56.00	56.00	56.00
2500	57.00	57.00	57.00	56.00	57.00	57.00
2750	57.00	57.00	57.00	56.00	56.00	58.00
3000	57.00	57.00	58.00	55.00	57.00	58.00
3250	56.00	57.00	57.00	56.00	58.00	57.00
3500	56.00	56.00	56.00	55.00	56.00	57.00
3750	56.00	56.00	58.00	55.00	56.00	58.00
4000	57.00	57.00	58.00	56.00	56.00	57.00
4250	56.00	57.00	58.00	54.00	57.00	57.00
4500	56.00	56.00	56.00	55.00	57.00	57.00
4750	56.00	57.00	57.00	56.00	57.00	58.00
5000	55.00	56.00	57.00	56.00	57.00	57.00

2nd Tempered

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	36.00	38.00	42.00	49.00	43.00	46.00
50	46.00	50.00	50.00	48.00	49.00	48.00
100	49.00	50.00	50.00	50.00	50.00	48.00
150	50.00	50.00	50.00	51.00	51.00	49.00
200	50.00	50.00	49.00	51.00	50.00	50.00
250	50.00	51.00	50.00	51.00	50.00	50.00
500	50.00	51.00	50.00	50.00	51.00	49.00
750	51.00	51.00	50.00	51.00	51.00	49.00
1000	51.00	51.00	50.00	52.00	52.00	50.00
1250	50.00	51.00	50.00	51.00	51.00	50.00
1500	51.00	51.00	52.00	50.00	51.00	51.00
1750	51.00	51.00	51.00	50.00	51.00	51.00
2000	50.00	50.00	50.00	50.00	51.00	51.00
2250	51.00	51.00	51.00	51.00	51.00	50.00
2500	50.00	51.00	51.00	52.00	51.00	51.00
2750	51.00	52.00	50.00	52.00	52.00	51.00
3000	51.00	51.00	52.00	52.00	52.00	51.00
3250	51.00	52.00	50.00	50.00	51.00	50.00
3500	51.00	53.00	52.00	51.00	51.00	51.00
3750	52.00	51.00	52.00	50.00	52.00	50.00
4000	51.00	51.00	51.00	51.00	51.00	49.00
4250	52.00	52.00	53.00	50.00	51.00	48.00
4500	51.00	53.00	52.00	51.00	51.00	50.00
4750	51.00	52.00	51.00	51.00	51.00	52.00
5000	51.00	51.00	52.00	51.00	51.00	50.00

1st Nitrided

Temperature	1020	1020	1020	1020	1020	1020
Duration	1	1	3	3	5	5
Quenching	Fan Cooling	Water Quench	Fan Cooling	Water Quench	Fan Cooling	Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	69	71	70	70	70	71
50	70	72	72	71	69	71
100	65	64	65	57	59	59
150	54	57	58	53	53	52
200	52	54	55	53	50	52
250	51	53	54	53	50	52
500	51	52	53	52	50	51
750	52	53	53	51	51	52
1000	50	53	52	51	51	51
1250	52	53	52	52	50	53
1500	51	53	53	51	51	52
1750	52	52	55	50	51	50
2000	51	52	54	51	52	52
2250	51	52	53	51	51	52
2500	50	53	53	50	51	52
2750	52	50	53	51	53	52
3000	51	52	53	52	51	51

2nd Nitrided

20	71	71	70	70	71	71
50	71	71	72	71	72	70
100	71	71	71	70	71	70
150	71	71	71	61	69	69
200	60	60	61	56	60	56
250	56	56	58	53	57	56
500	54	53	54	53	53	53
750	52	53	54	54	53	52
1000	52	52	54	53	54	53
1250	52	54	53	52	52	53
1500	51	53	55	52	52	53
1750	52	52	53	52	53	53
2000	52	53	52	51	53	52
2250	51	53	53	52	54	52
2500	51	53	52	52	52	52
2750	51	53	51	52	53	53
3000	51	51	53	52	54	51

3rd Nitrided

20	69	71	72	71	71	72
50	71	71	72	71	71	72
100	70	71	71	70	70	71
150	68	64	67	67	66	65
200	56	57	58	60	57	56
250	53	54	55	54	54	54
500	53	51	53	54	53	54
750	53	53	54	53	53	52
1000	53	53	53	51	55	52
1250	52	53	53	50	53	53
1500	51	53	53	53	53	53
1750	52	53	54	51	54	53
2000	49	54	54	52	53	52
2250	51	53	54	53	53	53
2500	52	52	53	54	53	51
2750	52	53	53	54	53	51
3000	52	51	51	53	53	53

- Pack Carburized Heat Treatment

As Quenched

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(µm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	66.00	66.00	66.00	66.00	61.00	59.00
50	68.00	66.00	66.00	66.00	65.00	62.00
100	67.00	65.00	67.00	67.00	65.00	63.00
150	65.00	64.00	67.00	67.00	64.00	62.00
200	65.00	62.00	67.00	67.00	65.00	62.00
250	64.00	59.00	67.00	66.00	66.00	63.00
300	65.00	54.00	67.00	66.00	66.00	62.00
350	63.00	53.00	67.00	65.00	65.00	61.00
400	58.00	51.00	67.00	62.00	66.00	61.00
450	57.00	51.00	67.00	59.00	65.00	61.00
500	53.00	52.00	66.00	57.00	66.00	61.00
550	53.00	52.00	65.00	55.00	65.00	60.00
600	52.00	52.00	60.00	55.00	64.00	59.00
650	53.00	52.00	59.00	55.00	64.00	60.00
700	51.00	52.00	57.00	54.00	62.00	59.00
750	53.00	52.00	56.00	54.00	62.00	60.00
800	52.00	53.00	56.00	55.00	62.00	59.00
850	55.00	54.00	55.00	56.00	61.00	58.00
900	52.00	55.00	55.00	55.00	61.00	58.00
950	55.00	55.00	55.00	53.00	61.00	59.00
1000	52.00	55.00	55.00	54.00	60.00	58.00
1250	56.00	56.00	55.00	54.00	59.00	58.00
1500	55.00	55.00	56.00	55.00	58.00	57.00
1750	57.00	55.00	56.00	55.00	57.00	57.00
2000	57.00	54.00	56.00	54.00	57.00	56.00
2250	59.00	54.00	56.00	55.00	56.00	56.00
2500	58.00	55.00	56.00	55.00	56.00	56.00
2750	58.00	55.00	56.00	55.00	56.00	56.00
3000	57.00	54.00	55.00	54.00	56.00	57.00
3250	57.00	55.00	55.00	55.00	57.00	57.00
3500	58.00	55.00	55.00	55.00	56.00	56.00
3750	56.00	55.00	55.00	55.00	57.00	56.00
4000	56.00	55.00	55.00	55.00	57.00	57.00
4250	56.00	56.00	56.00	55.00	56.00	56.00
4500	57.00	56.00	56.00	55.00	56.00	56.00
4750	58.00	57.00	56.00	55.00	56.00	56.00
5000	57.00	56.00	56.00	56.00	56.00	56.00

1st Tempered

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	51.00	41.00	54.00	57.00	49.00	53.00
50	57.00	56.00	61.00	63.00	57.00	64.00
100	58.00	56.00	62.00	63.00	57.00	64.00
150	58.00	55.00	61.00	63.00	57.00	64.00
200	59.00	56.00	61.00	62.00	57.00	64.00
250	58.00	56.00	60.00	62.00	57.00	64.00
500	58.00	58.00	60.00	62.00	58.00	63.00
750	57.00	56.00	57.00	59.00	58.00	63.00
1000	58.00	56.00	59.00	58.00	57.00	63.00
1250	57.00	56.00	59.00	58.00	57.00	61.00
1500	58.00	57.00	59.00	57.00	57.00	60.00
1750	59.00	58.00	58.00	58.00	56.00	58.00
2000	58.00	58.00	58.00	58.00	58.00	58.00
2250	59.00	57.00	60.00	59.00	58.00	58.00
2500	58.00	59.00	60.00	57.00	58.00	58.00
2750	57.00	57.00	59.00	57.00	58.00	58.00
3000	57.00	56.00	59.00	58.00	58.00	59.00
3250	58.00	57.00	58.00	57.00	58.00	58.00
3500	58.00	59.00	59.00	58.00	57.00	58.00
3750	58.00	58.00	59.00	56.00	57.00	59.00
4000	57.00	56.00	59.00	57.00	57.00	59.00
4250	57.00	57.00	58.00	59.00	57.00	58.00
4500	57.00	56.00	58.00	58.00	58.00	58.00
4750	59.00	58.00	57.00	58.00	59.00	57.00
5000	56.00	56.00	57.00	58.00	59.00	58.00

2nd Tempered

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1 Water Quench	1020 3 Fan Cooling	1020 3 Water Quench	1020 5 Fan Cooling	1020 5 Water Quench
Distance from surface(μm)	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc	Hardness Rc
20	51.00	49.00	50.00	48.00	43.00	30.00
50	57.00	57.00	58.00	58.00	57.00	59.00
100	58.00	59.00	58.00	59.00	58.00	58.00
150	59.00	60.00	59.00	59.00	57.00	58.00
200	58.00	58.00	59.00	60.00	58.00	59.00
250	57.00	58.00	58.00	62.00	58.00	58.00
500	58.00	60.00	59.00	60.00	58.00	59.00
750	59.00	58.00	58.00	58.00	57.00	58.00
1000	59.00	61.00	58.00	58.00	59.00	58.00
1250	58.00	60.00	58.00	58.00	57.00	58.00
1500	57.00	59.00	58.00	57.00	57.00	59.00
1750	58.00	59.00	58.00	57.00	57.00	58.00
2000	59.00	58.00	58.00	57.00	57.00	58.00
2250	58.00	59.00	60.00	57.00	57.00	60.00
2500	57.00	58.00	58.00	57.00	58.00	58.00
2750	59.00	59.00	59.00	58.00	58.00	58.00
3000	58.00	59.00	59.00	58.00	58.00	59.00
3250	58.00	59.00	59.00	57.00	56.00	59.00
3500	59.00	58.00	59.00	57.00	59.00	58.00
3750	59.00	61.00	58.00	56.00	59.00	59.00
4000	56.00	59.00	58.00	56.00	62.00	60.00
4250	59.00	61.00	59.00	57.00	58.00	59.00
4500	59.00	62.00	59.00	57.00	58.00	60.00
4750	58.00	58.00	57.00	59.00	59.00	62.00
5000	57.00	58.00	58.00	58.00	60.00	62.00

- Vacuum Heat Treatment

As Quenched

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1.5 Fan Cooling	1020 2 Fan Cooling
Distance from surface(µm)	Hardness Rc	Hardness Rc	Hardness Rc
50	56.00	57.00	56.00
250	58.00	58.00	56.00
500	57.00	56.00	56.00
750	58.00	57.00	56.00
1000	59.00	57.00	57.00
1250	59.00	57.00	57.00
1500	57.00	57.00	56.00
1750	57.00	58.00	56.00
2000	57.00	57.00	57.00
2250	58.00	56.00	56.00
2500	56.00	56.00	57.00
2750	57.00	58.00	56.00
3000	56.00	57.00	56.00
3250	55.00	56.00	56.00
3500	56.00	57.00	57.00
3750	56.00	58.00	56.00
4000	56.00	57.00	57.00
4250	56.00	58.00	56.00
4500	56.00	58.00	57.00
4750	56.00	58.00	58.00
5000	56.00	58.00	57.00

