İSTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

SURFACE TREATMENT OF HEAT TREATABLE STEELS VIA NITRIDING AND THIN CrN COATING

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Programme : Materials Engineering

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ISIL İŞLEM YAPILABİLİR ÇELİKLERDE NİTRÜRLEME VE İNCE CrN KAPLAMA YOLUYLA YÜZEY İŞLEMLERİ

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Özgür ALPASLAN

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TABLE OF CONTENTS

Page

TABLE OF CONTENTS ..... **vii**
ABBREVIATIONS ..... **ix**
LIST OF TABLES ..... **xi**
LIST OF FIGURES ..... **xiii**
SUMMARY ..... **xv**
ÖZET ..... **xvii**
1. INTRODUCTION **1**
2. DIFFUSION METHODS **3**
2.1 Nitriding 3
2.2 Plasma (Ion) Nitriding 6
2.2.1 Case structures and formation 6
2.2.2 Diffusion zone of a nitrided case 7
2.2.3 Compound layers in nitrided steels 8
2.2.4 Structure of gas-nitrided steel case 9
2.2.5 Structure of ion-nitrided steel case 9
2.2.6 Workpiece factors 10
2.2.7 Suitability of materials 10
2.2.8 Effect of prior microstructure 10
2.2.9 Hardness profiles 11
2.2.10 White layer properties 12
2.2.11 Fatigue strength 12
2.2.12 Advantages and disadvantages 13
2.2.13 Alternative to carbonitriding for dimensional control 13
3. DEPOSITION METHODS **15**
3.1 Thin Films Formed by Physical Vapor Deposition 15
3.2 Technological (Real) Surfaces 17
3.3 Surface Preparation 18
3.4 Atomistic Film Growth 19
3.5 Vaporization 19
3.6 Transport 20
3.7 Condensation and Nucleation 20
3.8 Developing Surface Roughness 20
3.9 Changes in Microstructure and Morphology during Deposition 20
4. DUPLEX TREATMENT 23
4.1 Principles of Duplex Treatment 24
4.1.1 Definition and classification 24
4.1.2 Metallurgical aspects 24
4.1.3 Mechanical aspects 25
4.2 Duplex Treated Steel Systems 25
5. EXPERIMENTAL PROCEDURE **29**
5.1 Sampling 29

5.2 Surface and Heat Treatment 30
5.2.1 Bulk hardening 31
5.2.2 Plasma nitriding 31
5.2.3 Thin film coating 32
5.3 Characterization Tests 33
5.3.1 Microstructure examination 33
5.3.2 XRD analysis 33
5.3.3 Surface roughness test 33
5.3.4 Microhardness test 34
5.3.5 Rockwell C adhesion test 34
5.3.6 Wear test 34
6. RESULTS and DISCUSSION 35
6.1 Microsructure Examination 35
6.2 XRD Analysis 38
6.3 Surface Roughness Test 39
6.4 Microhardness Test 40
6.5 Rockwell C Adhesion Test 44
6.6 Wear Test 47
7. CONCLUSIONS 51
REFERENCES 53
APPENDICES 55
CURRICULUM VITAE 89

ABBREVIATIONS

BH	**:** Bulk Hardening
N	**:** Nitriding
PVD	**:** Physical Vapor Deposition
XRD	**:** X Ray Diffraction
SEM	**:** Scanning Electron Microscope

LIST OF TABLES

Page

Table 5.1: Steel grades and their as received hardness values 29
Table 5.2: Chemical compositions of the steel grades 30
Table 5.3: Bulk hardening parameters of vacuum furnace 31
Table 5.4: Bulk hardening parameters of gas atmosphere furnace 31
Table 5.5: Plasma nitriding parameters 32
Table 5.6: CrN coating parameters 33
Table 6.1: Thickness of white layers and CrN coatings 37
Table 6.2: Surface roughness of the treated surfaces at different steps 40

LIST OF FIGURES

Page

Figure 2.1 : Nitride case profiles for various steels 4
Figure 2.2 : Influence of alloying elements on hardness and depth of nitriding..... 6
Figure 2.3 : Factors affecting the microhardness profile of a nitrided steel 7
Figure 2.4 : Compound layer of γ' (Fe4N) on the ion-nitrided surface of quenched and tempered 4140 steel line title 8
Figure 2.5 : Observable diffusion zone on the unetched (white) portion of an ion-nitrided 416 stainless steel 8
Figure 2.6 : Typical gas compositions and the resulting metallurgical configurations of ion-nitrided steel 10
Figure 2.7 : Hardness profile for various ion-nitrided materials..... 11
Figure 2.8 : Effect of nitriding on fatigue strength 12
Figure 3.1 : Surface morphology effects on pinhole formation 18
Figure 6.1 : Microstructure of 1.2738 steel at 200x magnification..... 35
Figure 6.2 : Microstructure of 1.2379 steel at 200x magnification..... 36
Figure 6.3 : XRD pattern of 1.2738 steel 38
Figure 6.4 : XRD pattern of 1.2379 steel 39
Figure 6.5 : Microhardness measurements of 1.2738 steel by different loads 41
Figure 6.6 : Microhardness measurements of 1.2379 steel by different loads 41
Figure 6.7 : Indentation depth versus applied load for 1.2738 steel 42
Figure 6.8 : Indentation depth versus applied load for 1.2379 steel 42
Figure 6.9 : Cross section microhardness measurements of 1.2738 steel..... 43
Figure 6.10 : Cross section microhardness measurements of 1.2379 steel..... 44
Figure 6.11 : Rockwell C indents on 1.2738 steel 45
Figure 6.12 : Rockwell C indents on 1.2379 steel 46
Figure 6.13 : Scale for Rockwell C adhesion test 47
Figure 6.14 : Wear rates determined by reciprocating ball on disc method 48
Figure 6.15 : Friction coefficients determined by reciprocating ball on disc method..... 49

SURFACE TREATMENT OF HEAT TREATABLE STEELS VIA NITRIDING AND THIN CrN COATING

SUMMARY

In this study effect of surface treatment on wear resistance and surface hardness of 1.8550, 1.7225, 1.2344, 1.2738 and 1.2379 quality steels were investigated. 1.8550 and 1.2738 alloys were received in quenched and tempered state, while the other grades were in annelaed state. Therefore 1.7225, 1.2344 and 1.2379 steel grades were quenched and tempered in the scope of this thesis.

As surface treatment, plasma nitriding and CrN coating via PVD technique were applied. After the surface treatment process characterization of the samples were made by microstructure examinations, XRD analyses, microhardness tests, surface roughness measurements, Rockwell C adhesion tests and wear tests.

As a result of plasma nitriding process, white layers have been formed on the surfaces of quenched and tempered 1.8550, 1.7225, 1.2344 and 1.2738 quality steels. However, the surface of the martensitic 1.2379 quality steel was free from white layer.

At indentation loads in between 10g and 10000 g, considerably higher surface hardness values were detected on the surfaces of the nitrided alloys when compared to their quenched and tempered state. CrN coating of the steel by PVD techniques resulted in a further increase in surface hardness. The surface hardness of CrN coated alloys gradually decreased with increasing indentation load. According to the Rockwell C adhesion tests, CrN coatings established relatively good bonding with the martensitic and nitrided substrates. Similar to the CrN coatings, some micro-cracks were also detected at the vicinity of the indents of the nitrided steels, without leading severe delamination.

Hardness measurements on the cross sections of the nitrided steels at indentation load of 25 g revealed that, the case depth of the 1.2379 alloy was very small compared to those of 1.8550, 1.7225, 1.2344 and 1.2738 quality steels.

White layer containing 1.8550, 1.7225, 1.2344 and 1.2738 quality nitrided steels exhibited lower wear resistance than their quenched and tempered states. For the white layer free 1.2379 quality nitrided steel, wear resistance was enhanced upon nitriding when compared to its quenched and tempered state.

CrN coating of martensitic and nitrided steels caused significant improvement in wear resistance and reduction in friction coefficent. The excellent wear resistance was obtained after CrN coating of nitrided martensitic steels.

ISIL İŞLEM YAPILABİLİR ÇELİKLERDE NİTRÜRLEME VE İNCE CrN KAPLAMA YOLUYLA YÜZEY İŞLEMLERİ

ÖZET

Bu çalışmada yüzey işlemlerinin, 1.8550, 1.7225, 1.2344, 1.2738 ve 1.2379 alaşımlarının aşınma direncine ve yüzey sertliğine etkileri incelenmiştir. 1.8550 ve 1.2738 kaliteleri sertleştirilmiş ve menevişlenmiş olarak, diğer alaşımlar is tavlanmış olarak alınmıştır.1.7225, 1.2344 ve 1.2379 alaşımlarına bu tez kapsamında sertleştirme ve menevişleme işlemleri uygulanmıştır.

Yüzey işlemi olarak plazma nitrürleme ve fiziksel buhar biriktirme yoluyla ince film kaplama teknikleri uygulanmıştır. Yüzey işlemlerinden sonra, numunelerin karakterizasyonu, için mikroyapı incelemesi, XRD analizi, mikrosertlik ölçümü, yüzey pürüzlülüğü ölçümü, Rockwell C yapışma testi ve aşınma testi yapılmıştır.

Plazma nitrürleme işleminin sonucunda 1.8550, 1.7225, 1.2344 ve 1.2738 alaşımların yüzeyinde beyaz tabaka oluşurken, 1.2379 alaşımında beyaz tabakanın oluşmadığı belirlenmiştir.

10g'dan başlayıp 10000g'a kadar yapılan sertlik ölçümlerinde, nitrürlenmiş alaşımların yüzey sertliklerinde, sertleştirilmiş ve menevişlenmiş hallerine göre kayda değer miktarda artışlar olduğu belirlenmiştir. Fiziksel buhar biriktirme yoluyla CrN kaplama işlemi yüzey sertliklerini daha da artırmıştır. CrN kaplanmış yüzeylerin sertlik ölçümlerinde indentasyon yükü arttıkça sertliğin azaldığı gözlenmiştir.

Rockwell C yapışma testinde, CrN kaplamaların martensitik ve nitrürlenmiş altlıklarla iyi bağ yaptığı gözlenmiştir. CrN kaplamalara benzer şekilde, nitrürlenmiş yüzeylerdeki indentasyonların çevresinde mikro çatlaklar görülmekle birlikte ciddi boyutta kabarma, kalkma türü bir durumla karşılaşılmamıştır.

Nitrürlenmiş numunelerin kesitleri boyunca 25g yük ile yapılan mikrosertlik ölçümleri, 1.2379 alaşımının sertlik derinliğinin, 1.8550, 1.7225, 1.2344 ve 1.2738 kalite çeliklere kıyasla daha az olduğunu ortaya çıkarmıştır.

Beyaz tabaka içeren nitrürlenmiş 1.8550, 1.7225, 1.2344 ve 1.2738 kalite çelikler, sertleştirilmiş ve menevişlenmiş hallerine göre daha az aşınma direnci göstermişlerdir. Beyaz tabakası olmayan nitrürlenmiş 1.2379 kalite çeliğin aşınma direnci ise sertleştirilmiş ve menevişlenmiş haline göre artmıştır.

Martensitik ve nitrürlenmiş çeliklerin CrN kaplanması aşınma direncinde belirgin bir artış ve sürtünme katsayısında azalmaya neden olmuştur. Nitrürlenmiş martensitik çeliklerin CrN kaplanması sonucunda en iyi aşınma direnci elde edilmiştir.

1. INTRODUCTION

Engineering components are subjected to various kinds of surface treatments to increase service life. These treatments increase surface hardness, improve wear and corrosion resistance and fatigue properties.

Surface treatments can be classified mainly as diffusion, deposition and duplex treatment methods. Nitriding is an example of diffusion method and thin film coating is a typical deposition technique. Duplex treatment is a combination of these two processes.

The objectives of this study are to determine the effects of some surface treatments on surface hardness and wear resistance of some steel grades.

In this study, bulk hardening, nitriding, thin film coating and nitriding followed by thin film coating methods were applied to the specimens. The purpose was to increase surface hardness and wear resistance and determine how much they affect these properties. Another purpose was to compare the effects of these different methods on different steels.

Five steel grades were selected and received for this study. These steels are commonly used in industry. Four kinds of treatments were applied to these steels. Totally twenty types of specimens were obtained and they were characterized by several testing methods.

2. DIFFUSION METHODS

The purpose of the diffusion methods is to increase surface hardness by the mechanism of subsurface modification by diffusion process. Carburizing, nitriding, boriding, carbonitriding processes are some of the typical diffusion methods [1].

Diffusion methods modify the chemical composition of the surface with hardening species such as carbon, nitrogen, or boron. Diffusion methods allow effective hardening of the entire surface of a part and are generally used when a large number of parts are to be surface hardened [1].

The basic process used is thermochemical because some heat is needed to enhance the diffusion of hardening species into the surface and subsurface regions of a part. The depth of diffusion exhibits a time-temperature dependence such that:

$$\text{Case depth} \propto K_{\text{time}}$$

where the diffusivity constant, K, depends on temperature, the chemical composition of the steel, and the concentration gradient of a given hardening species. In terms of temperature, the diffusivity constant increases exponentially as a function of absolute temperature. Concentration gradient depends on the surface kinetics and reactions of a particular process [1].

1.1 Nitriding

Nitriding is a surface-hardening heat treatment that introduces nitrogen into the surface of steel at a temperature range (500-550 °C), while it is in the ferritic condition. Thus, nitriding is similar to carburizing in that surface composition is altered but different in that nitrogen is added into ferrite instead of austenite. Because nitriding does not involve heating into the austenite phase field and a subsequent quench to form martensite, nitriding can be accomplished with a minimum of distortion and with excellent dimensional control [1].

Nitrogen has partial solubility in iron. It can form a solid solution with ferrite at nitrogen content up to about 6%. At about 6% N, a compound called gamma prime

(γ'), with a composition of Fe4N is formed. At nitrogen contents greater than 8%, the equilibrium reaction product is ε compound, Fe3N. The outermost surface can be all γ' and , if this is the case, it is referred to as the white layer (it etches white in metallographic preparation). Such a surface layer is undesirable: It is very hard but is so brittle that it may spall in use. Usually it is removed; special nitriding processes are used to reduce this layer or make it less brittle. The ε zone of the case is hardened by the formation of the Fe3N compound, and below this layer there is some solid solution strengthening from the nitrogen in solid solution (Fig. 2.1) [1].