1st Tempered

50	57.00	60.00	58.00
250	60.00	60.00	58.00
500	59.00	59.00	57.00
750	60.00	58.00	59.00
1000	59.00	59.00	58.00
1250	60.00	59.00	58.00
1500	60.00	60.00	59.00
1750	59.00	61.00	59.00
2000	59.00	60.00	58.00
2250	59.00	59.00	58.00
2500	59.00	61.00	59.00
2750	59.00	60.00	58.00
3000	59.00	59.00	59.00
3250	60.00	61.00	58.00
3500	61.00	60.00	58.00
3750	59.00	59.00	59.00
4000	59.00	60.00	58.00
4250	60.00	60.00	58.00
4500	60.00	60.00	58.00
4750	60.00	60.00	58.00
5000	59.00	61.00	58.00

2nd Tempered

50	47.00	52.00	54.00
250	49.00	53.00	53.00
500	49.00	54.00	53.00
750	50.00	54.00	52.00
1000	50.00	53.00	53.00
1250	49.00	55.00	53.00
1500	50.00	54.00	54.00
1750	49.00	54.00	53.00
2000	50.00	54.00	53.00
2250	50.00	54.00	53.00
2500	49.00	54.00	53.00
2750	49.00	55.00	54.00
3000	49.00	55.00	55.00
3250	48.00	56.00	55.00
3500	49.00	55.00	54.00
3750	50.00	53.00	54.00
4000	50.00	56.00	54.00
4250	51.00	55.00	53.00
4500	50.00	54.00	53.00
4750	50.00	55.00	53.00
5000	50.00	54.00	53.00

1st Nitrided

Temperature Duration Quenching	1020 1 Fan Cooling	1020 1.5 Fan Cooling	1020 2 Fan Cooling
Distance from surface(µm)	Hardness Rc	Hardness Rc	Hardness Rc
20	70	71	70
50	70	72	71
100	63	64	66
150	53	56	57
200	49	55	54
250	49	55	54
500	49	55	54
750	50	54	54
1000	50	54	54
1250	50	55	53
1500	49	56	54
1750	50	55	53
2000	50	55	53
2250	49	55	53
2500	50	55	53
2750	50	54	52
3000	49	54	53

2nd Nitrided

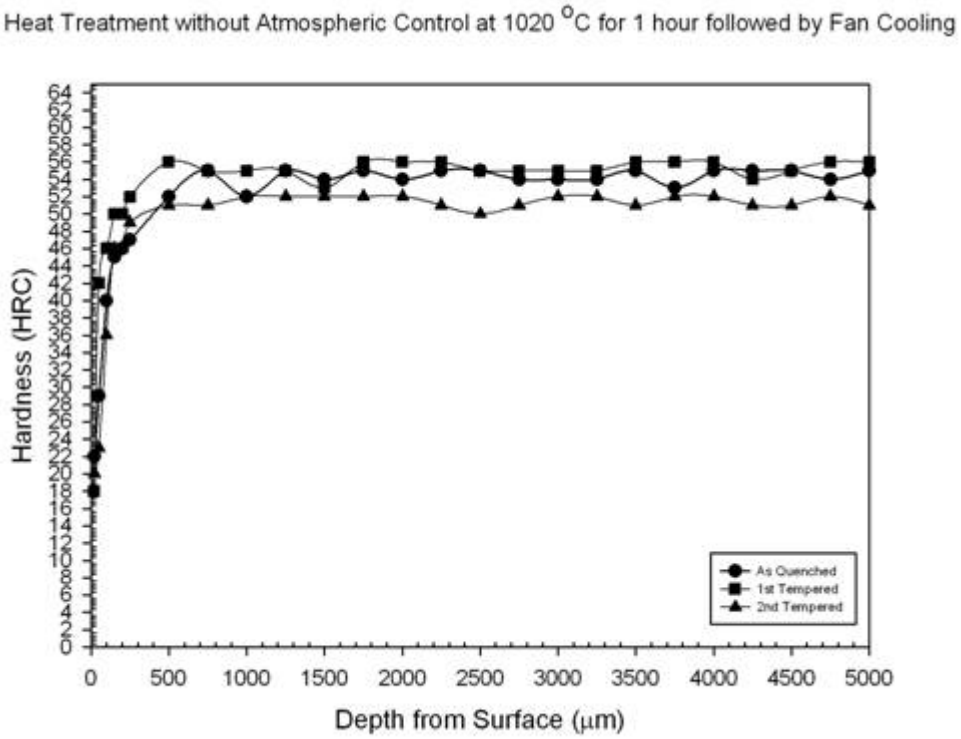
20	71	70	70
50	70	70	71
100	70	70	70
150	64	59	65
200	55	56	58
250	51	54	54
500	49	54	55
750	51	54	53
1000	49	53	54
1250	49	53	54
1500	50	54	53
1750	49	54	53
2000	50	54	53
2250	49	54	54
2500	50	54	53
2750	51	54	54
3000	50	54	54

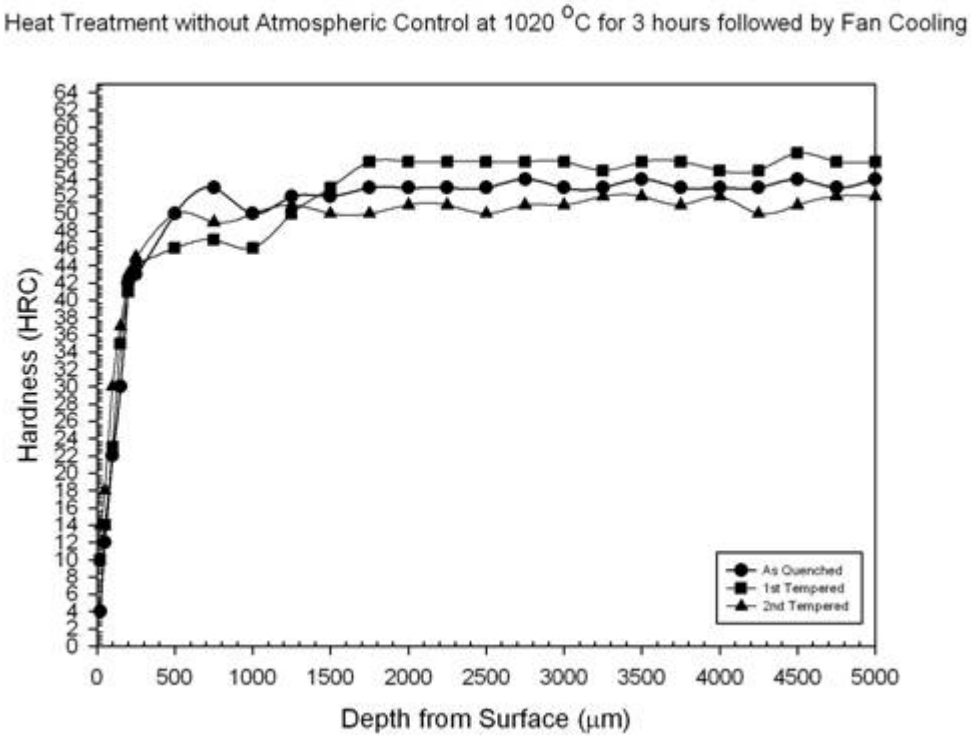
3rd Nitrided

20	71	71	71
50	71	71	70
100	70	70	71
150	69	70	70
200	58	61	60
250	54	58	57
500	50	54	53
750	50	54	55
1000	50	53	54
1250	50	54	53
1500	49	54	53
1750	50	54	54
2000	50	54	52
2250	49	54	54
2500	50	54	53
2750	50	54	53
3000	49	54	53

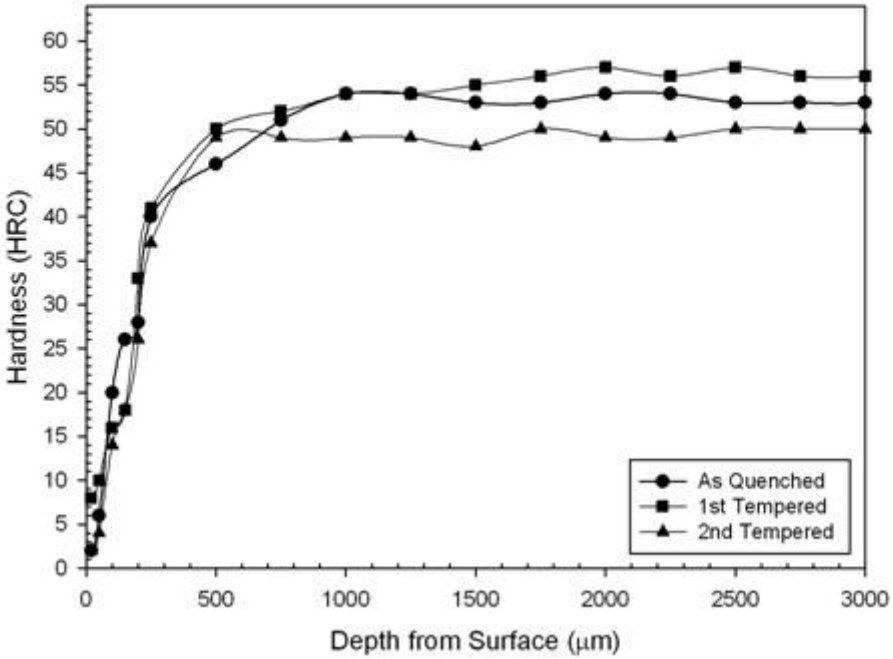
Appendix C. Hardness Profile

- Heat Treatment without Atmospheric Control

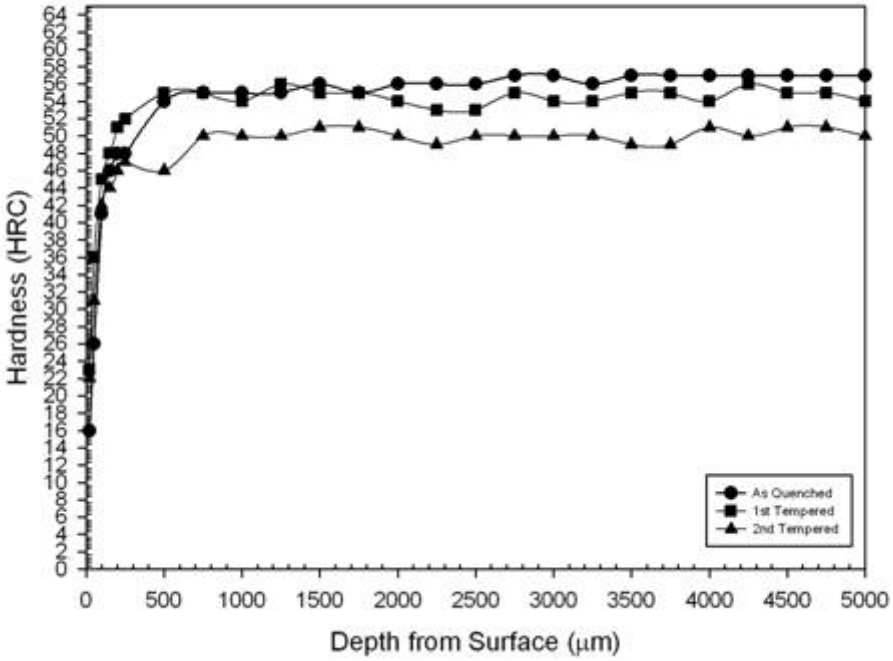




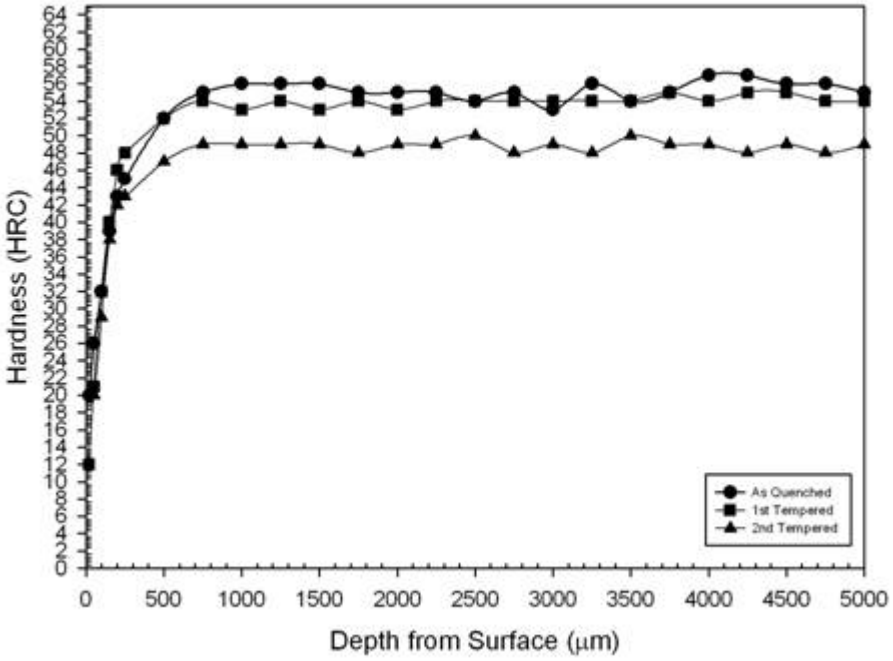
Heat Treatment without Atmospheric Control at 1020 °C for 5 hours followed by Fan Cooling



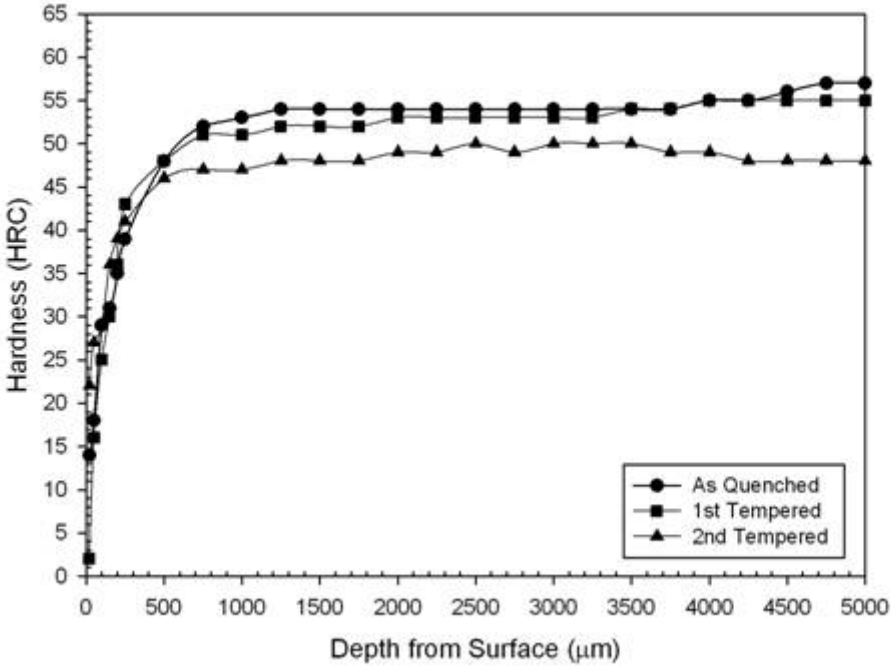
Heat Treatment without Atmospheric Control at 1020 °C for 1 hour followed by Water Quench



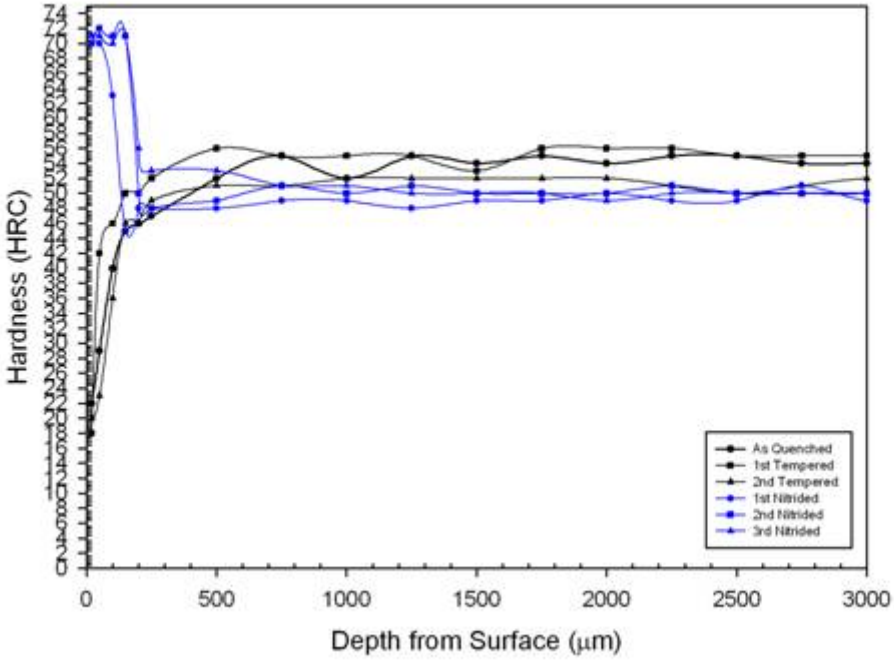
Heat Treatment without Atmospheric Control at 1020 °C for 3 hours followed by Water Quench



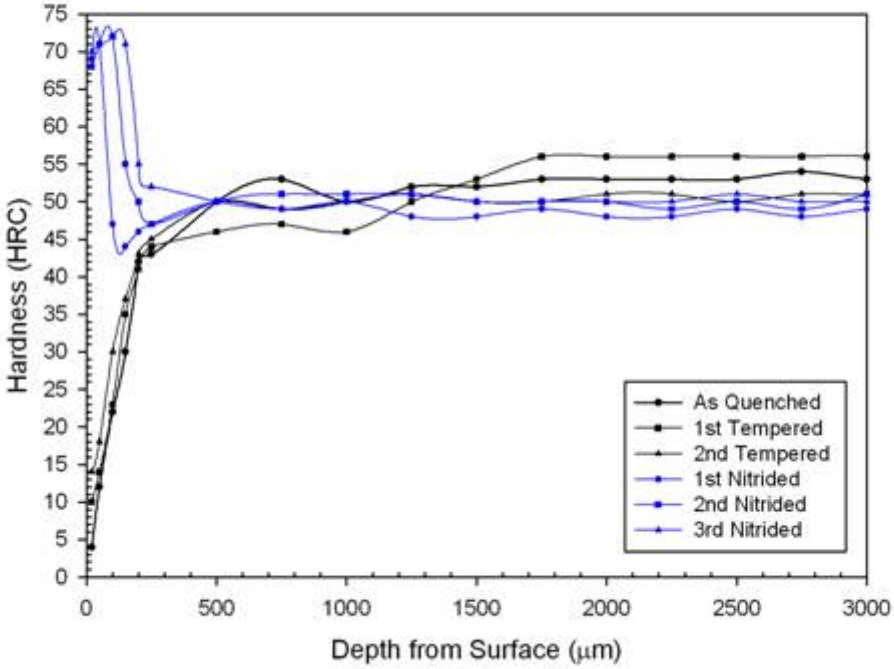
Heat Treatment without Atmospheric Control at 1020 °C for 5 hours followed by Water Quench



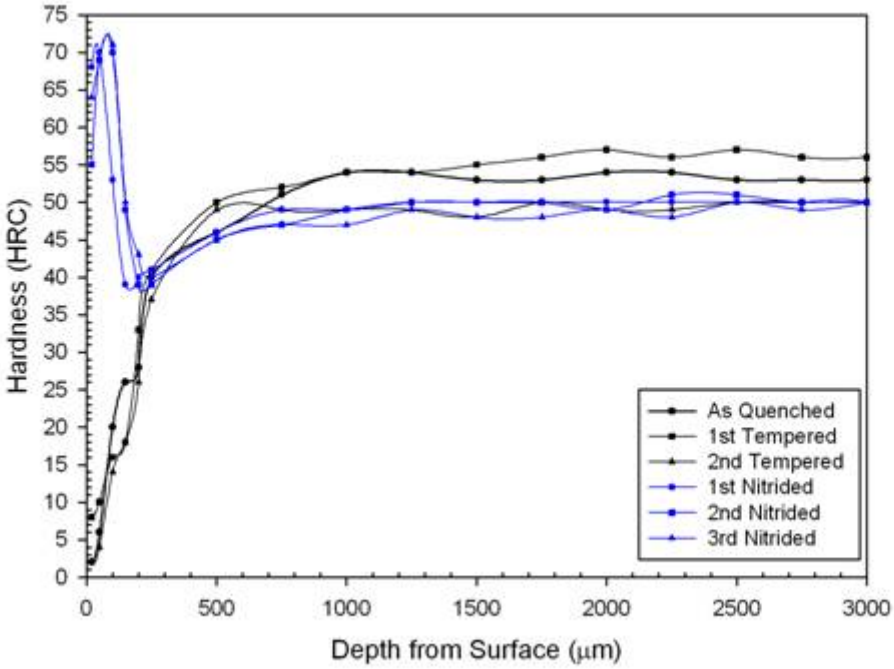
Heat Treatment without Atmospheric Control at 1020 ^{o}C for 1 hour followed by Fan Cooling