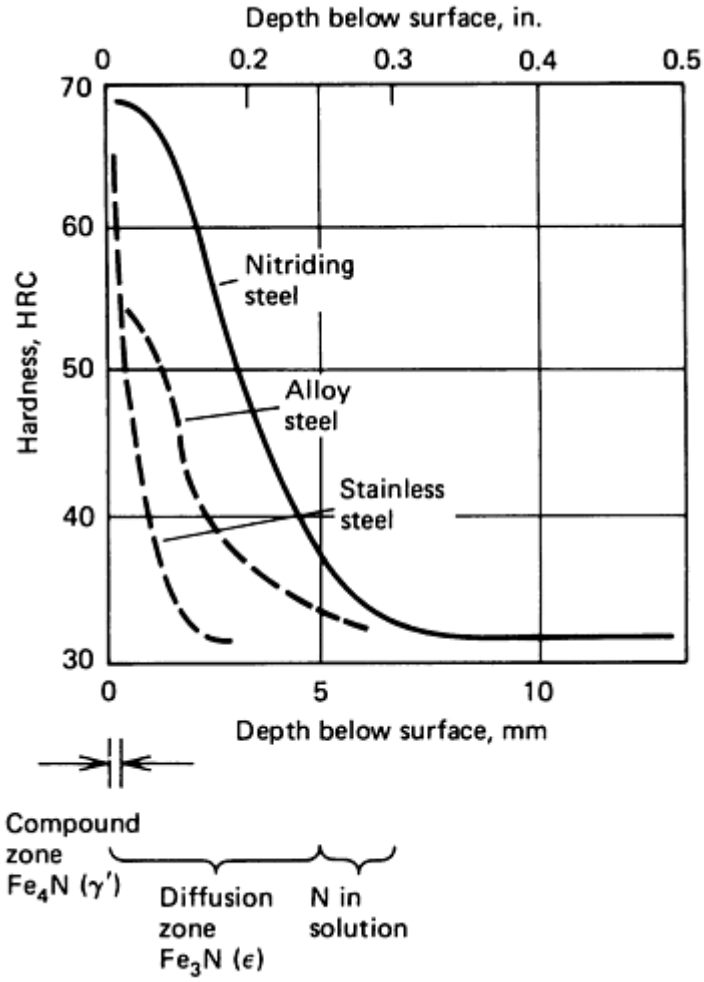


Figure 2.1 : Nitride case profiles for various steels [1].

Nitrided steels are generally medium-carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminum, chromium, vanadium and molybdenum. The most significant hardening is achieved with a class of alloy steels (nitralloy type) that contain about 1% Al (Fig.1). When these steels are nitrided,

aluminum forms AlN particles, which strain the ferrite lattice and create strengthening dislocations.

Titanium and chromium are also used to enhance case hardness (Fig. 2.2a), although case depth decreases as alloy content increases (Fig. 2.2b) [1]. Molybdenum will form stable nitrides at the nitriding temperature and will reduce the risk of surface embrittlement at the nitriding temperature [18].

Chromium will also form stable nitrides at the nitriding temperature; however, the high chromium content found in some stainless steels makes them more difficult to nitride. Chromium reacts with oxygen to form a chrome oxide barrier on the surface, which must be broken down by depassivation in order for nitriding to be effective. The higher the percentage of available chromium at the steel surface, the more difficult the steel will be to nitride. The positive side of this is usually high surface hardness values [18].

Vanadium in a nitriding steel also is conducive to the formation of stable nitrides. In addition, fine grain toughness will be exhibited within the formed case. Tungsten enables the steel to retain its hardness at high operating temperatures with no loss of surface hardness. Depending on the tungsten content and the general composition, the nitrided steel is able to operate at temperatures up to 590 °C (1100 °F) with enhanced wear characteristics and no appreciable loss of surface hardness [18].

Silicon is considered to be a good nitride former. Though it is usually present as either an oxidizer or a stabilizer, silicon generally is not of sufficient volume to be considered a strong nitride former [18].

The microstructure also influences nitridability because ferrite favors the diffusion of nitrogen and because a low carbide content favors both diffusion and case hardness. Usually alloy steels in the heat treated (quenched and tempered) state are used for nitriding [1].

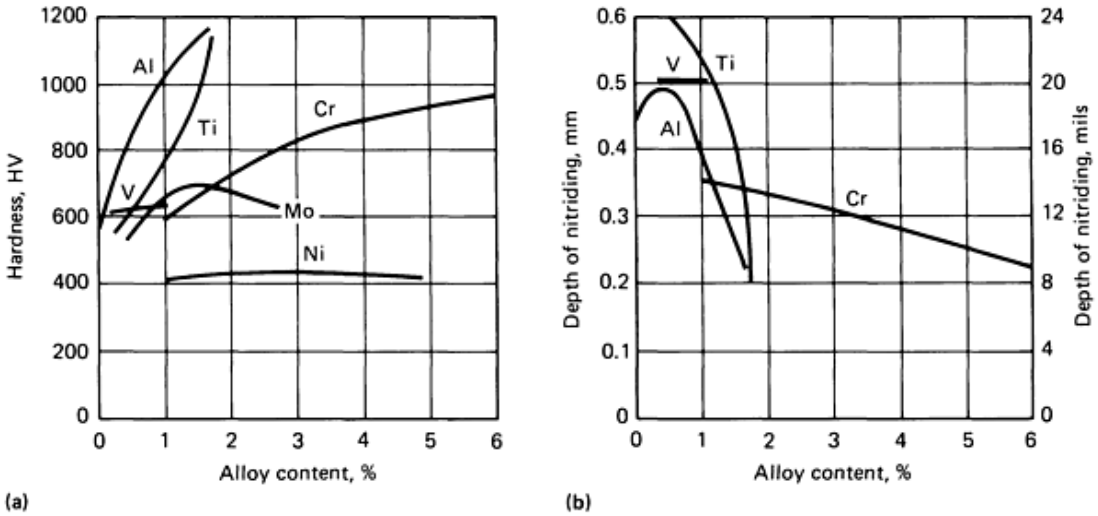


Figure 2.2 : Influence of alloying elements on (a) hardness after nitriding (base alloy, 0.35% C, 0.30% Si, 0.70% Mn) and (b) depth of nitriding measured at 400 HV (nitriding for 8 h at 520 °C, or 970 °F) [1].

Process methods for nitriding include gas (box furnace or fluidized bed), liquid(salt bath) and plasma (ion) nitriding. Times for gas nitriding can be quite long, from 10 to 130h depending on the application and the case depths are relatively shallow, usually less than 0.5mm. Plasma nitriding allows faster nitriding times and the quickly attained surface saturation of the plasma process results in faster diffusion. Plasma nitriding can also clean the surface by sputtering [1].

2.2. Plasma (Ion) Nitriding

Plasma, or ion, nitriding is a method of surface hardening using glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface and provides active nitrogen. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional (gas) nitriding. A key difference between gas and ion nitriding is the mechanism used to generate nascent nitrogen at the surface of the work [2].

2.2.1. Case structures and formation

The case structure of a nitrided steel, which may include a diffusion zone with or without a compound zone (Fig. 2.3), depends on the type and concentration of alloying elements and the time-temperature exposure of a particular nitriding

treatment. Moreover, because the formation of a compound zone and/or a diffusion zone depends on the concentration of nitrogen, the mechanism used to generate nascent nitrogen at the surface of the workpiece also affects the case structure [2].

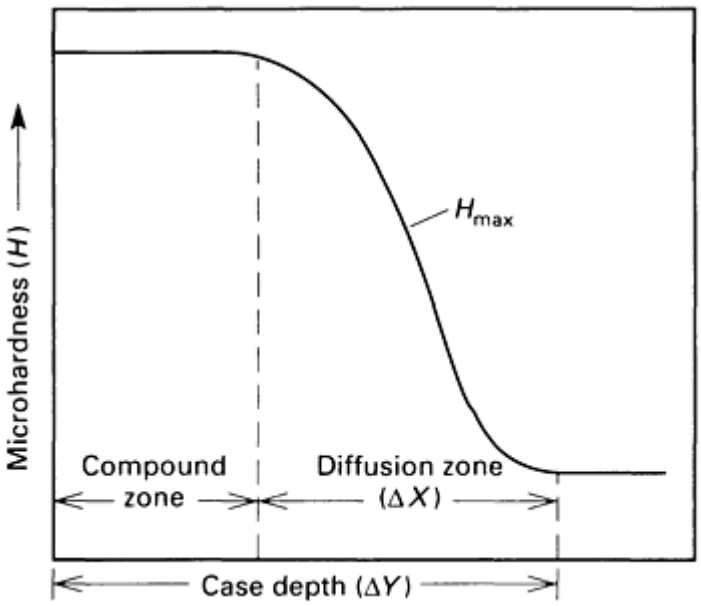


Figure 2.3 : Factors affecting the microhardness profile of a nitrided steel. The hardness of the compound zone is unaffected by alloy content, while the hardness of the diffusion zone is determined by nitride-forming elements (Al, Cr, Mo, Ti, V, Mn). ΔX is influenced by the type and concentration of alloying elements; ΔY increases with temperature and decreases with alloy concentration [2].

2.2.2. Diffusion zone of a nitrided case

The diffusion zone of a nitrided case can best be described as the original core microstructure with some solid solution and precipitation strenghtening. In iron-base materials, the nitrogen exists as single atoms in solid solution at lattice sites or interstitial positions until the limit of nitrogen solubility (0.4 wt% N) in iron is exceeded. This area of solid-solution strengthening is only slightly harder than the core. The depth of the diffusion zone depends on the nitrogen concentration gradient, time at a given temperature, and the chemistry of the workpiece [2].

As the nitrogen concentration increases toward the surface, very fine, coherent precipitates are formed when the solubility limit of nitrogen is exceeded. The precipitates can exist both in the grain boundaries and within the lattice structure of the grains themselves. These precipitates, nitrides of iron or other metals, distort the lattice and pin crystal dislocations and thereby substantially increase the hardness of the material [2].

In most ferrous alloys, the diffusion zone formed by nitriding cannot be seen in a metallograph because the coherent precipitates are generally not large enough to resolve. In Fig. 2.4, for example, martensite in the diffusion zone cannot be visually distinguished from that in the core. In some materials, however, the nitride precipitate is so extensive that it can be seen in an etched cross section. Such is the case with stainless steel (Fig. 2.5), in which the chromium level is high enough for extensive nitride formation [2].

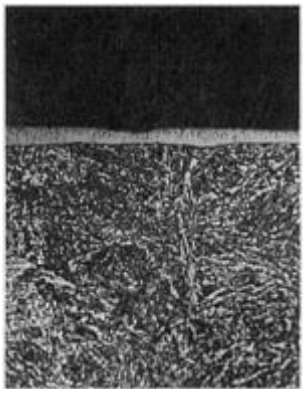


Figure2.4 : Compound layer of γ' (Fe4N) on the ion-nitrided surface of quenched and tempered 4140 steel. The γ' compound layer is supported by a diffused case, which is not observable in this micrograph. Nital etched. 500x [2].

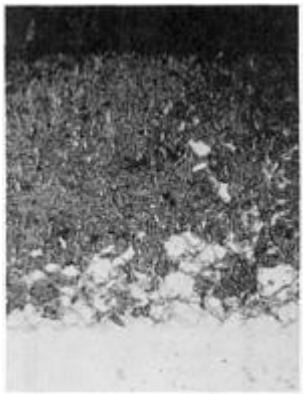


Figure 2.5 : Observable diffusion zone on the unetched (white) portion of an ion nitrided 416 stainless steel. Nital etched. 500x [2].

2.2.3. Compound layers in nitrided steels

The compound zone is the region where the γ' (Fe4N) and ε(Fe2-3N) intermetallics are formed. Because carbon in the material aids ε formation, methane is added to the process gas when an ε layer is desired. Hydrogen also tends to catalyze Fe2N

formation. These compound layers are called white layers because they appear white on a polished, etched cross section [2].

2.2.4. Structure of gas-nitrided steel case

Gas nitriding with ammonia produces a compound zone that is a mixture of the γ'and ε compounds; the mixture is due to the variability of ammonia dissociation, and therefore of nitriding potential, as the compound layer is formed. In conventional gas nitriding, the nascent nitrogen is produced by introducing ammonia (NH3) to a work surface that is heated to at least 480 °C (900 °F). Under these conditions, the ammonia, catalyzed by the metal surface, dissociates to release nascent nitrogen into the work and hydrogen gas into the atmosphere of the furnace. The nitriding potential, which determines the rate of introduction of nitrogen to the surface, is determined by the NH3 concentration at the work surface and its rate of dissociation. This nitriding potential, which can vary significantly in the gas process, is responsible for the limited control of microstructure in the nitrided case [2].

X-ray diffraction has shown that from the outer surface to the beginning of the diffusion zone the dominant compound changes from ε to γ'. However, both phases exist throughout the entire white layer, which is referred to as a dual-phase layer [2].

The dual-phase layer has two characteristics that make it susceptible to fracture:

· Weak bonding at the interface between phases
· Different thermal-expansion coefficients in the two phases

Layers that are particularly thick or that are subjected to temperature fluctuation in service are particularly prone to failure [2].

Another mechanical weakness in the gas-nitrided white layer is porosity in the outer region of the layer. As the compound zone builds, ammonia dissociation becomes more sluggish without the catalytic action of the steel surface, and gas bubbles begin to form in the layer [2].

2.2.5. Structure of ion-nitrided steel case

In the ion-nitriding process, nitrogen gas (N2) can be used instead of ammonia because the gas is dissociated to form nascent nitrogen under the influence of the glow discharge. Therefore the nitriding potential can be precisely controlled by the

regulation of the N2 content in the process gas. This control allows precise determination of the composition of the entire nitrided case, selection of a monophase layer of either ε or γ', or total prevention of white-layer formation (Fig. 2.6) [2].

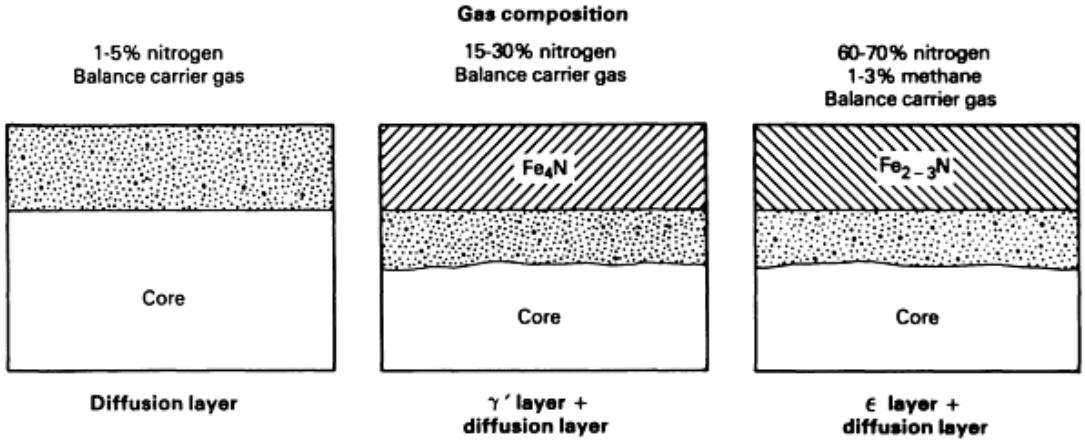


Figure 2.6 : Typical gas compositions and the resulting metallurgical configurations of ion-nitrided steel [2].

2.2.6. Workpiece factors

The nitrogen concentration achieved during nitriding affects the depth and hardness of the case. In addition, the microstructure and resulting mechanical properties of a nitrided case also depends on the original composition and microstructure of the workpiece [2].