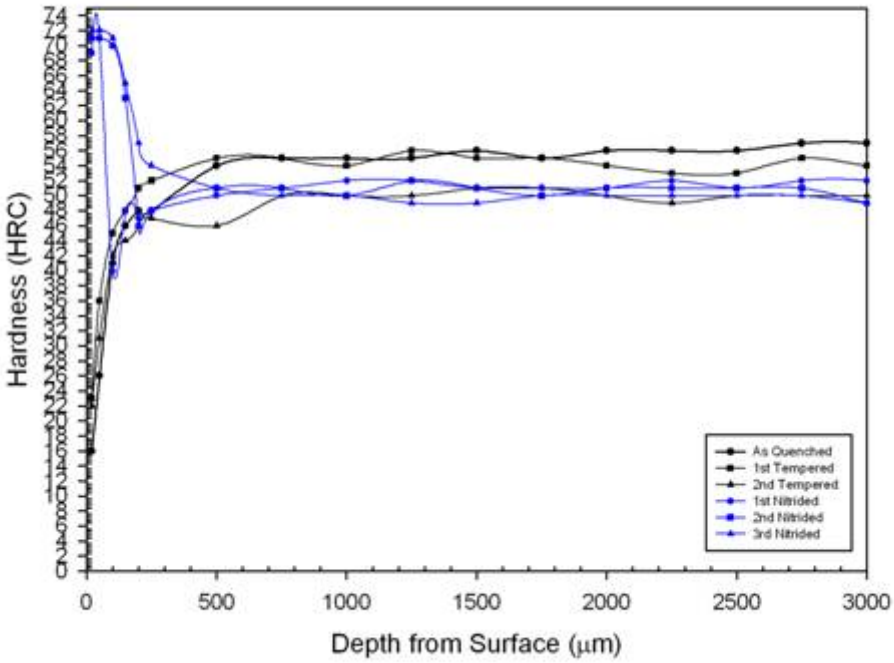
Heat Treatment without Atmospheric Control at 1020 ^{o}C for 3 hours followed by Fan Cooling



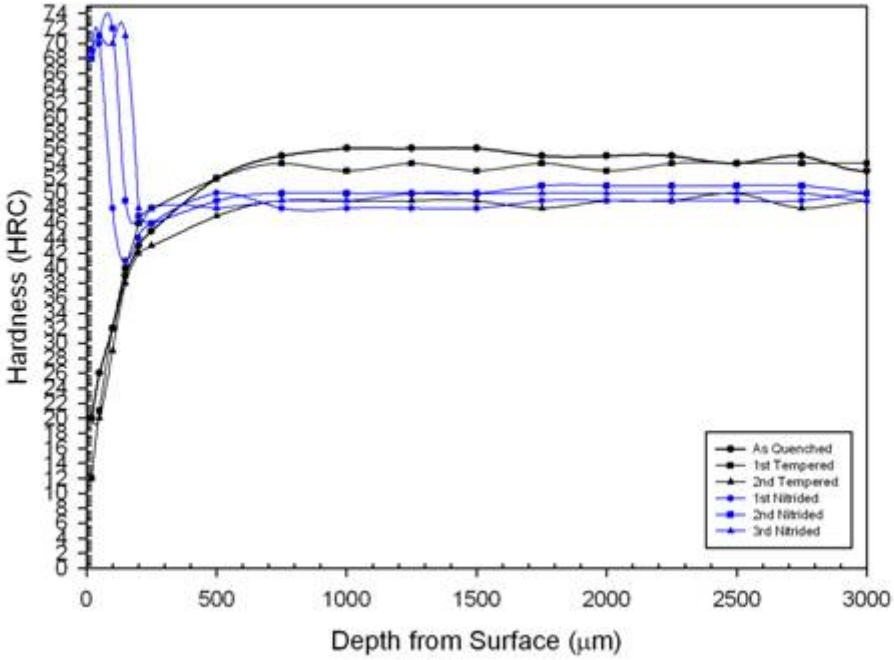
Heat Treatment without Atmospheric Control at 1020 °C for 5 hours followed by Fan Cooling



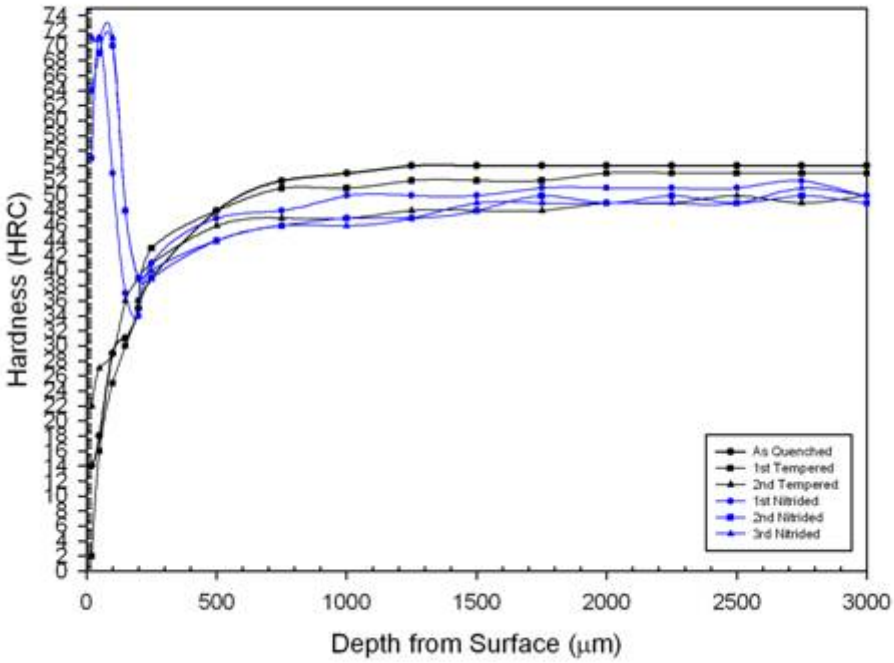
Heat Treatment without Atmospheric Control at 1020 °C for 1 hour followed by Water Quench



Heat Treatment without Atmospheric Control at 1020 °C for 3 hours followed by Water Quench

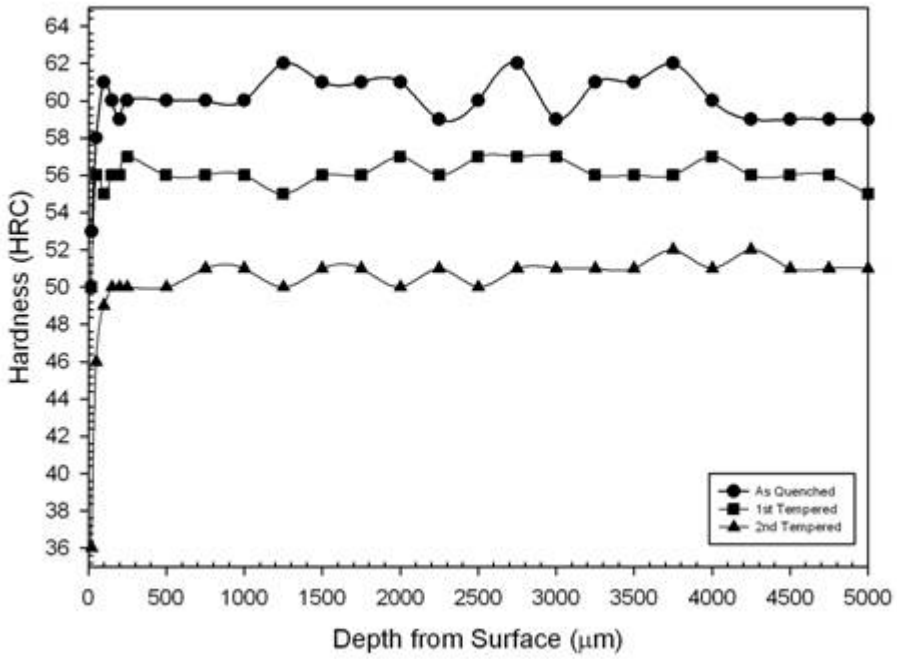


Heat Treatment without Atmospheric Control at 1020 °C for 5 hours followed by Water Quench

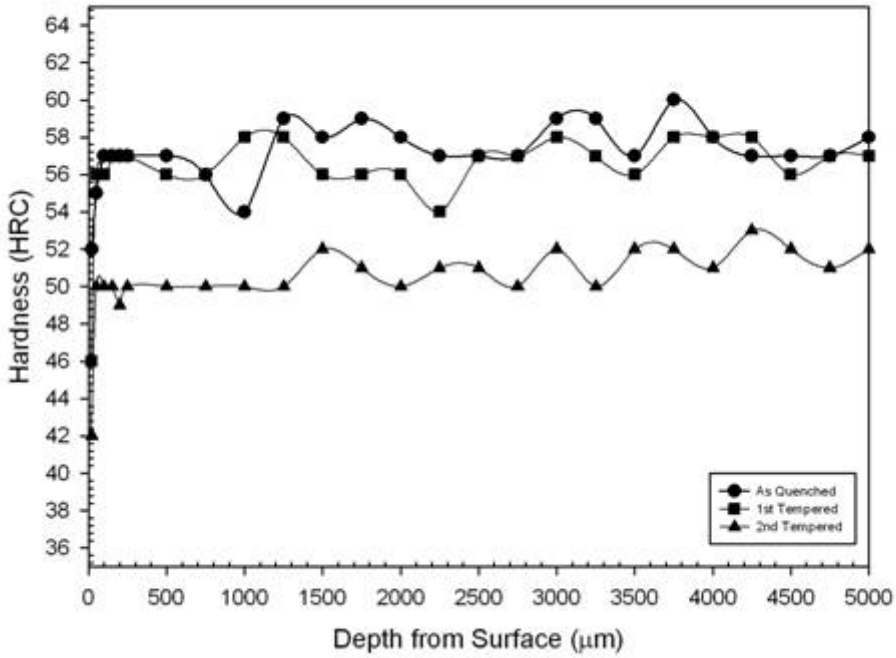


- Stainless Steel Foil Wrapping

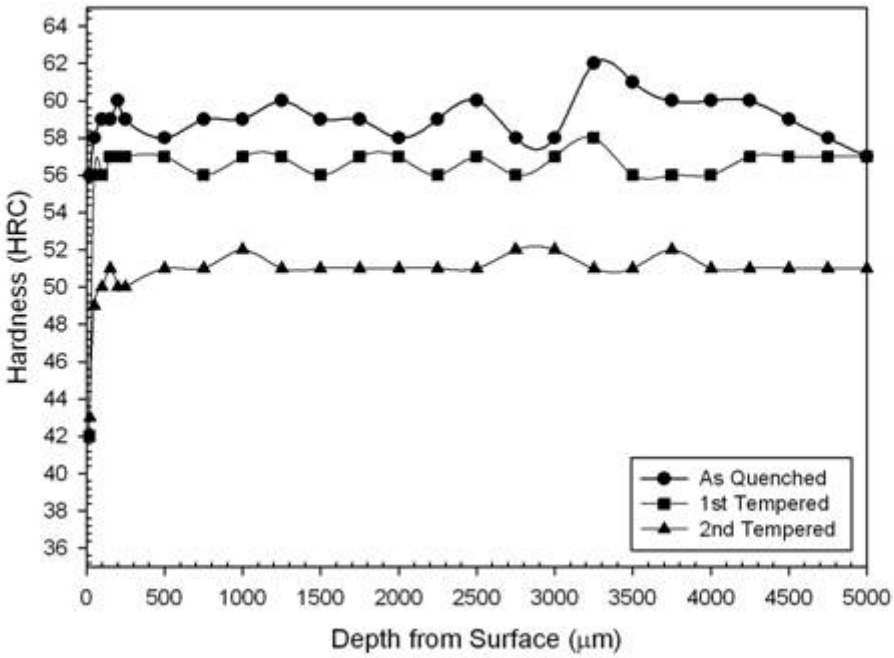
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 1 hour followed by Fan Cooling



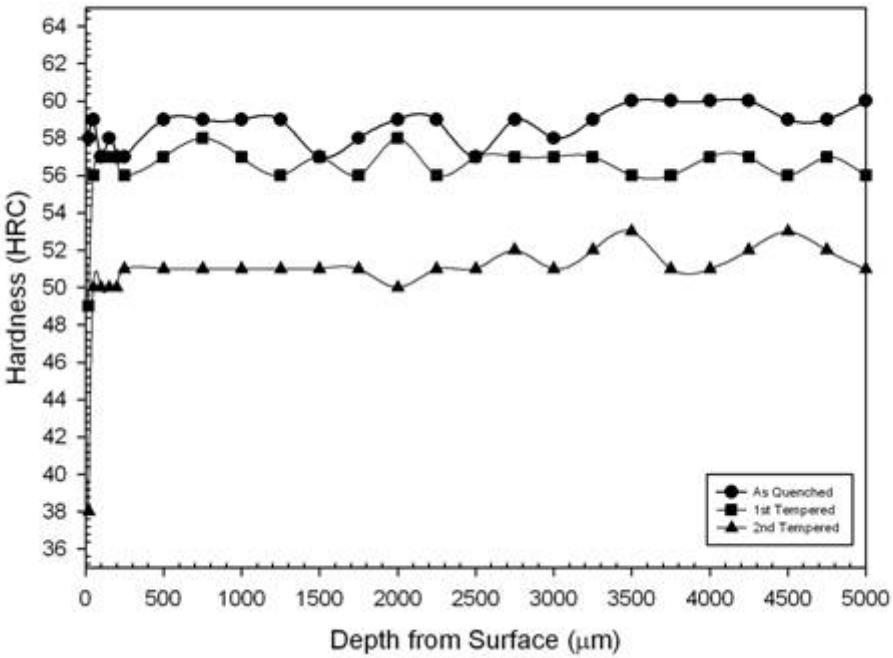
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 3 hours followed by Fan Cooling



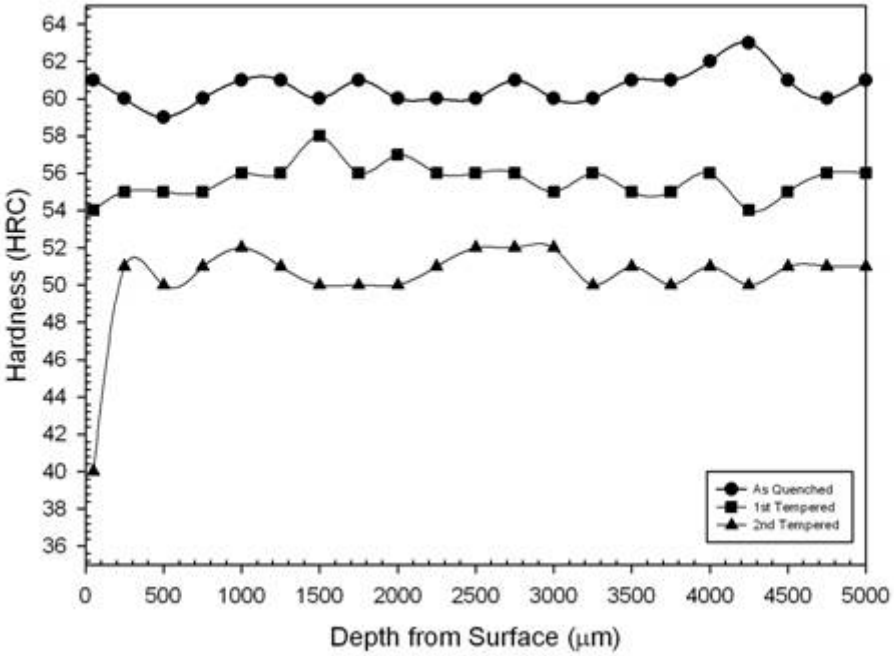
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 5 hours followed by Fan Cooling



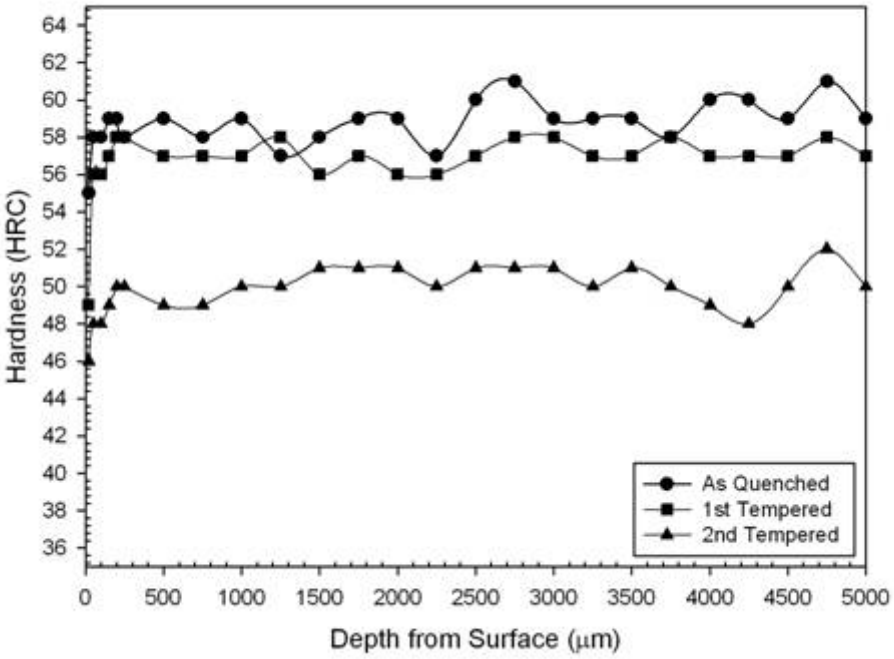
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 1 hour followed by Water Quench



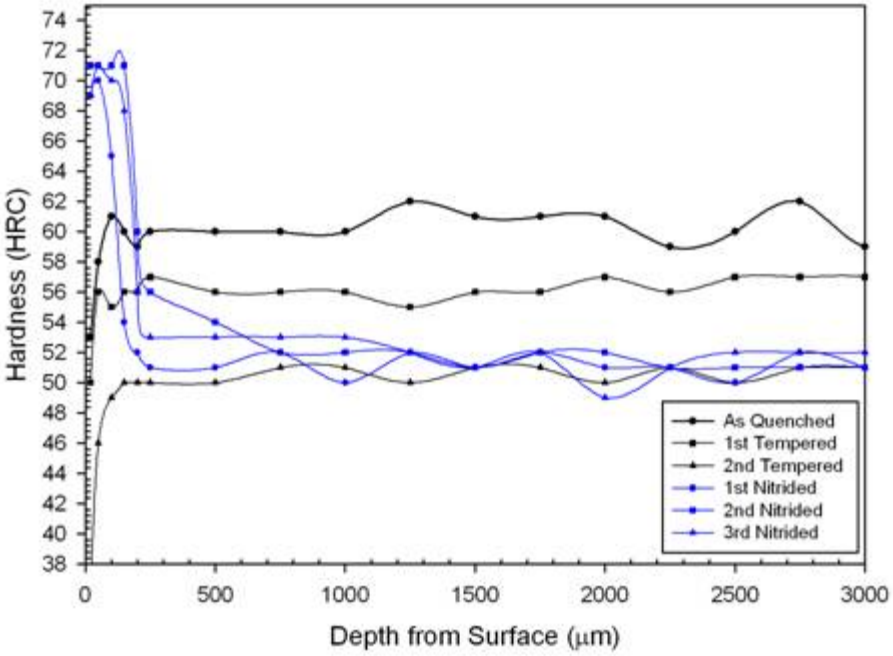
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 3 hours followed by Water Quench



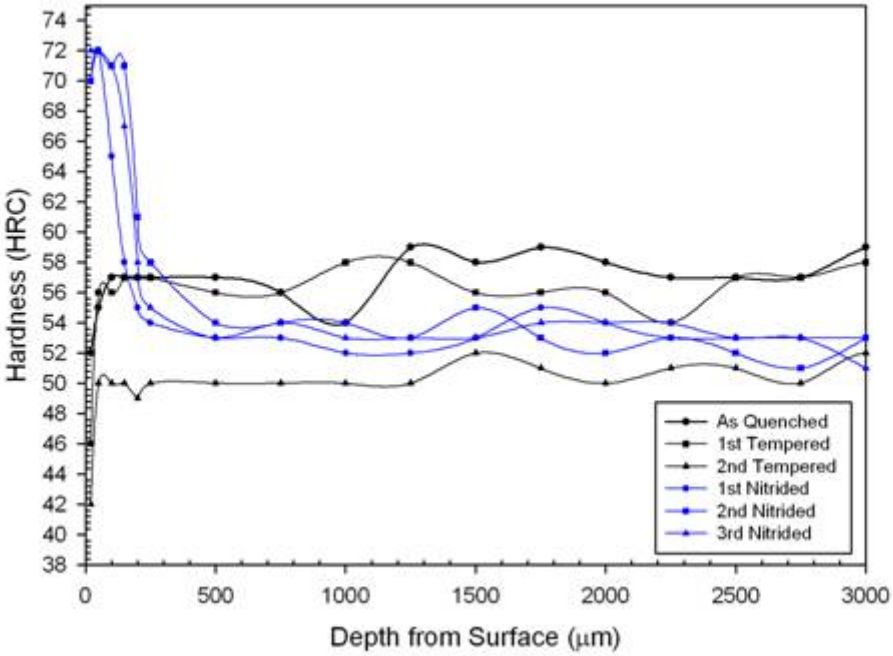
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 5 hours followed by Water Quench