2.2.7. Suitability of materials

In general, the response of a material to nitriding depends on the presence of strong nitride-forming elements. Plain carbon steels can be nitrided, but the diffused case is not significantly harder than the core. The strongest nitride formers are aluminum, chromium, molybdenum, vanadium and tungsten. Because the white layer constituents are only compounds of iron and nitrogen, the hardness of these layers is essentially independent of alloy content [2].

2.2.8. Effect of prior microstructure

As with other diffusion methods, the initial microstructure can also influnce the response of a material to nitriding. In the case of alloy steels, a quenched and tempered structure is considered to produce the optimum nitriding results. The tempering temperature should be 15 to 25 °C above the anticipated nitriding

temperature to minimize further tempering of the core during the nitriding process [2].

If the nitriding of nonmartensitic matrix is desired, it is important that prior heat treatment must be accompanied by as fast a cooling as possible to provide a relatively low-temperature austenite transformation and retain a high percentage of the nitride forming element in solution for subsequent precipitation [2].

2.2.9. Hardness profiles

There are hardness profiles for typical ion-nitrided alloys in Fig. 2.7. The hardness increase of an ion-nitride layer is virtually the same as for any nitriding process that provides the same nitrogen concentration profile. As previously mentioned, the hardness of the diffused case depends on precipitation hardening, while that of the white layer depends on the type and thickness of the compound formed. Because the white layers are compounds of only iron and nitrogen, the hardness of these layers is essentially independent of alloy content [2].

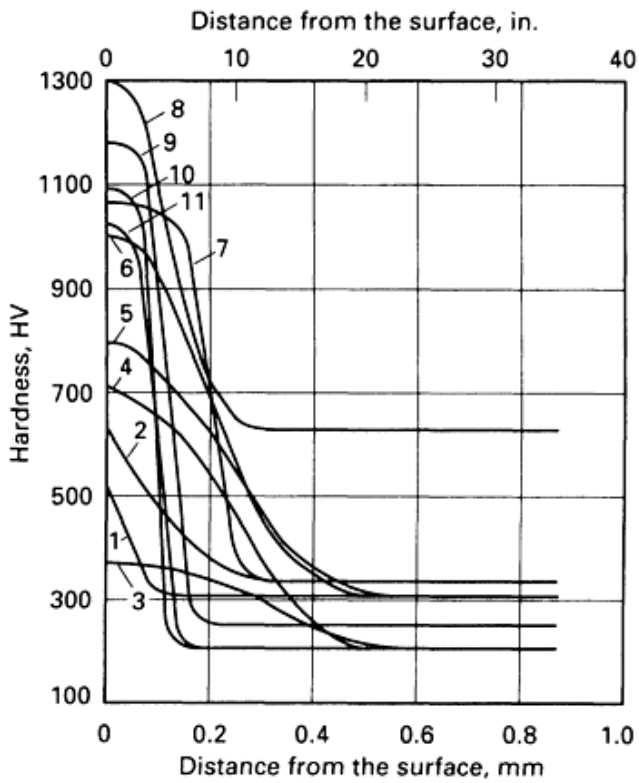


Figure 2.7 : Hardness profile for various ion-nitrided materials. 1, gray cast iron; 2, ductile cast iron; 3, AISI 1040; 4, carburizing steel; 5, low-alloy steel; 6, nitriding steel; 7, 5% Cr hot-work steel; 8, cold-worked die steel; 9, ferritic stainless steel; 10, AISI 420 stainless steel; 11, 18-8 stainless steel [2].

2.2.10. White layer properties

In general, case depth and white-layer composition should be selected for the anticipated operating conditions of the nitrided component. The ε layer is best for wear and fatigue applications that are relatively free of shock loading or high localized stresses. The γ' layer is somewhat softer and less wear resistant, but is tougher and more forgiving in severe loading situations. The white layer also provides increased lubricity. In addition to mechanical properties, the white layer, which is relatively inert, provides increased corrosion resistance in a variety of environments [2].

2.2.11. Fatigue strength

In addition to hardness and wear resistance, fatigue strength is significantly improved by nitriding (Fig. 2.8). The formation of precipitates in the diffused case results in lattice expansion. The core material, in an attempt to maintain its original dimension, holds the nitrided case in compression. This compressive stress essentially lowers the magnitude of an applied tensile stress on the material and thus effectively increases the endurance limit of the part [2].

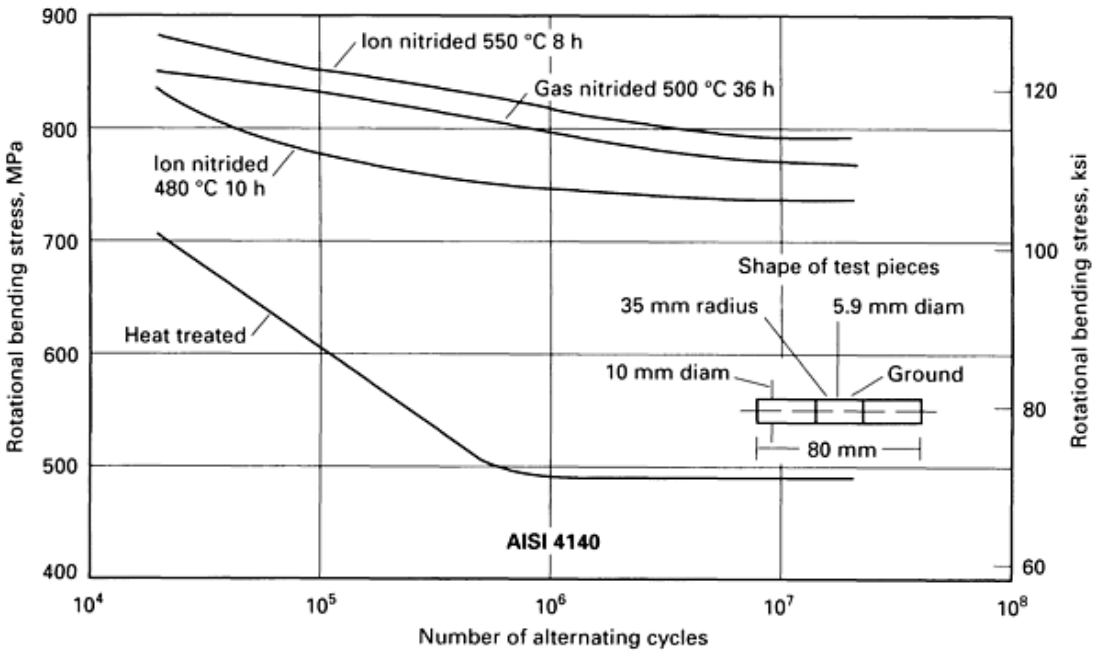


Figure 2.8 : Effect of nitriding on fatigue strength [2].

2.2.12. Advantages and disadvantages

Ion nitriding when compared to conventional (gas) nitriding, offers more precise control of the nitrogen supply at the workpiece surface and the ability to select either an ε or a γ' monophase layer or to prevent white-layer formation entirely. Other advantages of ion nitriding are:

- Improved control of case thickness
- Lower temperatures (as low 375 °C,or 700 °C, due to plasma activation, which does not exist in gas nitriding)
- Lower distortion
- No environmental hazard (freedom from handling ammonia)
- Reduced energy consumption
- Ability to automate
- Ability to shield areas where nitriding is not desired by simple mechanical masking

A disadvantage of the ion process is the need to fixture parts to avoid localized overheating [2].

2.2.13. Alternative to carbonitriding for dimensional control

Ion nitriding is becoming a replacement for carbonitriding in some areas. The driving force for this decision is the growing industry focus on dimensional control and the desire to reduce or eliminate machining after heat treatment. The distortion of carbonitrided parts occurs in three ways:

· Heating to the austenitic range relieves residual stress

· Oil quenching introduces high thermal stresses and some localized plastic deformation

· The expansion of the case during martensite formation can cause some part distortion

Ion nitriding can be performed at temperatures as low as 375 °C (700 °F), which minimizes the amount of residual stres relieved. Because loads are gas cooled, they do not experience distortion from temperature gradients or martensite formation [2].

3. DEPOSITION METHODS

The purpose of deposition methods is to harden the surface by involving an intentional buildup or addition of a new layer. Thin films (physical vapor deposition, sputtering, ion plating), coatings (electrochemical plating, chemical vapor deposition, ion mixing) or weld overlays (hardfacings) are examples of deposition methods. Films, coatings, and overlays generally become less cost effective as production quantities increase, especially when the entire surface of workpieces must be hardened [3].

The fatigue performance of films, coatings, and overlays may also be a limiting factor, depending on the bond strength between the substrate and the added layer. Fusion-welded overlays have strong bonds, but the primary surface-hardened steels used in wear applications with fatigue loads include heavy case hardened steels and flame- or induction-hardened steels. Nonetheless, coatings and overlays can be effective in some applications. With tool steels, for example, TiN and Al_2O_3 coatings are effective not only because of their hardness but also because their chemical inertness reduces crater wear and the welding of chips to the tool. Overlays can be effective when the selective hardening of large areas is required [3].

1.2 Thin Films Formed by Physical Vapor Deposition

The properties of atomistically deposited films depend strongly on the material being deposited, the substrate surface chemistry and morphology, the surface preparation process, and the details of the deposition process and the deposition parameters. The origin of the unique properties of physical vapor deposition (PVD) film can be understood by understanding the film formation process [3].

The formation of a useful and commercially attractive engineered surface using any PVD process (vacuum deposition, sputter deposition, or ion plating) involves several stages:

1. Choice of the substrate (real surface) and development of an appropriate surface preparation process
2. Selection of the film material(s) to produce the surface properties required
3. Choice of the PVD process to provide reproducible properties, compatibility with subsequent processing, and long-term stability
4. Development of the fabrication process parameters, parameter limits, and the monitoring/control techniques
5. Development of appropriate characterization techniques to determine the film properties and stability of the product
6. Creation of written specifications and manufacturing processing instructions to cover the substrate material, surface preparation, deposition process, and characterization procedures

The properties of a film of a material formed by any PVD process depends on four factors:

- **Substrate surface condition**--e.g., surface morphology (roughness, inclusions, particulate

contamination), surface chemistry (surface composition, contaminants), mechanical properties, surface flaws, outgassing, preferential nucleation sites, and the stability of the surface

- **Details of the deposition process and system geometry**--e.g., angle-of-incidence distribution of the depositing adatom flux, substrate temperature, deposition rate, gaseous contamination, and concurrent energetic particle bombardment (flux, particle mass, energy)
- **Details of film growth on the substrate surface**--e.g., substrate temperature, nucleation, interface formation, interfacial flaw generation, energy input to the growing film, surface mobility of the depositing adatoms, growth morphology of the film, gas entrapment, reaction with deposition ambient (including reactive deposition processes), and changes in the film properties during deposition
- **Postdeposition processing and reactions**--e.g., reaction of film surface with the ambient, thermal or mechanical cycling, corrosion, interfacial degradation, burnishing of soft surfaces, shot peening, and overcoating (topcoat)

In order for the film to have reproducible properties, each of these factors must be reproducible [3].

3.2. Technological (Real) Surfaces

Technological surfaces or engineering surfaces are terms that are used to describe the real surfaces of engineering materials. These layers, along with the underlying bulk material, are the real substrate that must be altered to produce the desired surface properties. Invariably the real surface differs chemically from the bulk material by having surface layers of reacted and adsorbed material such as oxides and hydrocarbons. The surface chemistry, morphology, and mechanical properties of the real surface can be very important to the adhesion and film formation process. The underlying bulk material can be important to the performance of the surface. For example, a wear coating on a soft substrate will not function well if, under load, it is fractured by the deformation of the underlying substrate. Also, good film adhesion cannot be obtained when the substrate surface is mechanically weak, because failure can occur in the near-surface material. The bulk material can influence the surface preparation and the deposition process by continual outgassing and outdiffusion of internal constituents [3].

Some of the surface properties that affect the formation and properties of the deposited film are:

· Surface chemistry--affects the adatom-surface reaction and nucleation density. Chemistry can affect the stability of the interface formed by the deposition.

· Contamination (particulate and film, local or uniform)--affects surface chemistry and nucleation of the adatoms on the surface. Particulate contamination generates pinholes in the deposited film.

· Surface morphology--affects the angle-of-incidence of the depositing atoms and thus the film growth. Geometrical shadowing of the surface from the depositing adatom flux reduces surface coverage. Surface morphology can affect the film properties and stability.

· Mechanical properties--affects film adhesion and deformation under load

· Outgassing and outdiffusion--affects nucleation and film contamination

· Homogeneity of the surface--affects uniformity of film properties over the surface

In particular, the surface morphology can have an important effect on the film properties. Figure 3.1 shows the effect of surface morphology and particulate contamination on surface coverage and pinhole formation. Also, the surface morphology can affect the average angle-of-incidence of the adatom flux, which has

a large effect on the development of the columnar morphology in atomistically deposited films [3].

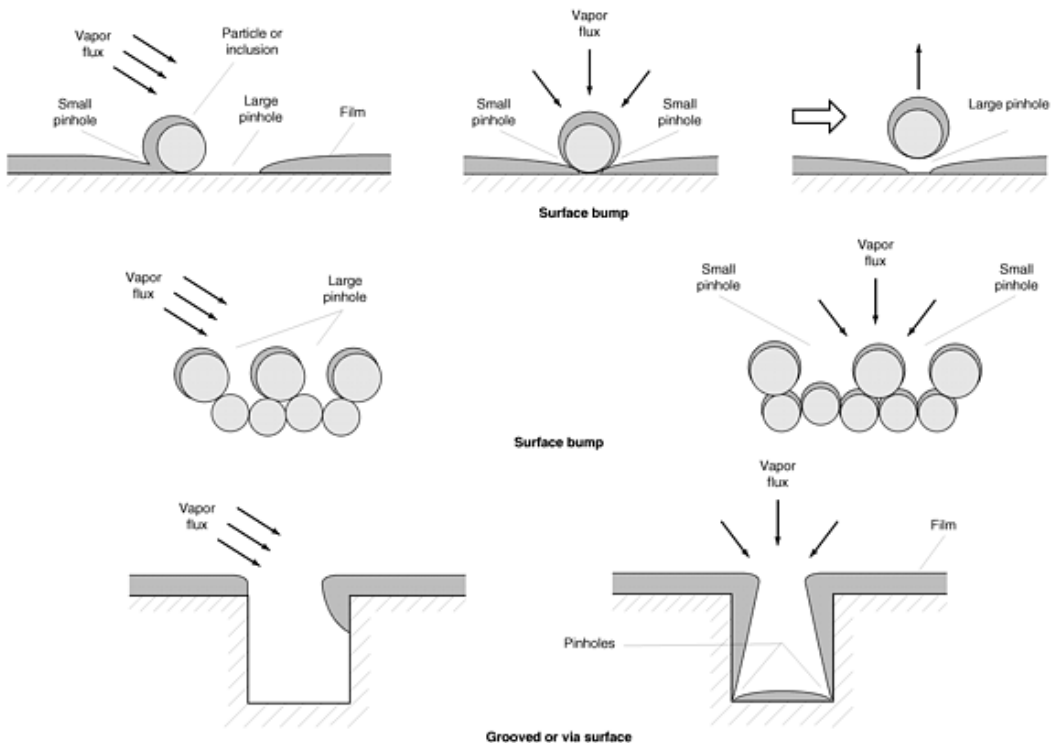


Figure 3.1 : Surface morphology effects on pinhole formation [3].

The nature of the real surface depends on its formation, handling, and storage history. In order to have reproducible film properties, the substrate surface must be reproducible. This reproducibility is attained by careful specification of the substrate material, careful incoming inspection procedures, careful surface preparation, and appropriate handling and storage of the material [3].

3.3. Surface preparation

Surface preparation is the process of preparing a surface for the film/coating deposition process. Surface preparation may mean cleaning (removal of contaminants), but it can also include surface treatments to change the properties of the surface in a desirable way, such as roughening or smoothing the surface, making a harder surface by plasma treatment (i.e., plasma nitriding) or shot peening, or "activating" the surface, such as the oxygen plasma treatment of a polymer surface. Often surface preparation consists of two distinct stages. The first is "external cleaning," which takes place outside the deposition system in a controlled

environment. This processing environment is designed to control recontamination after cleaning. For example, to control recontamination by particulates, a filtered air "cleanroom" is used. External cleaning can consist of both "gross cleaning," which removes a portion of the substrate surface material, and "specific cleaning," which removes specific contaminants such as hydrocarbons or salts. The second stage of surface preparation is "in situ cleaning," which is performed in the deposition system. For example, hydrocarbon contamination can be removed from some surfaces by exposing them to an oxygen plasma in the deposition system [3].

Care must be taken to ensure that the surface preparation process does not change the surface in an undesirable or uncontrolled manner, such as selective leaching of one phase of a two-phase surface. One objective of any surface preparation procedure is to produce as homogeneous a surface as possible. Reproducible surface preparation, as well as associated handling and storage techniques, are obtained by having appropriate specifications for the process, handling, and storage procedures used. In addition, recontamination of the prepared surface in the deposition chamber and by the deposition process is a major consideration [3].

3.4. Atomistic Film Growth

Atomistic film growth occurs as a result of the condensation of atoms ("adatoms") on a surface. The stages of film formation are:

1. Vaporization of the material (adatoms) to be deposited
2. Transport of the material to the substrate
3. Condensation and nucleation of the adatoms
4. Nuclei growth
5. Interface formation
6. Film growth--nucleation and reaction with previously deposited material
7. Changes in structure during the deposition process--interface and film
8. Postdeposition changes due to postdeposition treatments, exposure to the ambient, subsequent processing steps, in-storage changes, or in-service changes [3].

3.5. Vaporization

In physical vapor deposition, vapors can be formed by thermal and nonthermal techniques. Thermal techniques require heating, such as vacuum evaporation and

sublimation. Nonthermal vaporization includes sputtering, arc vaporization, laser ablation, and others [3].

3.6. Transport

The vaporized material can be transported through a vacuum, gas, or plasma. The vacuum environment allows control of the contamination in the ambient environment to any desired level. The gaseous environment may thermalize energetic particles and cause vapor phase nucleation, depending on the gas density. The plasma environment "activates" reactive species, making them more chemically reactive [3].

3.7. Condensation and Nucleation

Atoms that impinge on a surface in a vacuum environment either are reflected immediately, reevaporate after a residence time, or condense on the surface. The ratio of the condensing atoms to the impinging atoms is called the sticking coefficient. If the atoms do not immediately react with the surface, they will have some degree of surface mobility over the surface before they condense. Re-evaporation is a function of the bonding energy between the adatom and the surface, the surface temperature, and the flux of mobile adatoms. For example, the deposition of cadmium on a steel surface having a temperature greater than about 200 °C (390 °F) will result in total re-evaporation of the cadmium [3].

3.8. Developing Surface Roughness

On an atomistic scale, surface morphology can vary from very smooth, such as that of a flowed glass surface, to very rough, such as is found with sintered materials. Generally, as the film grows the surface roughness increases because some features or crystallographic planes grow faster than others. The roughness may not be uniform over the surface, or there can be local areas of roughness due to scratches, vias, embedded particles, particulate contamination, and so on that lead to variations of the film properties in these areas [3].

3.9. Changes in Microstructure and Morphology during Deposition

Film microstructure, morphology, and properties can be influenced by processes that occur after adatom condensation but during film growth. The processes that change the film properties include:

· Mass transport, such as growth of the interfacial region and crystal defect formation and void coalescence
· Recrystallization and grain growth
· Phase precipitation and growth
· Chemical reaction of codeposited species
· Stress annealing

Many of these changes are time- and temperature-dependent and therefore depend on the thermal history of the film during deposition. This thermal history depends on the deposition temperature, condensation energy release, deposition rate, deposition time, thermal conductivity of the film and substrate materials, heat removal mechanisms, and so on [3].

4. DUPLEX TREATMENT

Despite the fact that great achievements have been made in the domain of existing first generation surface engineering technologies, real designed surfaces with economically viable technically enhanced performance were rarely produced until duplex surface engineering, also referred to as second generation surface engineering, emerged. For instance, thin coatings such as PVD TiN can provide a surface with dramatically improved tribological properties in terms of low friction and high resistance to wear, but catastrophical failure will occur if the substrate plastically deforms under a high applied load; on the other hand deep hardened layers produced by such surface modification techniques as energy beam surface alloying can sustain high contact stresses but still exhibit higher friction and wear rates when compared to most ceramic coatings [4].

The tribological performance of components covered with hard physical vapor deposited (PVD) coatings depends both on the properties of the coating and the substrate. Duplex coatings that consist of a nitrided steel substrate and a hard PVD coating, combine the high hardness and the good wear properties of PVD coatings with enhanced fatigue and corrosion resistance and load carrying properties of the hardened substrate [5], [8], [9].

PVD hard ceramic coatings provide surfaces with low friction and high wear resistance; however, in the field of extrusion dies this technique has some disadvantages. The main point is the large difference in hardness between coating and substrate which results in coating failure. The duplex treatment, which combines the hardening of the substrate by nitriding prior to the physical vapor deposition process of the hard coatings, reduces the hardness gradient between the coated surface and substrate resulting, thus, in an improved adhesion and an increase of the durability of the tools [6], [10]. by a tough and supportive sub-surface for the hard coating[7], [10].

4.1. Principles of Duplex Treatment

4.1.1. Definition and classification

Duplex treatment or duplex surface engineering, as the name implies, involves the sequential application of two or more established surface technologies to produce a surface composite with combined properties which cannot be obtained through any individual surface technology. According to the interactions between the two individual processes and their relative contributions to the combined effects of the composite layer, duplex surface engineering may fall into two general groups: in the first group (Type I), two individual processes complement each other and the combined effects result from both processes; in the second group (Type II), one process supplements and reinforces the other, thus serving as pre- or post-treatment, and the resultant properties are mainly related to one process. PVD treatment of pre-nitrided steel is a typical example of the first group while electron beam surface melting of a sprayed overlay is a typical example of the second group [4].

4.1.2. Metallurgical aspects

Although the possible combinations of surface technologies are virtually unlimited and the list of duplex surface technologies could be endless, to date only a limited number of duplex treatments have been developed, and few of them have yet found real applications. It should be pointed out that duplex treatments are not simply mixing two surface treatments which may individually produce desirable properties. This is because a duplex treated component is typical of a multi-layer system and the resultant performance of a duplex system depends more on the combined effects from the two individual processes, rather than the expected effect provided by individual processes, i.e. synergy of the processes usually occurs. For instance, inappropriate combinations and/or incorrect control will lead to worse rather than improved combined effects. Accordingly, it is essential to identify correctly the metallurgical reactions so that the effects resulting from the first process are not deteriorated by the second process [4].

4.1.3. Mechanical aspects

It has been found that in most coating systems plastic deformation initiates in the substrate near the coating–substrate interface when subject to relatively high intensity loading, and plastic deformation does not initiate in the coating until a large plastic zone has been developed in the substrate. The load bearing capacities of coating–substrate systems thus depends upon the substrate properties. Clearly, deep case hardening can significantly enhance the load bearing capacity of a coating-substrate system [4].

According to the local shear strain or stress criterion, which may be most suitable for compression-dominated contact, an interface crack or adhesive failure may initiate in the layered media if the plastic shear strain at the interface is beyond a critical value. The magnitudes of shear stress and strain along interfaces vary significantly with the friction coefficient. Thus, low friction coatings such as nitrides and oxides used as the top coating layer for duplex systems not only increase wear resistance but also diminish interfacial shear stress and strain, and thus reduce the tendency for debonding of top coatings. In this respect, DLC or diamond coating are more effective since they possess the lowest friction against most engineering surfaces [4].

4.2. Duplex Treated Steel Systems

PVD treatment of pre-nitrided steel is the most widely researched and well documented duplex treatment process. Plasma nitriding produces a relatively thick (~500 μm) and hard (900–1000 HV) subsurface, and at the same time a thin iron nitride compound layer is formed at the outmost surface. The thickness of the compound layer is a function of the active nitrogen capacity of the plasma and the processing temperature and time. It has been shown that the nature and thickness of this iron nitride phase can have a profound effect on the quality of the titanium nitride deposited and on the bonding strength to the nitrided subsurface. In one duplex system after plasma nitriding, the nitrided surface was coated with titanium nitride about 3 μm thick by various PVD processes. Depending on the nitriding and the coating process conditions, as well as the surface preparation prior to coating, a variety of coating–nitrided combinations were produced, including (a) ceramic coating/dense compound layer, (b) ceramic coating/diffusion layer (c) ceramic coating/decomposed compound layer (black layer) [4].

As a result of the combined effects of the two processes engineering components exhibit low friction and wear (a characteristic of ceramic coatings), and a high load bearing capacity and high fatigue strength, characteristics of the nitrided subsurface. In addition improved coating- subsurface adhesion strength can be also achieved provided these two processes are properly combined and carefully controlled. On the other hand, incorrect process control will lead to the formation of a soft 'black' layer below the coating by thermochemical decomposition of the outer part of the previously present iron nitride layer, which severely deteriorates the load bearing capacity of the composite through reduced bonding strength between the outermost titanium nitride and the nitrided subsurface. The problem of the formation of undesirable 'black' layer has been addressed by grinding off the compound layer prior to coating or avoiding the formation of compound layer during the nitriding process ('bright nitriding'). Reducing the PVD process temperature to <450°C is effective in avoiding the undesirable decomposition of iron nitride layer [4].

An ideal PVD ceramic coating-nitrided steel duplex system can thus be designed with a view to achieving combined improvements in tribological behaviour, corrosion resistance and fatigue strength based on the above discussion, as follows:

1) hardening and tempering of low alloy steel to obtain a combination of good core properties and nitriding response;

2) plasma nitriding to produce a dense compound layer which is essential for achieving excellent corrosion resistance, and also to produce a deep hardened case which serves as strong support for the hard ceramic coating, and to form an intensive near surface compressive stress, which assists in conferring excellent fatigue strength;

3) removing the outer part of the iron nitride formed in the plasma nitriding process by micro blasting or polishing to secure high adhesion strength between the iron nitride and the ceramic coating, and to eliminate a possible negative effect on the corrosion resistance associated with interfacial porosity;

4) PVD-nitride coating at temperatures below 450°C to produce a very hard, wear and corrosion-resistant ceramic coating without appreciably impairing the beneficial effects resulting from the plasma nitriding treatment [4].

In addition to the discontinuous duplex process mentioned above, continuous processes have recently been investigated to produce such ceramic coating/nitrided steel systems. A typical continuous process involves plasma nitriding followed by ceramic coating (PVD or PCVD) in the same equipment without interruption. Although the integrated duplex processes have the advantages of possibly better process control, simple logistics and better delivery time, they have the economic disadvantage of using an expensive PVD coating unit for a nitriding treatment which can be up to 60 h [4].

5. EXPERIMENTAL PROCEDURE

5.1. Sampling

Five different steel grades were received for this study. These steels are commonly used in industry. They are suitable for various kinds of heat and surface treatment applications. As received hardness values and compositions of these alloys are shown in Tables 5.1 and 5.2.

Table 5.1 : Steel grades and their as received hardness values.

	Steel	Definition	Diameter(mm)	Hardness
1	1.8550 34CrAlNi7	Nitriding steel	35	282 HB
2	1.7225 42CrMo4	Heat treatable steel	32	200 HB
3	1.2344 X40CrMoV5-1	Hot work tool steel	28	207 HB
4	1.2738 40CrNiMo8-6-4	Plastic mold steel	26.5	36 HRC
5	1.2379 X153CrMoV12	Cold work tool steel	25	219 HB

DIN 1.8550 34CrAlNi7 alloy is a nitriding steel used for large cross sections such as extruder screws. It corresponds to AISI A355 steel.

DIN 1.7225 42CrMo4 alloy is a heat treatable (or structural steel) used commonly for many engineering applications and it is very suitable for quenching, tempering, nitriding, induction hardening and so on. It corresponds to AISI 4140 steel.

DIN 1.2344 X40CrMoV5-1 alloy is a hot work tool steel generally used at applications above 200 °C for extrusion and forging dies. It corresponds to AISI H13 steel.

DIN 1.2738 40CrNiMo8-6-4 alloy is a plastic mold steel especially used for synthetic plastic molding dies.

DIN 1.2379 X153CrMoV12 alloy is a cold work tool steel generally used at applications below 200 °C for cutting dies, sockets, thread rolling dies. It corresponds to AISI D2 steel.

Table 5.2 : Chemical compositions of the steel grades.

Steel	Chemical composition (wt%)									
	C	Si	Mn	P	S	Cr	Mo	Ni	Al	V
1	0.30	0.26	0.70	0.010	0.013	1.67	0.16	0.91	0.811	0.01
2	0.39	0.30	0.68	0.012	0.002	1.15	0.20	0.08	0.016	0.01
3	0.38	0.90	0.45	0.017	0.002	5.09	1.48	0.10	0.030	0.97
4	0.37	0.29	1.31	0.020	0.007	1.94	0.25	1.05	0.014	0.07
5	1.50	0.35	0.32	0.018	0.002	11.3	0.75	0.22	0.037	0.77

They were cut into 10 mm thick pieces perpendicular to rolling direction, then both surfaces were grinded step by step using SiO2 based abrasive papers starting from 60 Grit to 800 Grit.

5.2. Surface and Heat Treatment

Each alloy was classified into four groups according to treatment :

Group 1 Bulk hardening (BH)

Group 2 Bulk hardening + thin film coating (BH + PVD)

Group 3 Bulk hardening + nitriding (BH + N)

Group 4 Bulk hardening + nitriding + thin film coating (BH + N + PVD)

These treatments were also selected according to the fact that they are commonly preferred for industrial and commercial needs especially for the steels of this study.

Plasma nitriding is an environmentally harmless technology and great number of treatment parameters that can be arbitrarily selected and precisely preset within wide limits make it possible to produce specific structures and properties not found in conventionally nitrided materials. For these reasons, plasma nitriding is in many cases superior to conventional nitriding processes [11].