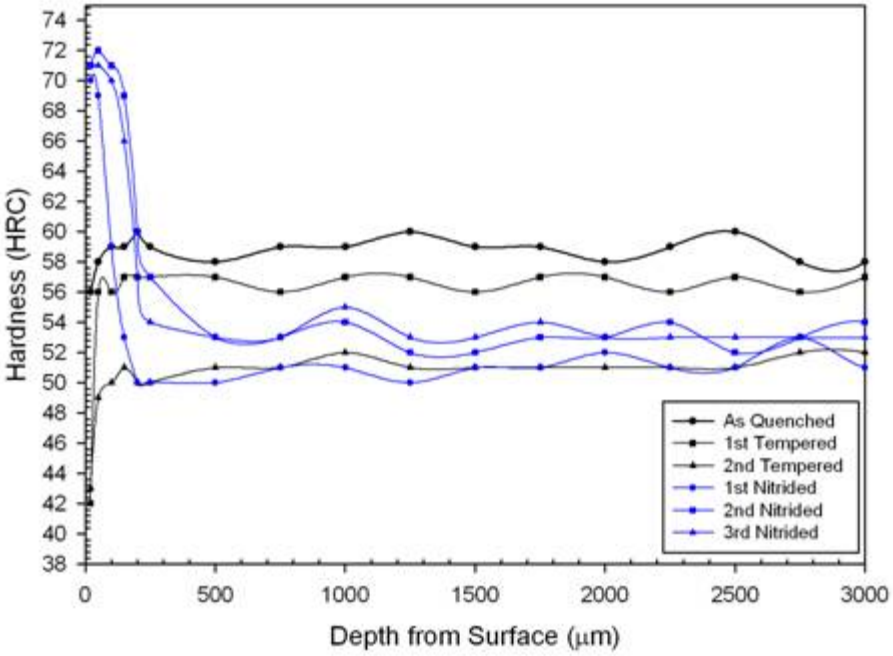
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 1 hour followed by Fan Cooling



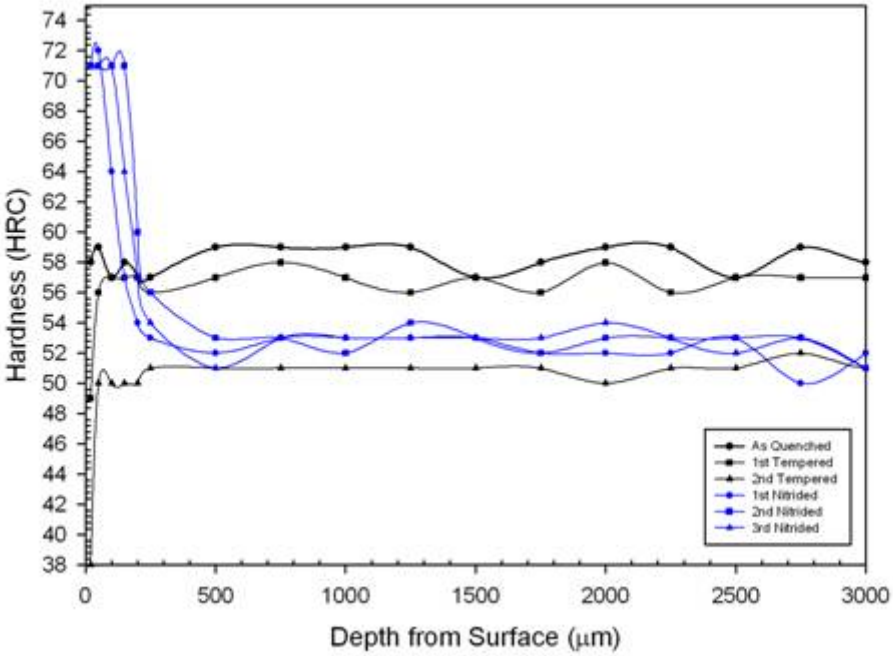
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 3 hours followed by Fan Cooling



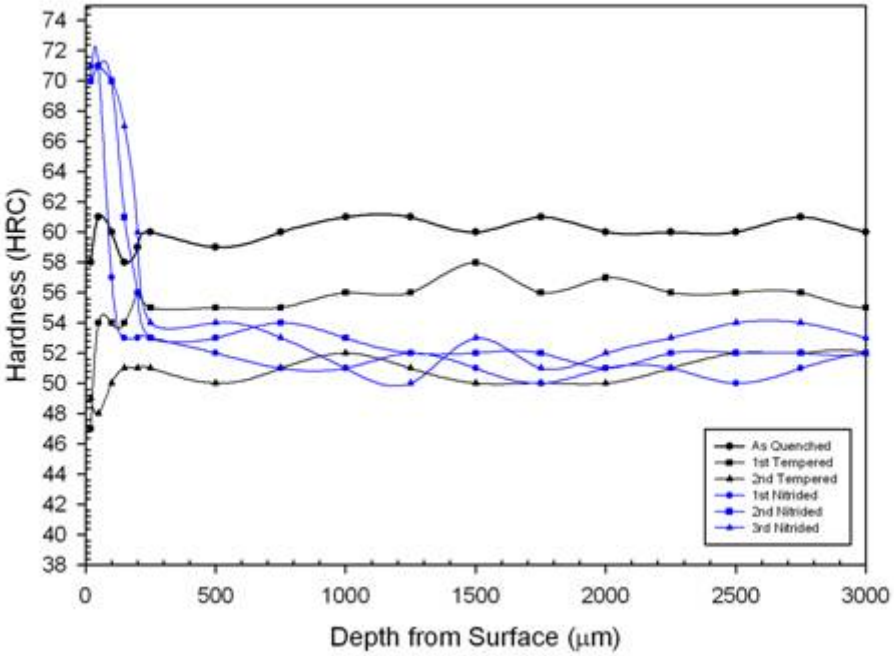
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 5 hours followed by Fan Cooling



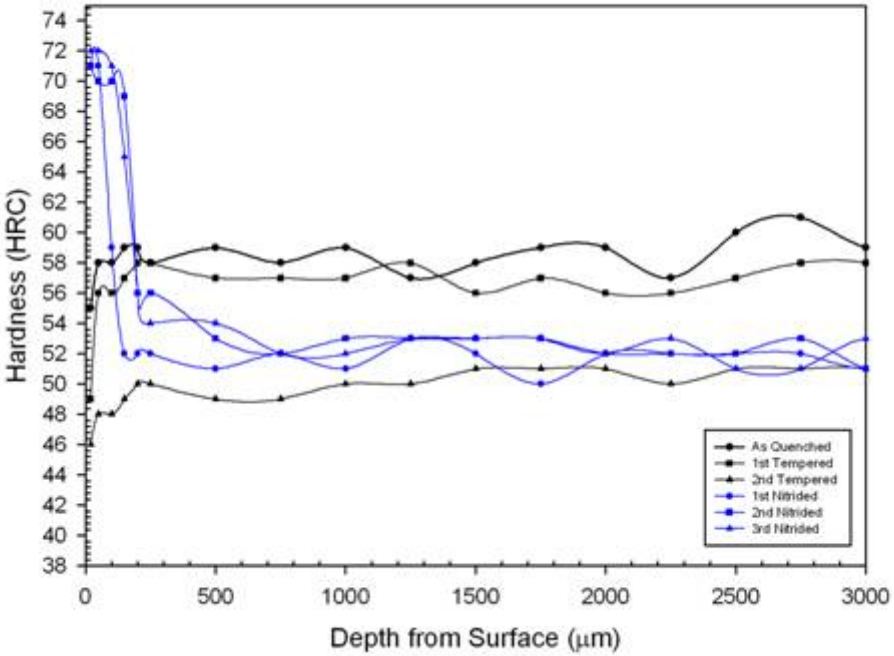
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 1 hour followed by Water Quench



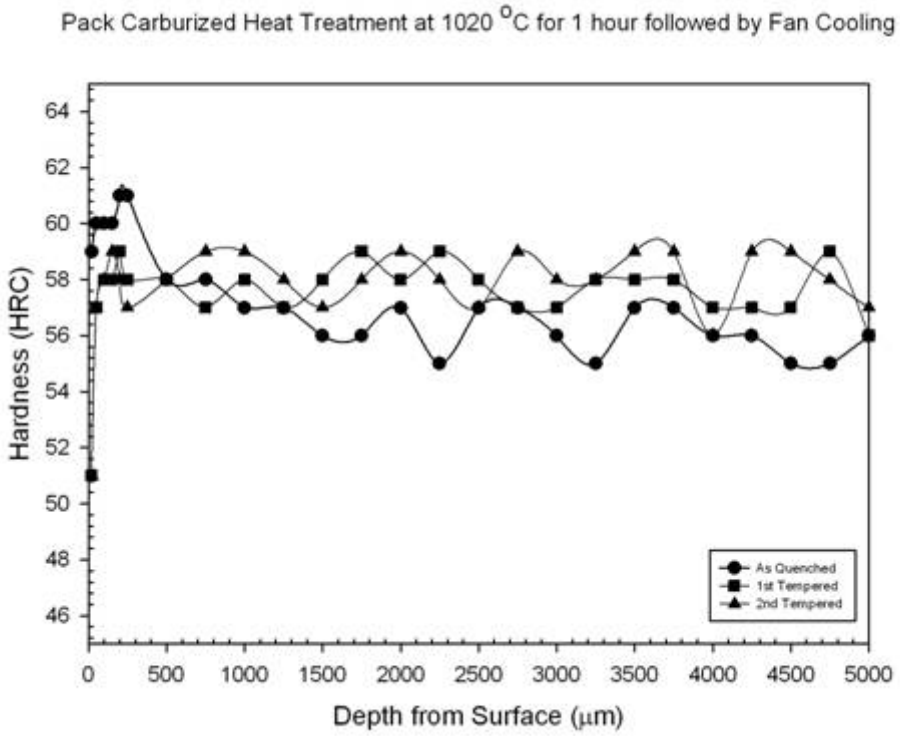
Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 3 hours followed by Water Quench

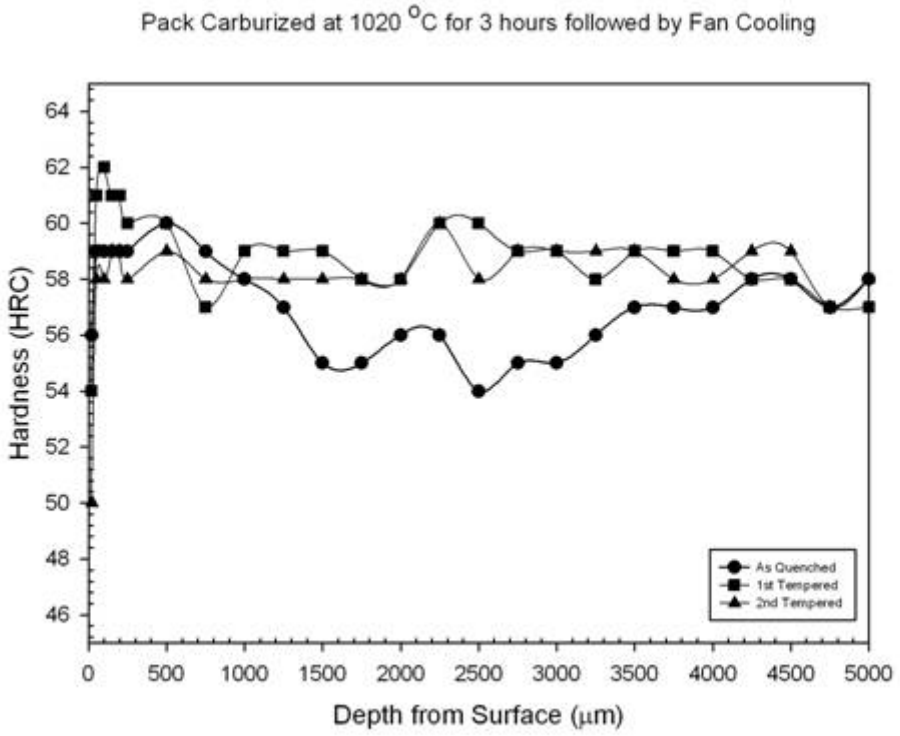


Heat Treatment with Stainless Steel Foil Wrapping at 1020 ^{o}C for 5 hours followed by Water Quench