Chromium nitride (CrN) has become recently very popular as a coating material due to its good mechanical properties. It can be succesfully made by physical vapor

deposition methods [12]. CrN coating has relatively high toughness and low hardness, high coating thickness and low surface roughness values.

Duplex treatment which is plasma nitriding followed by thin film coating here in this study, is commonly used in production of hot working dies, injection molding and deep drawing dies.

5.2.1. Bulk hardening

1.8550 and 1.2738 steels were received in as hardened condition, so bulk hardening was applied to 1.7225, 1.2344 and 1.2379 steels. 1.2344 and 1.2379 steels were bulk hardened in vacuum furnace and 1.7225 steel was bulk hardened in gas atmosphere furnace at "Tam Çelik Isıl İşlem" plant. Bulk hardening parameters and hardness values obtained as a result of these processes are given below in Tables 5.3 and 5.4.

Table 5.3 : Bulk hardening parameters of vacuum furnace.

Steel	Austenitizing Temperature(°C)	1st Tempering Temperature(°C)	2nd Tempering Temperature(°C)	Hardness (HRC)
1.2344	1035	565	600	50
1.2379	1040	520	520	60

Table 5.4 : Bulk hardening parameters of gas atmosphere furnace.

Steel	Austenitizing Temperature (°C)	Warm Bath Temperature (°C)	Tempering Temperature (°C)	%C of atmosphere	Hardness (HRC)
1.7225	850-860	180	565	0.45	35

5.2.2. Plasma nitriding

Group 3 and Group 4 specimens were nitrided at "İstanbul Isıl İşlem" plant via plasma nitriding technique by using pulse plasma nitriding furnace. Parameters of this process are given in Table 5.5.

Nitriding times and temperatures were selected according to commercial applications. 1.2379 steel has a microstructure containing many carbides especially because of the tendency of Cr to form carbides. At relatively longer holding times for 1.2379 steel, carbide particles come together and form bigger carbides. Big carbides destroys the homogeneity of the microstructure and hardness distribution, so shorter

holding time is chosen commercially for 1.2379 steel to avoid formation of big carbides.

Table 5.5 : Plasma nitriding parameters.

Steel	Nitriding Temperature (°C)	Holding Time (h)	Nitriding Media
1.8550	530	24	25% N2 + 75% H2
1.7225	500	8	25% N2 + 75% H2
1.2344	530	24	25% N2 + 75% H2
1.2738	500	8	25% N2 + 75% H2
1.2379	480	4	25% N2 + 75% H2

5.2.3. Thin film coating

Group 2 and Group 4 specimens were thin film(CrN) coated via physical vapor deposition (PVD) process (cathodic arc evaporation technique) at " Ionbond Tinkap" plant. Group 4 specimens were shot peened after nitriding to remove white layers. One of the purposes of removing white layer is to increase the adhesion between coating and substrate because white layer is thermally unstable, so it tends to decompose during coating deposition process [16], [17]. Because white layer is brittle, it can be broken in a brittle manner, so load bearing capacity can be destroyed, the other purpose of removing white layer is to prevent this effect. Then all the specimens were polished by using 1 micron diamond paste to a surface roughness value of Ra : 0.02 μm before coating process. Thin film coating parameters are given in Table 5.6.

Table 5.6 : CrN coating parameters.

Type of coating	CrN
Coating temperature	279-293 °C
Cathode current	50 amperes
Bias voltage	-110 volts
Vacuum value before coating	4x10-5 torr
Nitrogen partial pressure	5mtorr
Coating duration	80 min.
Expected coating hardness	2500 HV

5.3. Characterization Tests

5.3.1. Microstructure examination

Two types of specimens were prepared for each group. One was perpendicular to rolling direction for microstructure examination. The other one was along rolling direction for observing the coatings and white layers and measuring the thicknesses of them. Examinations were carried out by using " Olympus PME-3 ", an inverted type optical microscope.

5.3.2. XRD analysis

X-ray diffraction analyses were applied on treated surfaces, by using " GBC X-ray Diffractometer". CuKα radiation was used for phase identification.

5.3.3. Surface roughness test

After bulk hardening, before and after PVD coating, before and after nitriding, surface roughness values were measured using " Mitutoyo Surftest-402 ", a surface profilometer.

5.3.4. Microhardness test

Again two types of specimens were prepared for each group. The one perpendicular to rolling direction was for measuring microhardness values perpendicular to treated surfaces with different loads such as 25, 50, 100, 200, 300, 500, 1000 and 10000 grams. The one along rolling direction was for measuring the case depths and the change of hardness from surface to core and also for determining the effects of the treatments. Measurements were applied by using " Matsuzawa MHT-2 ", a microhardness tester.

5.3.5. Rockwell C adhesion test

Indentations were applied on the Group 2, Group 3 and Group 4 specimens by 150 kg load and diamond cone indenter using " Matsuzawa DXT-3 ", a Rockwell hardness tester.

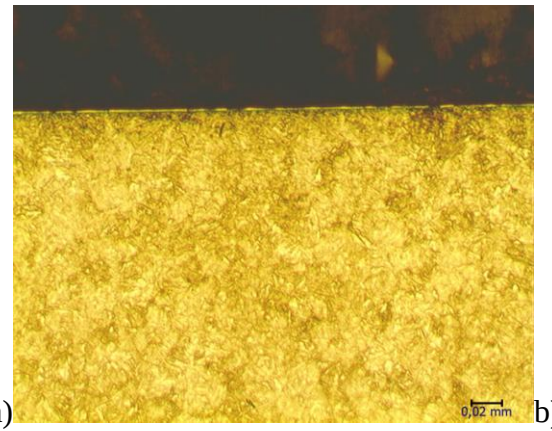
5.3.6. Wear test

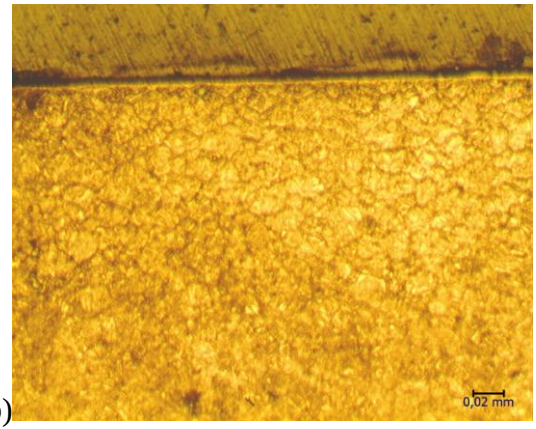
Wear tests were conducted under dry sliding wear testing conditions on a reciprocating wear tester at normal atmospheric conditions, by using "TRIBOtechnic TRIBOtester". Wear tests were carried out by rubbing Al_2O_3 ball having a diameter of 6 mm to the samples under a normal load of 5N. Sliding stroke, total sliding distance and sliding velocity were 2 mm, 20000 mm and 3 $mm.s^{-1}$, respectively.

6. RESULTS and DISCUSSION

6.1. Microstructure Examination

Microstructures of the steels subjected to different treatments are given in following figures. Fig. 6.1 shows the microstructure of 1.2738 steel that has white layer and Fig. 6.2. shows the microstructure of white layer-free 1.2379 steel.

a) 

b) 

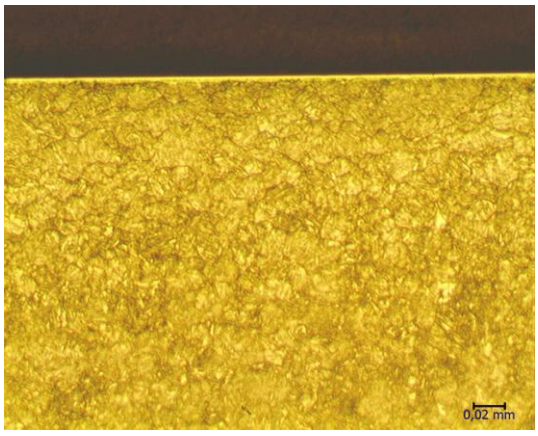
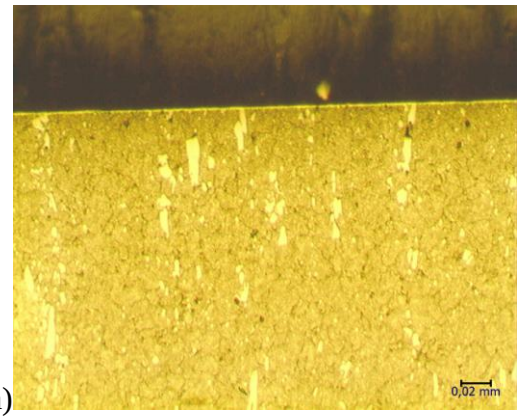
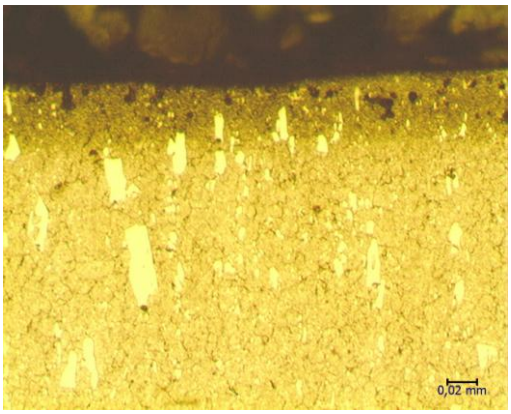
c) 

Figure 6.1 : Microstructure of 1.2738 steel at 200x magnification
a) Bulk hardened+thin film coated
b) Bulk hardened+nitrided
c) Bulk hardened+nitrided+thin film coated.

Both the surface and core microstructure of 1.2738 steel are shown in Fig. 6.1. The matrix is tempered martensite. CrN coating layer can be seen in Fig. 6.1a. White layer and diffusion zone can be seen in Fig. 6.1b. Fig. 6.1c shows CrN coating layer and diffusion zone.

a) 

b) 

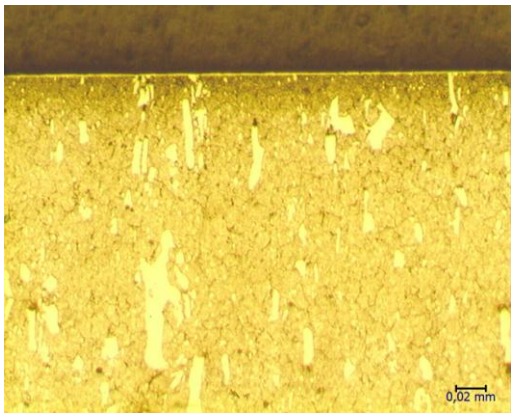
c) 

Figure 6.2 : Microstructure of 1.2379 steel at 200x magnification
a) Bulk hardened+thin film coated
b) Bulk hardened+nitrided
c) Bulk hardened+nitrided+thin film coated.

Both the surface and core microstructure of 1.2379 steel are shown in Fig. 6.2. Matrix consists tempered martensite and carbides. Fig. 6.2a shows CrN coating layer. Diffusion zone can be seen in Fig. 6.2b, see no white layer on the surface as a result of short holding time as stated in 5.2.3. Fig. 6.1c shows CrN coating layer and diffusion zone.

Microstructures of 1.8550, 1.7225 and 1.2344 steels are given in Appendices, A1, A2, and A3 respectively.

App. A1a shows CrN coating layer, App. A1b shows white layer and diffusion zone. CrN coating layer and diffusion zone can be seen in App. A1c. Matrix is tempered martensite.

App. A2a shows CrN coating layer, App. A2b shows white layer and diffusion zone. CrN coating layer and diffusion zone can be seen in App. A2c. Matrix is tempered martensite.

App. A3a shows CrN coating layer, App. A3b shows white layer and diffusion zone. CrN coating layer and diffusion zone can be seen in App. A3c. Matrix is composed of tempered martensite and some tiny carbides.

Thickness values of coatings and white layers formed on the treated surfaces of the steels are given in Table 6.1.

Table 6.1 : Thickness of white layers and CrN coatings.

	BH + PVD	BH + N	BH + N + PVD
	Average thickness of coating (μm)	Average thickness of white layer (μm)	Average thickness of coating (μm)
1.8550	2.1	2.4	2
1.7225	2.1	4.8	2.1
1.2344	2.1	2.6	2.1
1.2738	2.1	5	2.1
1.2379	1.9	-	2

Because the PVD coating duration for five steel grades were the same as given in Table 5.6., coating thicknesses are almost the same. As given in Table5.5., nitriding duration for 1.8550 and 1.2344 steels were 24h and nearly the same thickness of white layers were obtained. Similarly, 1.7225 and 1.2738 steels were nitrided for 8h, and this resulted in again almost the same white layer thicknesses.

Nitriding time for 1.2379 was relatively shorter as stated in 5.2.2., so white layer did not form on the surface.

6.2 XRD Analysis

XRD patterns of 1.2738 and 1.2379 steels are given below in Fig. 6.3 and Fig. 6.4. Patterns of 1.8550, 1.7225 and 1.2344 steels are given in App.4-7, App.8-11 and App.12-15, respectively.

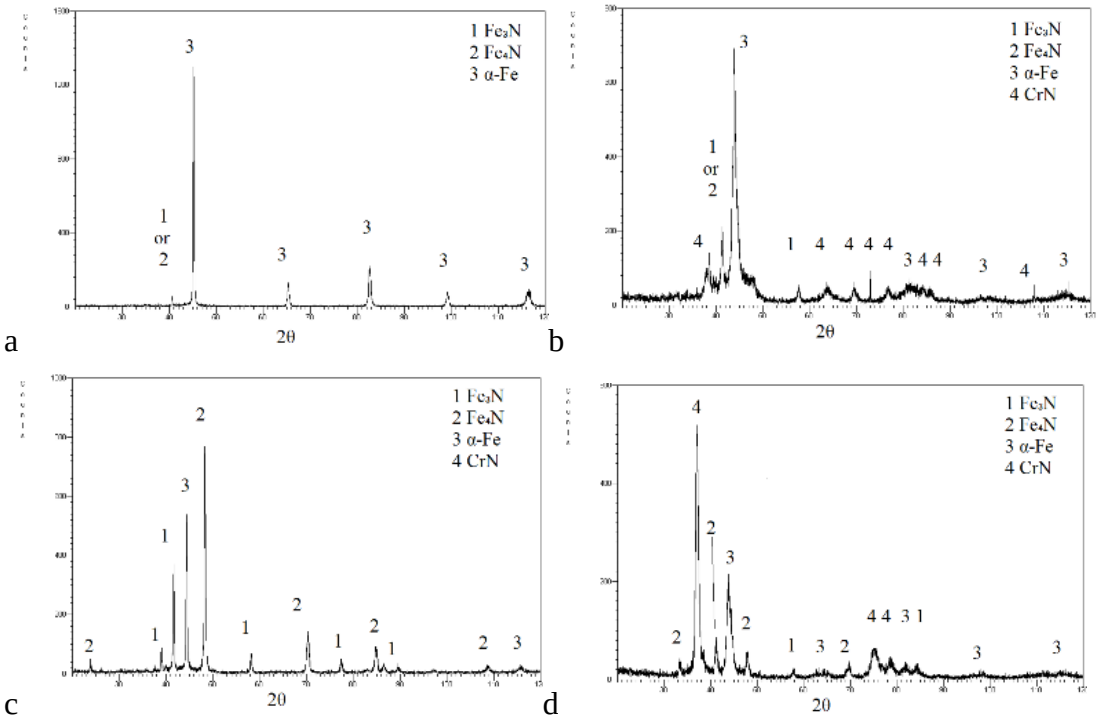


Figure 6.3 : XRD pattern of 1.2738 steel a)BH b)BH+PVD c)BH+N d)BH+N+PVD.

Fig. 6.3a shows mainly peaks of α-Fe phase. Mainly CrN and α-Fe peaks appeared in pattern above shown in Fig. 6.3a. Peaks of ε-Fe_3N and γ'-Fe_4N phases were detected in Fig. 6.3c, this means compound layer was consisted of ε-Fe_3N and γ'-Fe_4N phases. Peaks of steel matrix (α-Fe), compound layer (ε-Fe_3N and γ'-Fe_4N) and CrN were detected in Fig. 6.3d.

XRD pattern below in Fig. 6.4a shows mainly peaks of α-Fe phase and some Fe_4N phases for bulk hardened 1.2379 steel. Mainly CrN and α-Fe peaks appeared in pattern shown in Fig. 6.4b. Peaks of ε-Fe_3N and γ'-Fe_4N phases were detected in bulk hardened and plasma nitrided 1.2379 steel and are shown above in Fig. 6.4c. This shows that compound layer was consisted of ε-Fe_3N and γ'-Fe_4N phases. In the case of bulk hardened, nitrided and thin film coated (duplex treated) 1.2379 steel as shown in Fig. 6.4d, peaks of steel matrix (α-Fe), compound layer (ε-Fe_3N and γ'-Fe_4N) and CrN were detected.

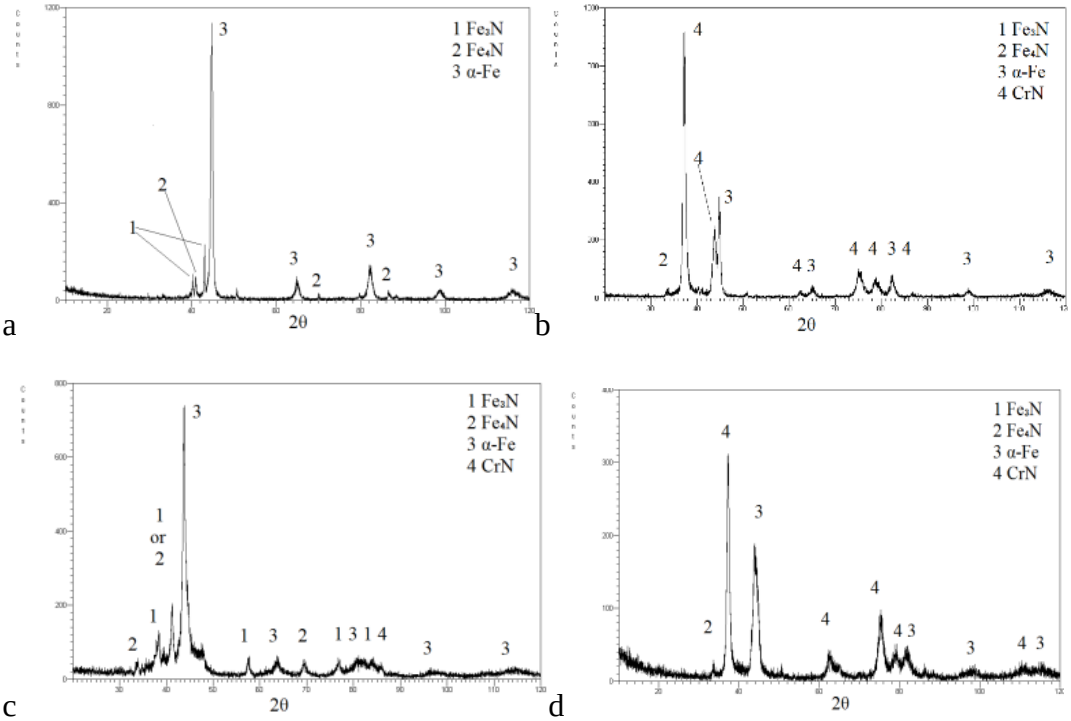


Figure 6.4 : XRD pattern of 1.2379 steel a)BH b)BH+PVD c)BH+N d)BH+N+PVD.

Similer phases were detected in each treated state of 1.8550, 1.7225 and 1.2344 steels.

6.3 Surface Roughness Test

At different steps, surface roughness values of treated surfaces were measured and results are given in Table 6.2. As can be seen on the table, PVD coating after nitriding did not increase the surface roughness, besides this PVD coating after bulk hardening made a slight increase. Surface roughness of 1.7225 and 1.2738 steels were not seriously affected from nitriding process, but surface roughness of 1.2344, 1.2379 and especially 1.8550 steels increased.

Table 6.2 : Surface roughness of the treated surfaces at different steps.

	Surface Roughness (μm)				
	After BH (polished)	After PVD	After N	Before PVD (Shot peened and polished)	After PVD
1.8550	0.02	0.03	0.20	0.02	0.02
1.7225	0.02	0.05	0.05	0.02	0.02
1.2344	0.02	0.04	0.12	0.02	0.02
1.2738	0.02	0.04	0.07	0.02	0.02
1.2379	0.02	0.02	0.11	0.02	0.02

6.4. Microhardness Test

Curves drawn for 1.2738 and 1.2379 steels according to the data of microhardness measurements perpendicular to treated surfaces by different loads are given in Fig. 6.5 and 6.6. Curves for 1.8550, 1.7225 and 1.2344 steels are given in Appendices A16,17 and 18. Higher hardness values were measured by smaller loads on the surfaces of thin film coated alloys. Because the case depth of 1.2379 steel is shallow, a sharp decrease can be observed at 10000 g load. It can be clearly seen in both of the figures that, curves of BH+PVD states and BH+N+PVD states are almost parallel and curves of BH+N+PVD states shifted upwards as a result of relatively higher hardness values of diffusion zone between the substrate and CrN coating.

Indentation depth for each load was also calculated and hardness versus indentation depth curves are given in Fig. 6.7, Fig. 6.8 and Appendices A.19, A.20 and A21.

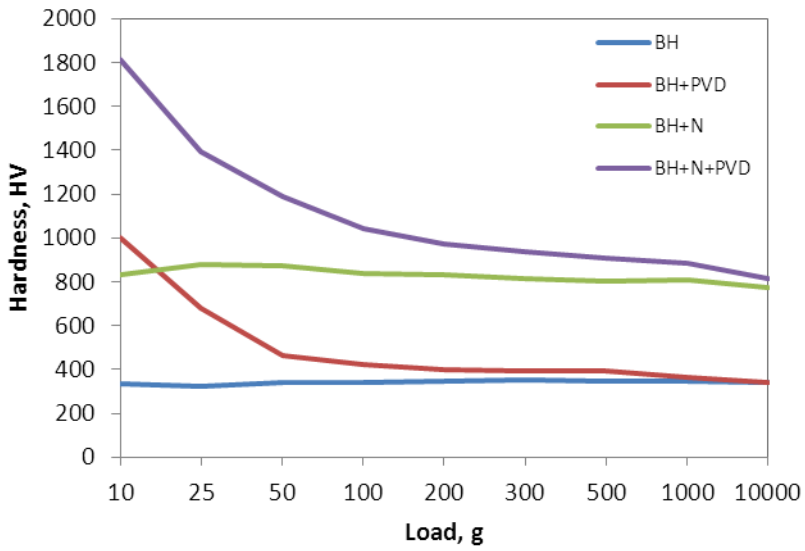


Figure 6.5 : Microhardness measurements of 1.2738 steel by different loads.

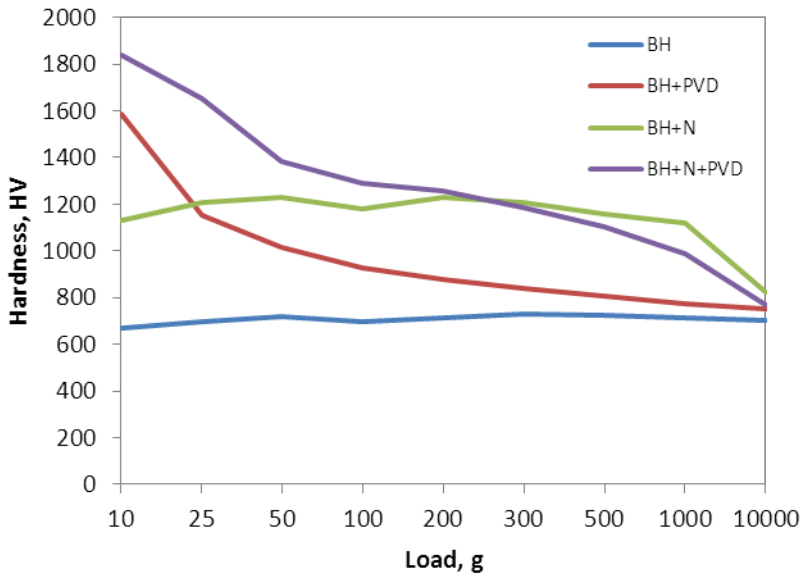


Figure 6.6 : Microhardness measurements of 1.2379 steel by different loads.

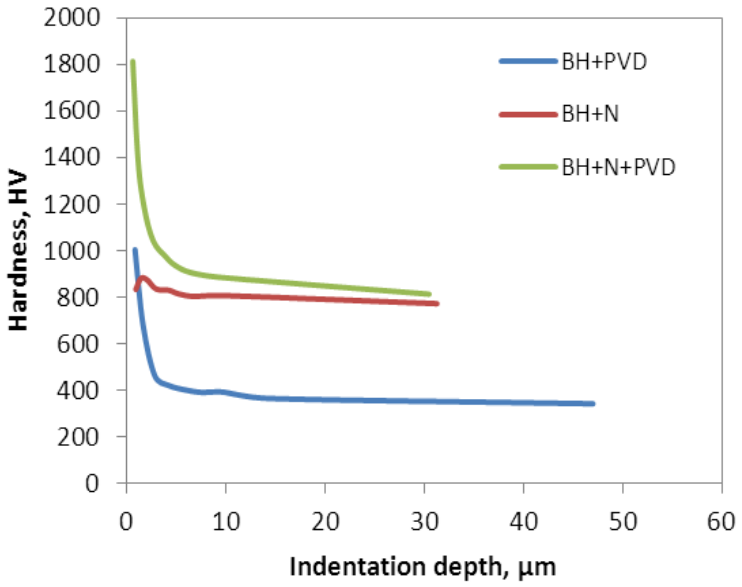


Figure 6.7 : Indentation depth versus applied load for 1.2738 steel

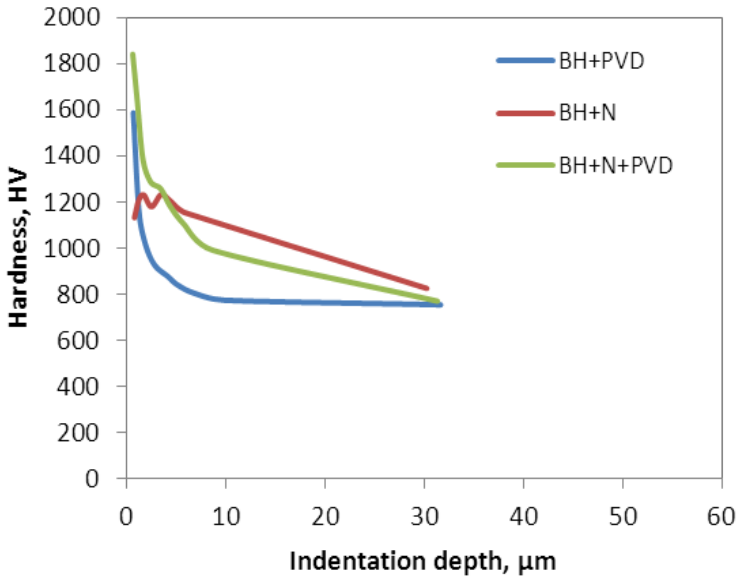


Figure 6.8 : Indentation depth versus applied load for 1.2379 steel

Curves drawn according to the data of microhardness measurements along the cross-sections are given in Fig 6.9 and 6.10 for 1.2738 and 1.2379 steels and in Appendices A22, A23 and A24 for 1.8550, 1.7225 and 1.2344 steels, respectively. Case depths formed by nitriding can be seen in these curves. 1.2379 alloy has a very small case depth with respect to other steels. Case depth of nitrided and thin film coated (duplex treated) 1.2379 steel was destroyed after CrN coating process, in other words softening occurred at the surface as can be seen in the diagram given in Fig. 6.8. As it is also reported in Ref.13, the reason may be substrate softening as a result of outward diffusion of nitrogen. Another cause may be the shot peening before CrN coating, hard surface might be destroyed by this operation.

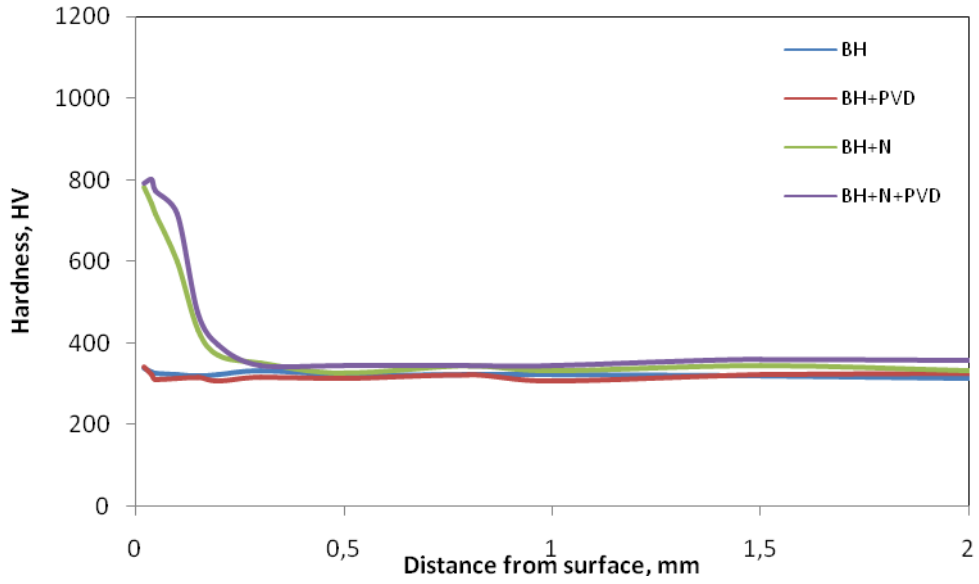


Figure 6.9 : Cross section microhardness measurements of 1.2738 steel.