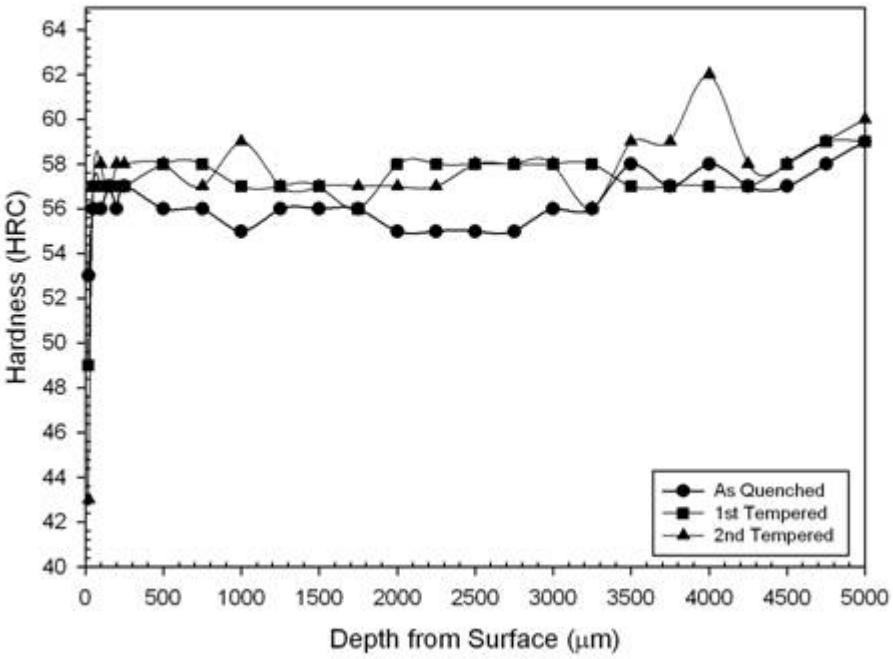


- Pack Carburization

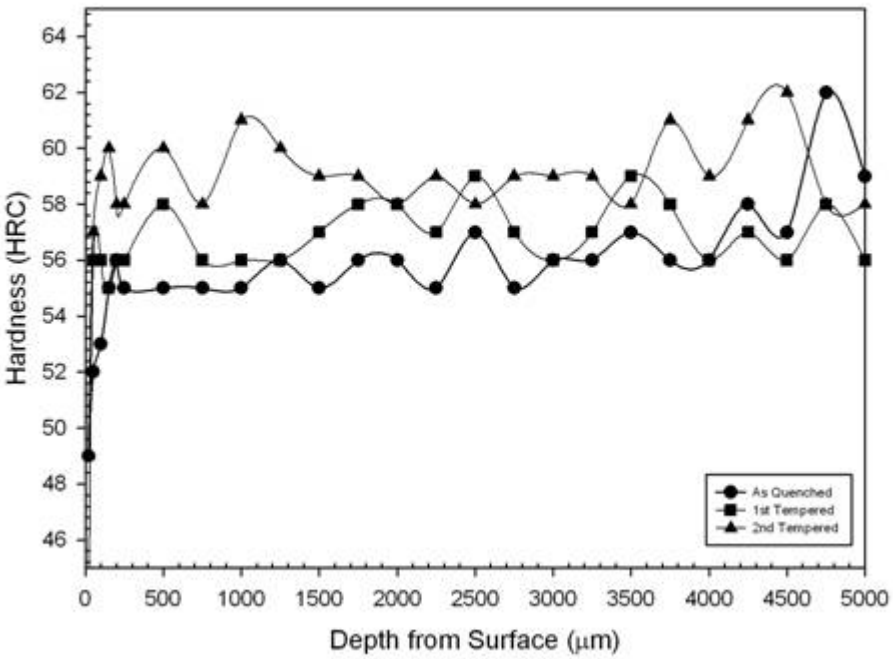


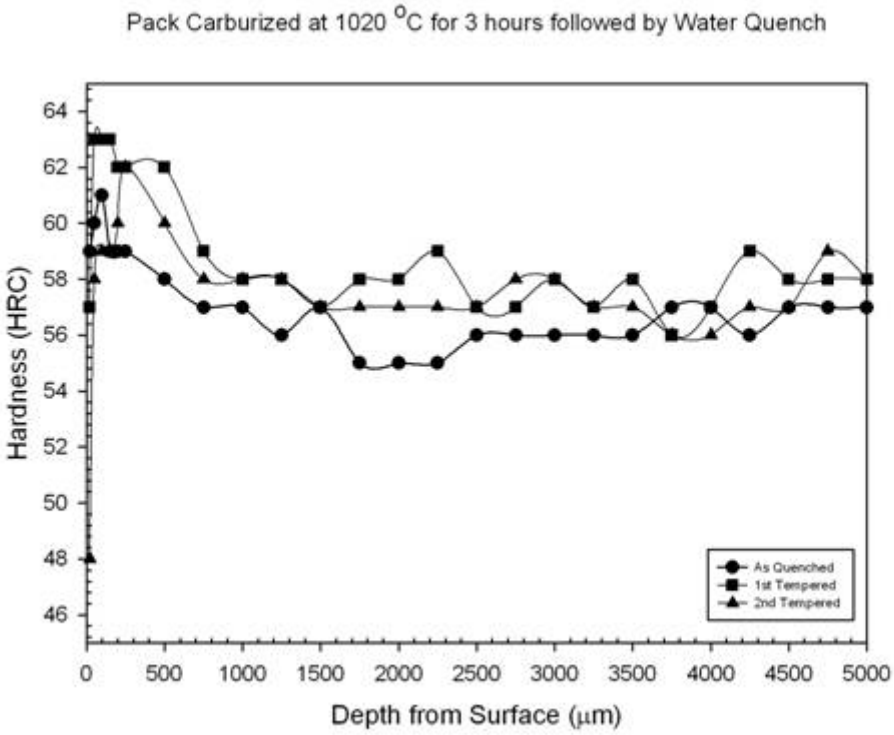


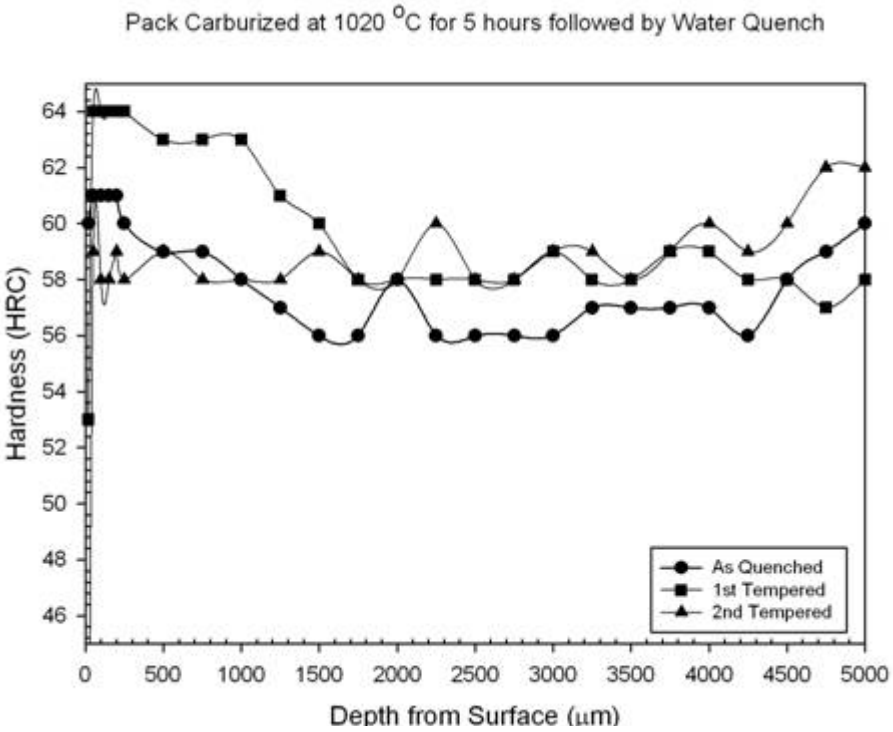
Pack Carburized at 1020 ^{o}C for 5 hours followed by Fan Cooling



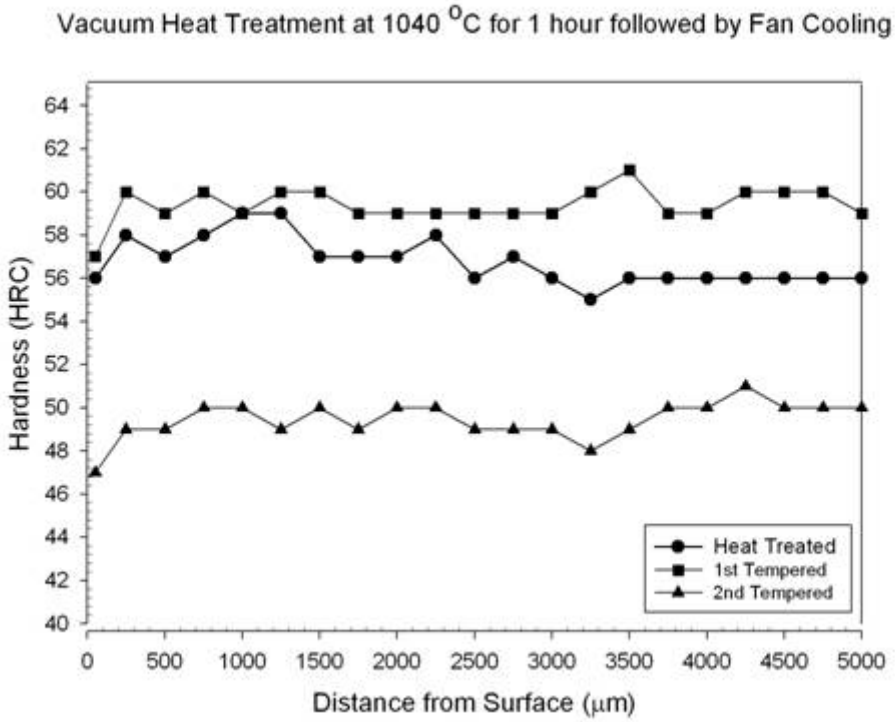
Pack Carburized at 1020 ^{o}C for 1 hour followed by Water Quench