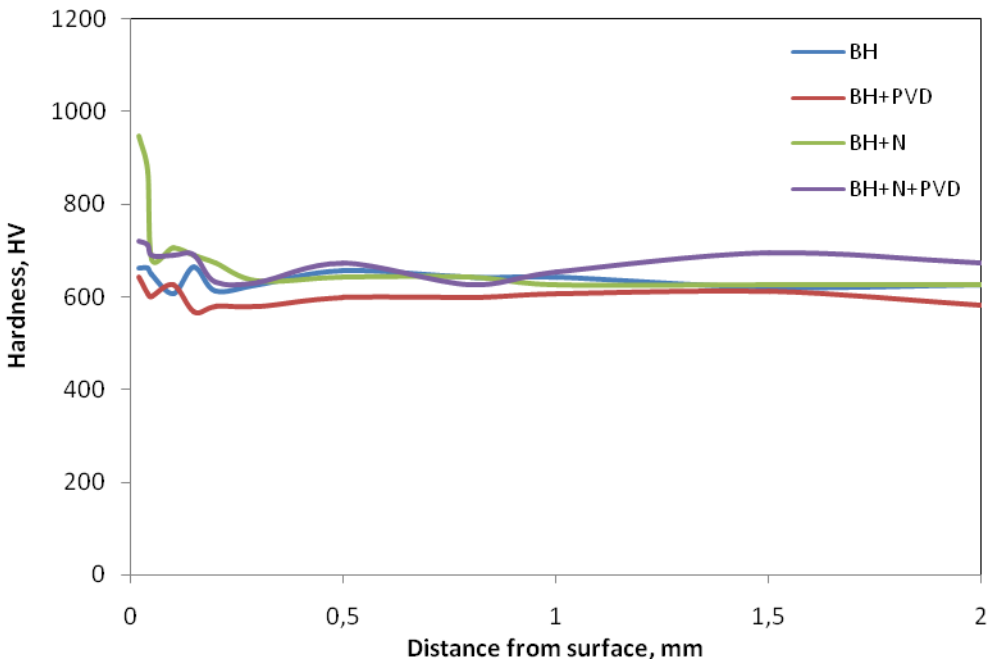


Figure 6.10 : Cross section microhardness measurements of 1.2379 steel.

6.5 Rockwell C Adhesion Test

HRC indents on thin film coated, nitrided, nitrided and thin film coated (duplex treated) surfaces are given in Fig. 6.11 and Fig. 6.12 for 1.2738 and 1.2379 steels and in Appendices 25-27 for 1.8550, 1.7225 and 1.2344 steels. Scale for this test is given in Fig. 6.13. HF1,…,HF4 define a sufficient adhesion whereas HF5 and HF6 represent insufficient adhesion [15].

Cracks and some delamination were detected in bulk hardened and CrN coated state of 1.2738 steel. Circular cracking occurred in nitrided state. Almost no cracking and delamination were detected at duplex treated state. These cracks and delaminations are at the level between HF1 and HF4. It can be said that adhesion is sufficient especially at duplex treated condition. Decreasing of the indent diameter in duplex treated state with respect to bulk hardened and thin film coated state is another remark and shows the effect of diffusion zone formed by plasma nitriding under the coating.

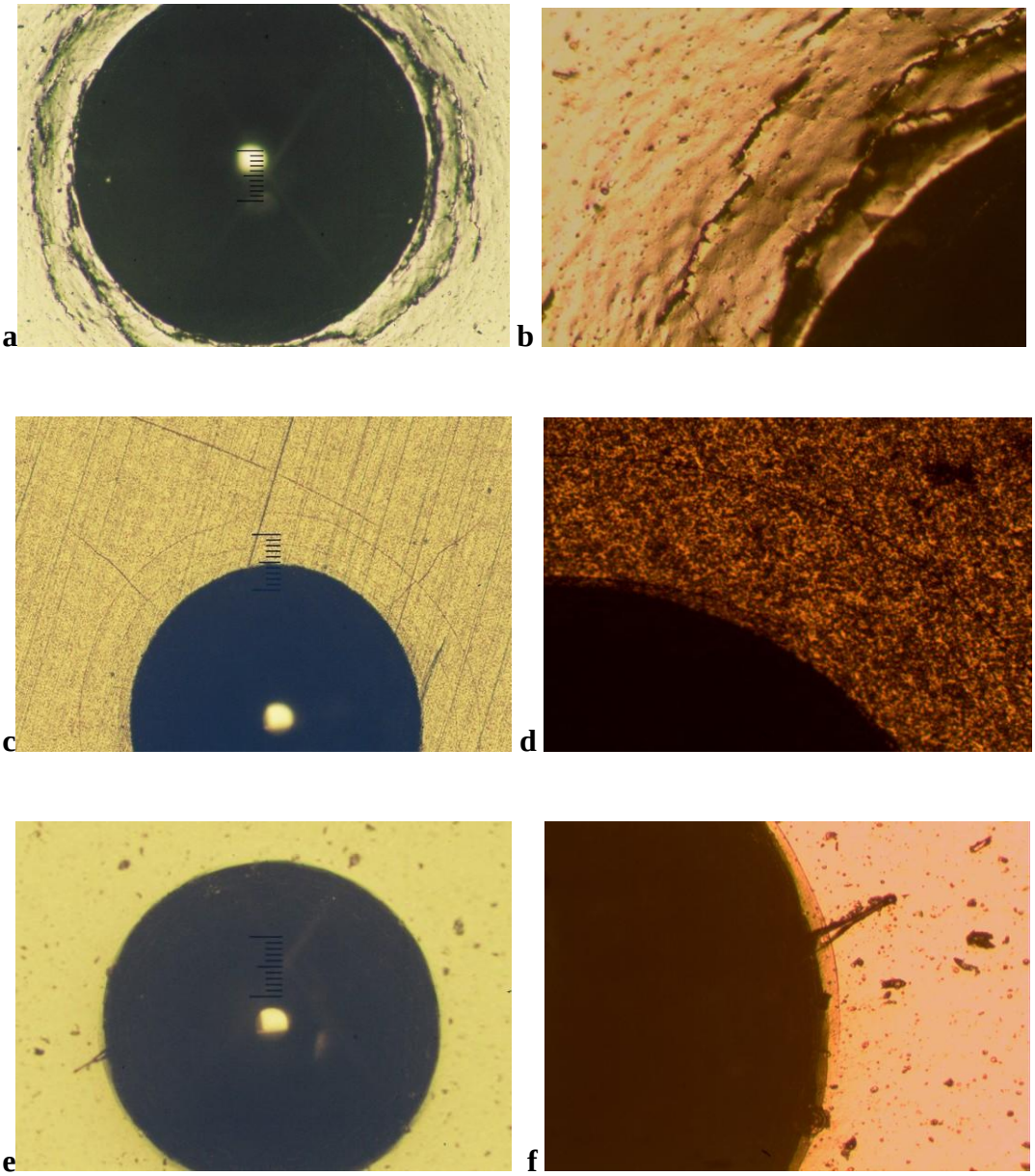


Figure 6.11 : Rockwell C indents on 1.2738 steel at 100x and 200x magnification a),b) BH+PVD, c), d) BH+N, e),f) BH+N+PVD.

Some microcracks and delamination were detected in bulk hardened and CrN coated state of 1.2379 steel. Radial cracking was detected in nitrided and duplex treated conditions. These are again between the sufficient adhesion limits.

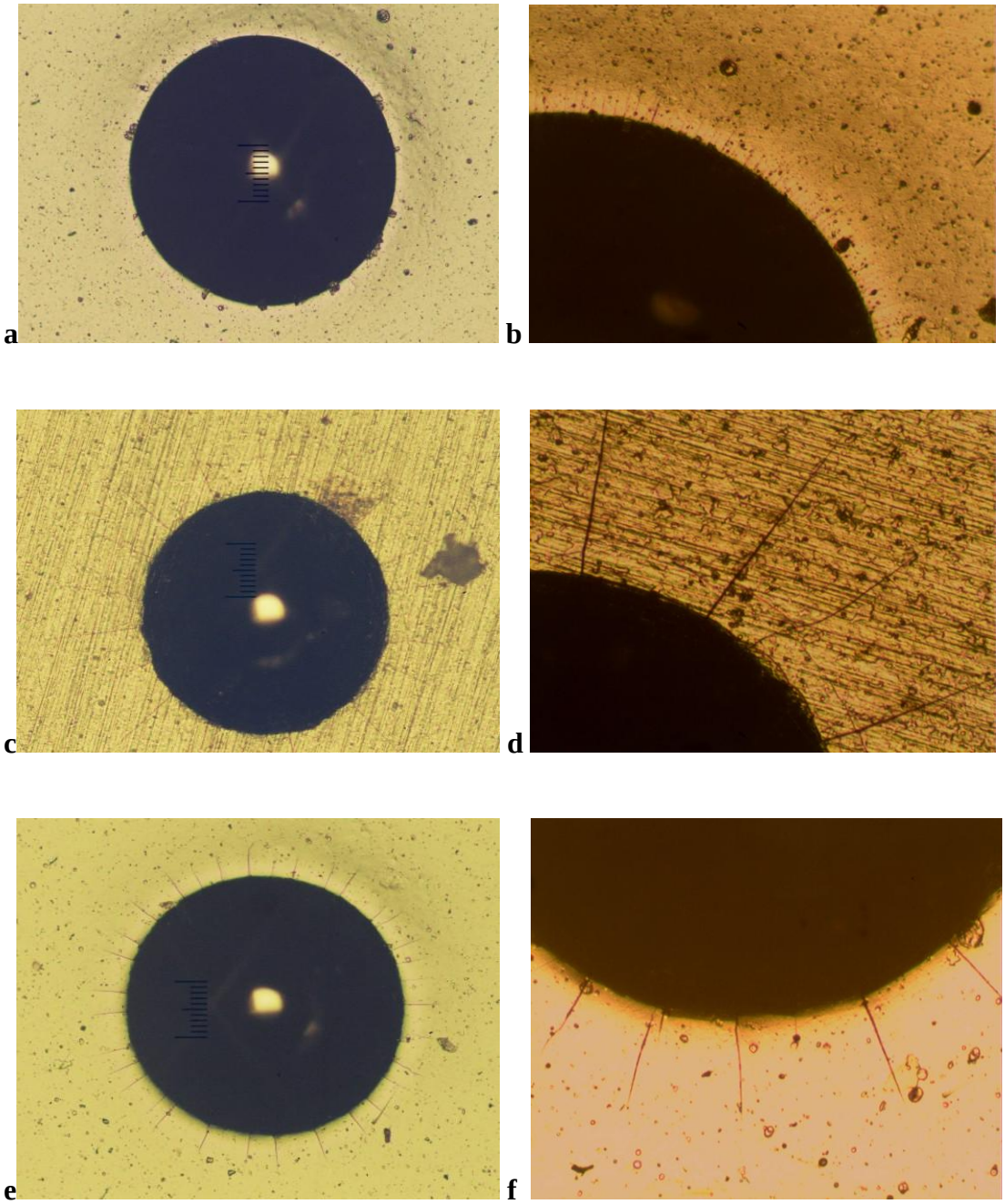


Figure 6.12 : Rockwell C indents on 1.2379 steel at 100x and 200x magnification a),b) BH+PVD, c),d) BH+N, e),f) BH+N+PVD.

Similar results were obtained in 1.8550, 1.7225 and 1.2344 steels. Cracking, circular cracking and some delamination were detected. It can be said that good adhesion was obtained espacially in duplex treated states.

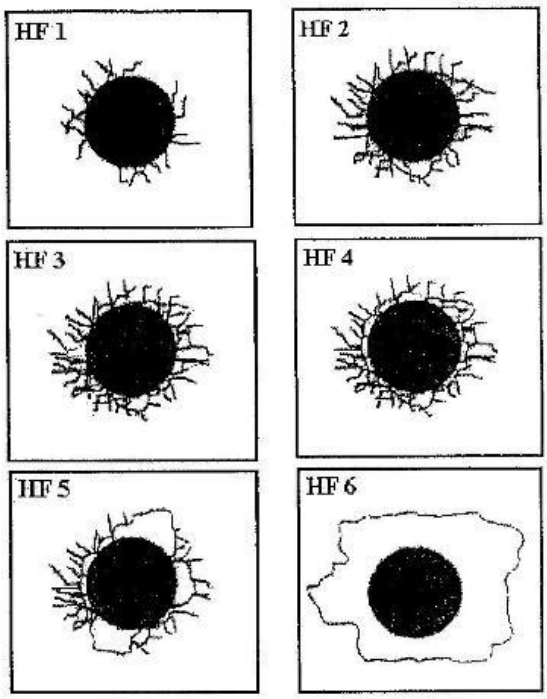


Figure 6.13 : Scale for Rockwell C adhesion test [15].

6.6 Wear Test

The 2D profiles of the wear tracks formed on the surfaces of the samples are shown in Appendices A28-47. After calculation of the wear track areas from their 2D profiles, results of wear test were evaluated according to wear ratio so that the wear ratio of the sample which had the biggest wear track on its surface (nitrided 1.8550 alloy), is taken as 100 (Fig. 6.14). Analysis of the wear rates of the examined samples revealed that the applied nitriding process detrimentally affected the wear performance when compared to the bulk hardened state (with the exception of 1.2379 steel). These results are in contrast with the results of the hardness measurements. In references [6], [11] and [14], it is stated that similar results were obtained. High surface hardness accompanied by low wear resistance for the steels having white layer on their surfaces after nitriding process. It should be noted that 1.2379 steel, which was free from white layer after nitriding, exhibited higher wear resistance and higher surface hardness than its bulk hardened state. Application of PVD process resulted in a significant improvement in wear resistance. When compared to the bulk hardened and CrN coated state, bulk hardening+nitriding+CrN coating process exhibited higher surface hardness and wear resistance.

During wear testing, friction curves of samples were also recorded (Appendices A48-52).

In Fig. 6.15 steady state friction coefficient of samples are presented. When compared to the bulk hardened and nitrided states, CrN coating leaded a reduction in friction coefficent.