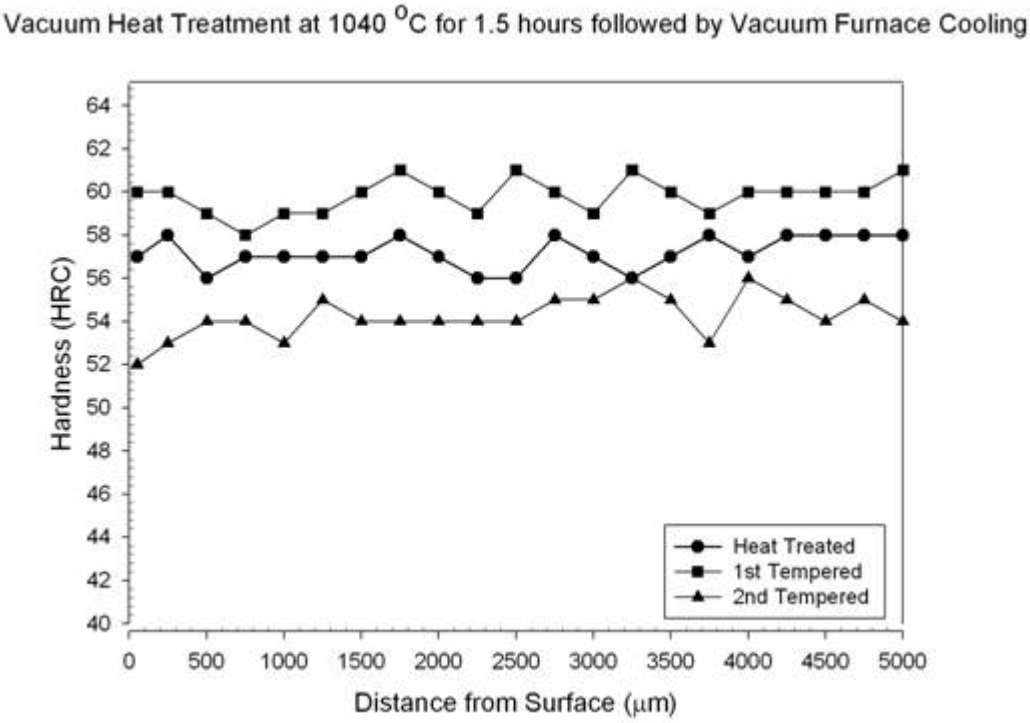



Pack Carburized at 1020 °C for 3 hours followed by Water Quench
Hardness (HRC)
Depth from Surface (μm)
As Quenched
1st Tempered
2nd Tempered

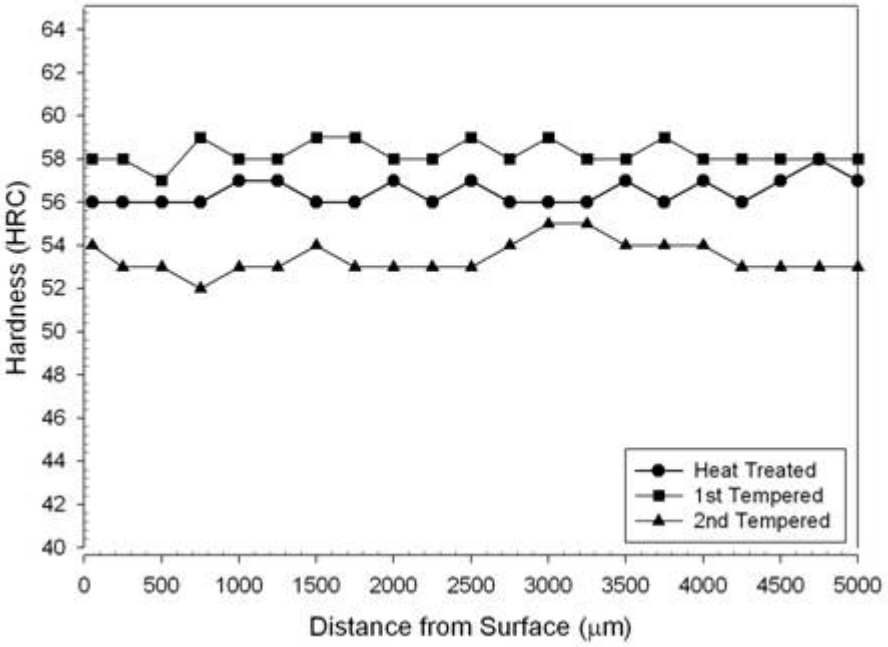

Pack Carburized at 1020 °C for 5 hours followed by Water Quench
Hardness (HRC)
Depth from Surface (μm)
As Quenched
1st Tempered
2nd Tempered

- Vacuum Treatment

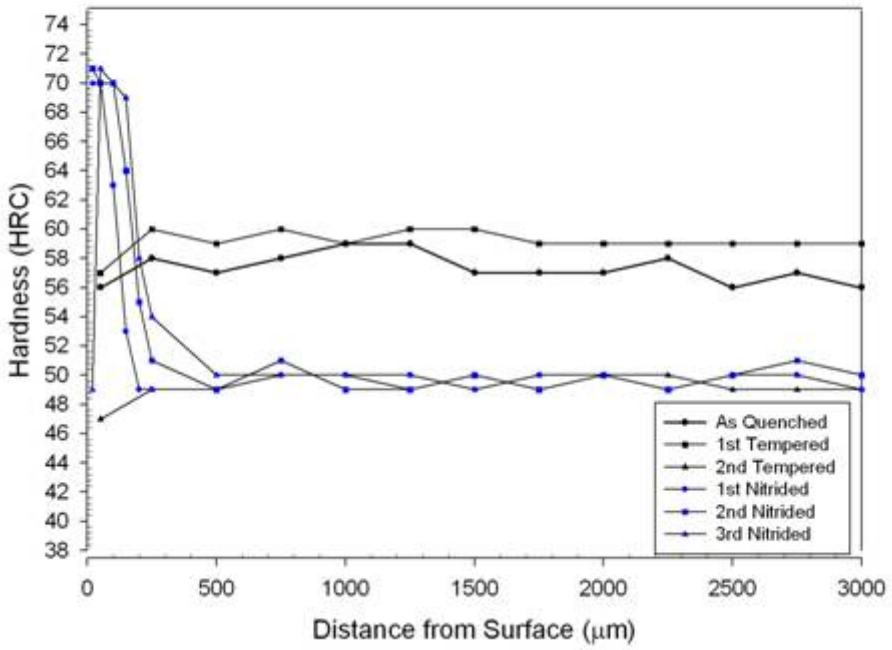




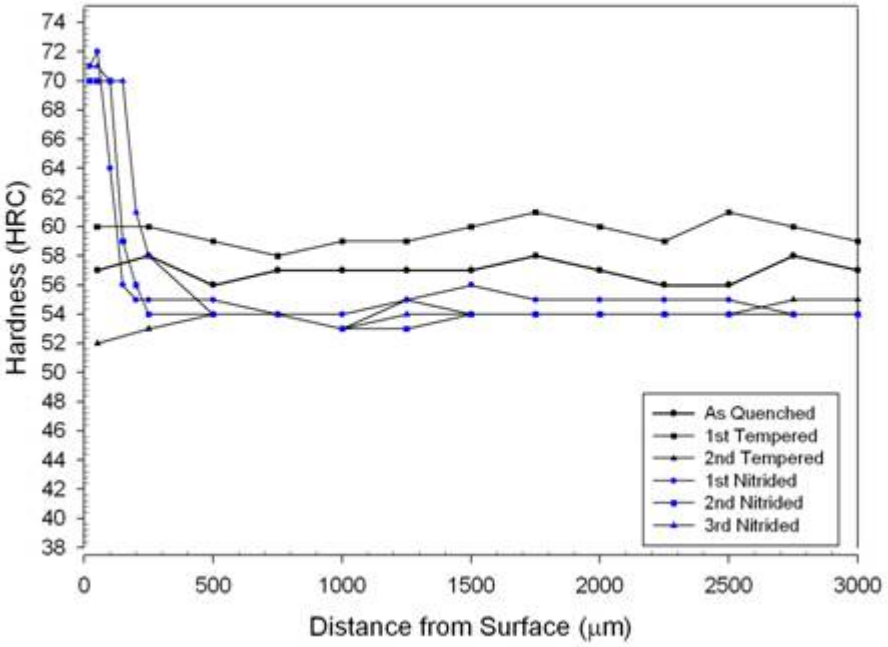
Vacuum Heat Treatment at 1040 ^{o}C for 2 hours followed by Vacuum Furnace Cooling



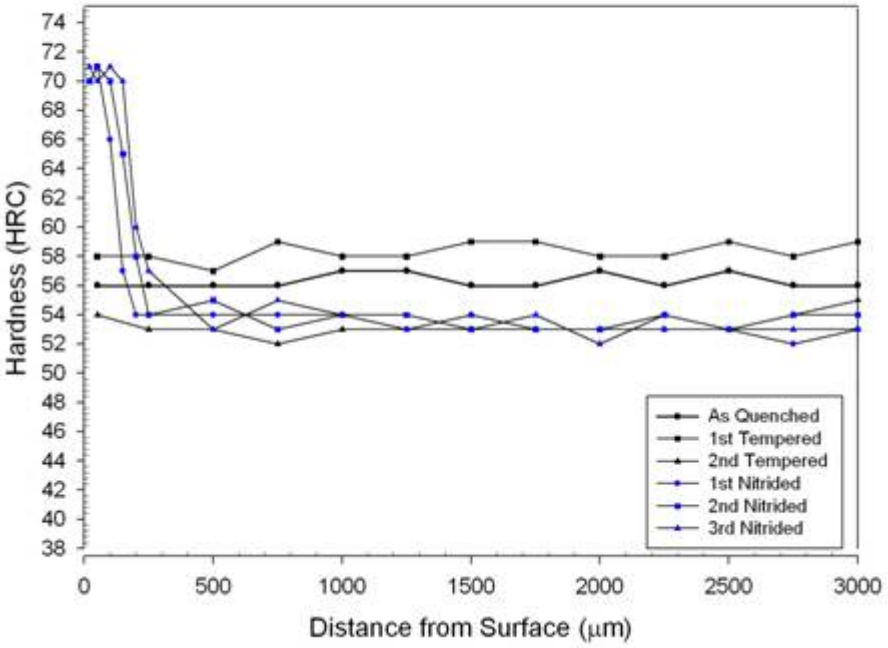
Vacuum Heat Treatment at 1040 ^{o}C for 1 hour followed by Fan Cooling



Vacuum Heat Treatment at 1040 ^{o}C for 1.5 hours followed by Fan Cooling



Vacuum Heat Treatment at 1040 ^{o}C for 2 hours followed by Fan Cooling



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