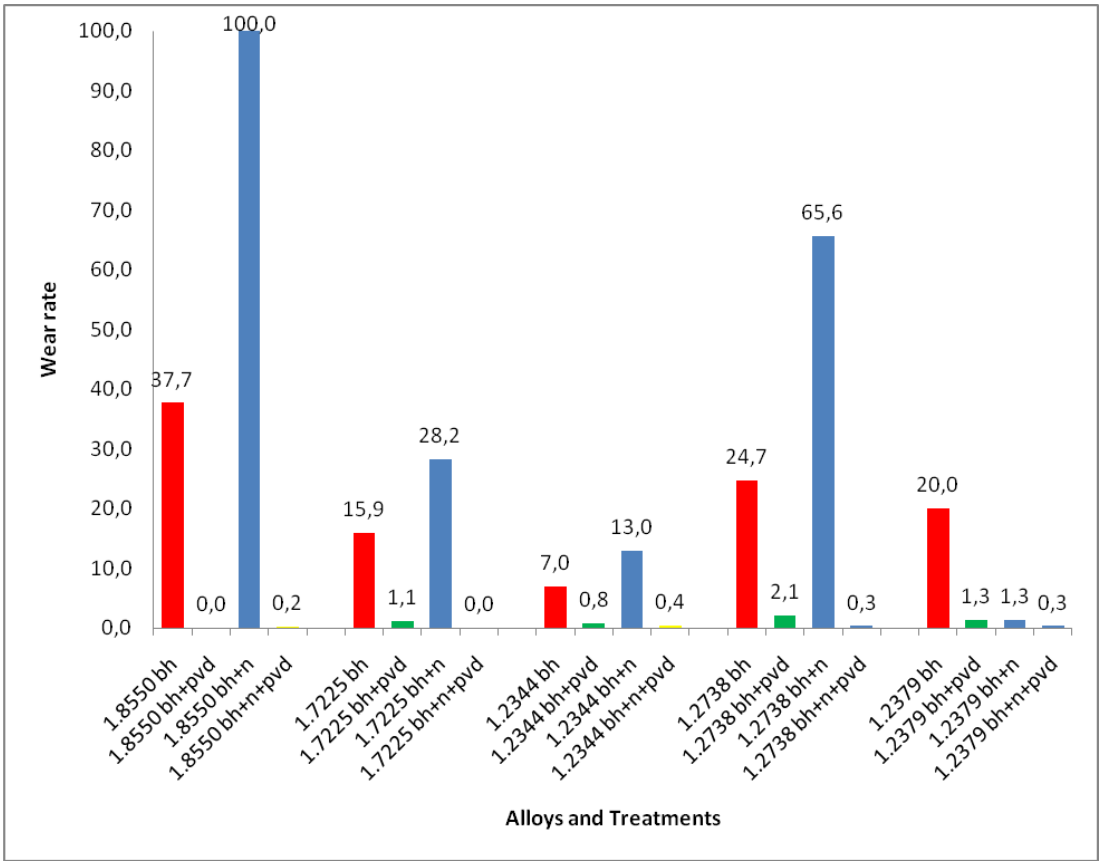


Figure 6.14 : Wear rates determined by reciprocating ball on disc method.

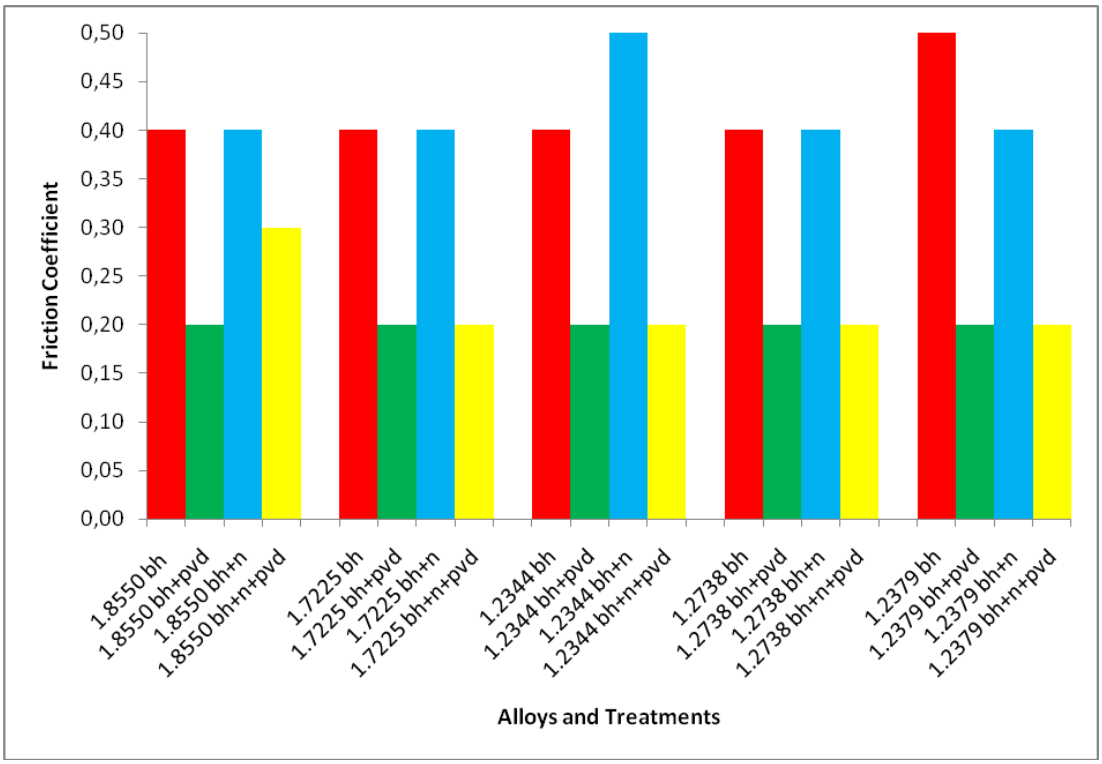


Figure 6.15 : Friction coefficients determined by reciprocating ball on disc method.

7. CONCLUSIONS

The results of this study can be summarized as follows :

1.After the plasma nitriding process white layers composed of Fe2-3N or Fe4N have been formed on the surfaces of quenched and tempered 1.8550, 1.7225, 1.2344 and 1.2738 quality steels. However the surface of the martensitic 1.2379 quality steel was free from white layer because of relatively shorter nitriding time.

2.At indentation loads in between 10g and 10000 g, considerably higher surface hardness values were obtained on the surfaces of the nitrided alloys when compared to their quenched and tempered state. CrN coating of the steel by PVD techniques resulted in a further increase in the surface hardness. The surface hardness of CrN coated alloys gradually decreased with increasing indentation load. According to the Rockwell C adhesion tests, CrN coatings established relatively good bonding with the martensitic and nitrided substrates. Similar to the CrN coatings, some micro-cracks were also detected at the vicinity of the indents of the nitrided steels, without leading delamination.

3.White layer containing 1.8550, 1.7225, 1.2344 and 1.2738 quality nitrided steels exhibited lower wear resistance than their quenched and tempered states. For the white layer free 1.2379 quality nitrided steel, wear resistance was enhanced upon nitriding when compared to its quenched and tempered state.

4. CrN coating of martensitic and nitrided steels caused significant improvement in wear resistance and reduction in friction coefficent. The excellent wear resistance was obtained at duplex treated steels, in others words after CrN coating of nitrided martensitic steels.

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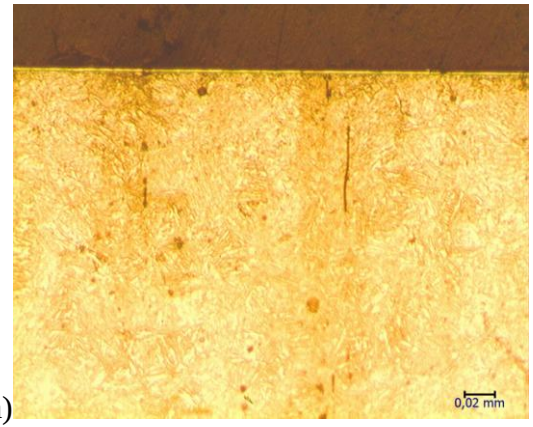
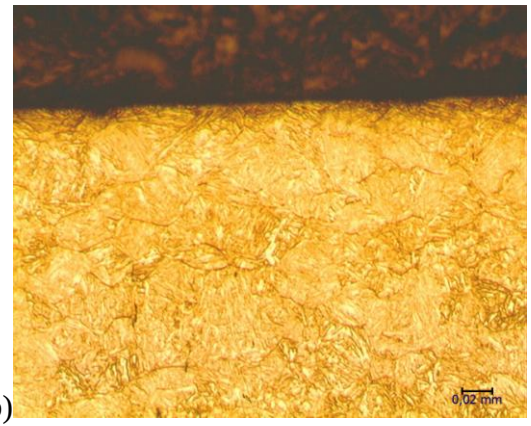
APPENDICES

APPENDIX A.1 : Microstructure of 1.8550 steel at 200x magnification

APPENDIX A.1 : Microstructure of 1.8550 steel at 200x magnification

a) 

b) 

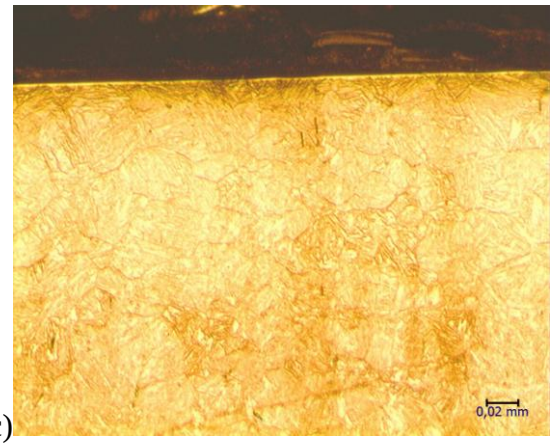
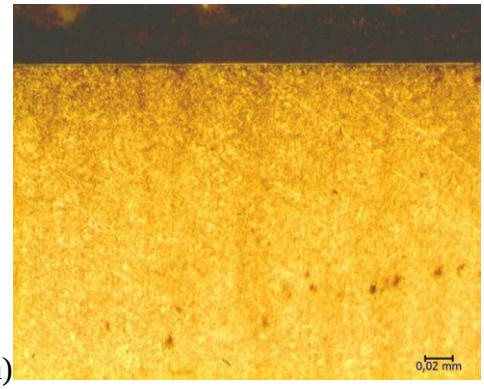
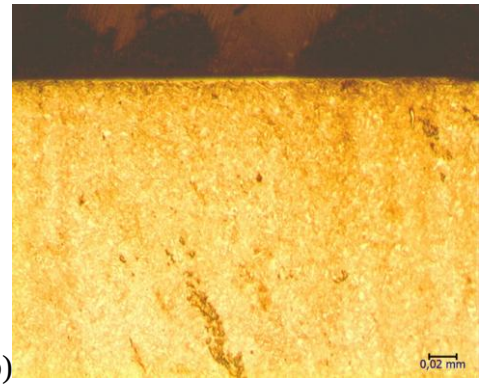
c) 

Fig. A.1) a) Bulk hardened+thin film coated b) Bulk hardened+nitrided c) Bulk hardened +nitrided+thin film coated

APPENDIX A.2 : Microstructure of 1.7225 steel at 200x magnification

a) 

b) 

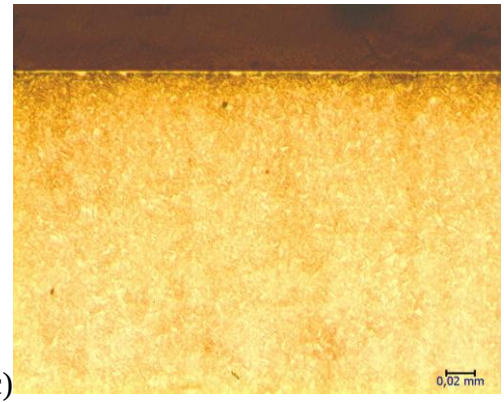
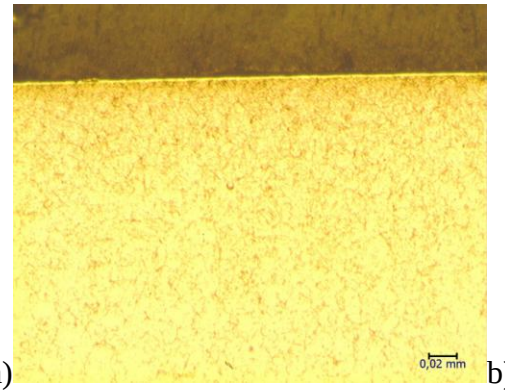
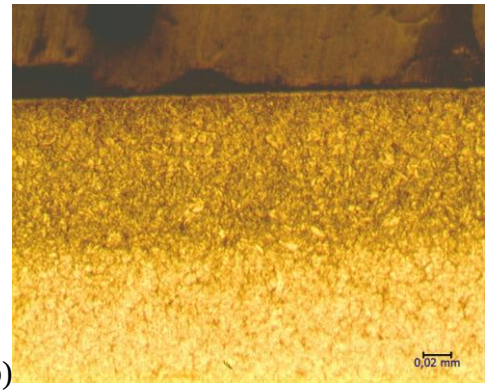
c) 

Fig. A.2) a) Bulk hardened+thin film coated b) Bulk hardened+nitrided
c) Bulk hardened +nitrided+thin film coated

APPENDIX A.3 : Microstructure of 1.2344 steel at 100x magnification

a) 

b) 

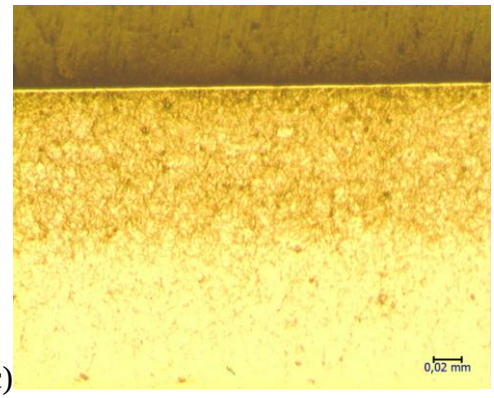
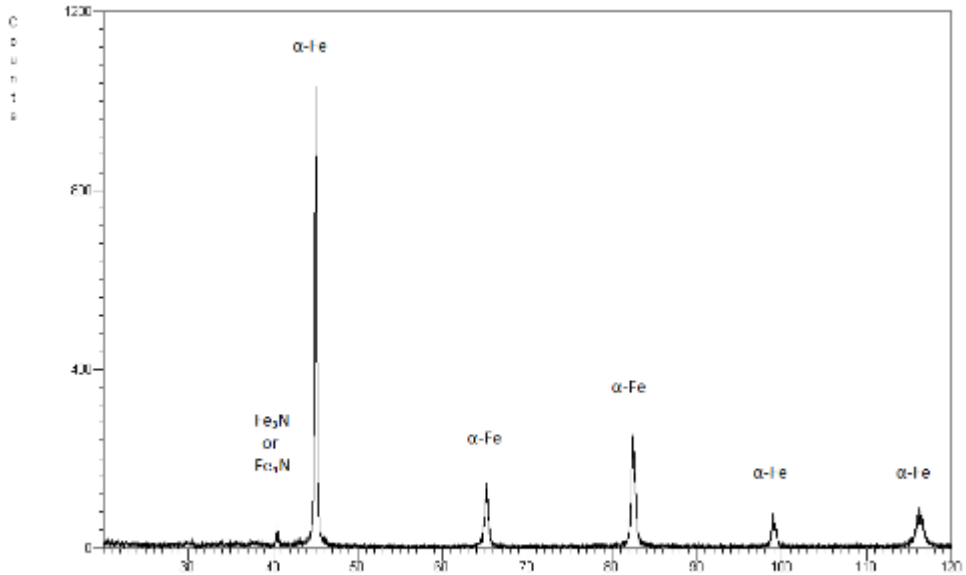
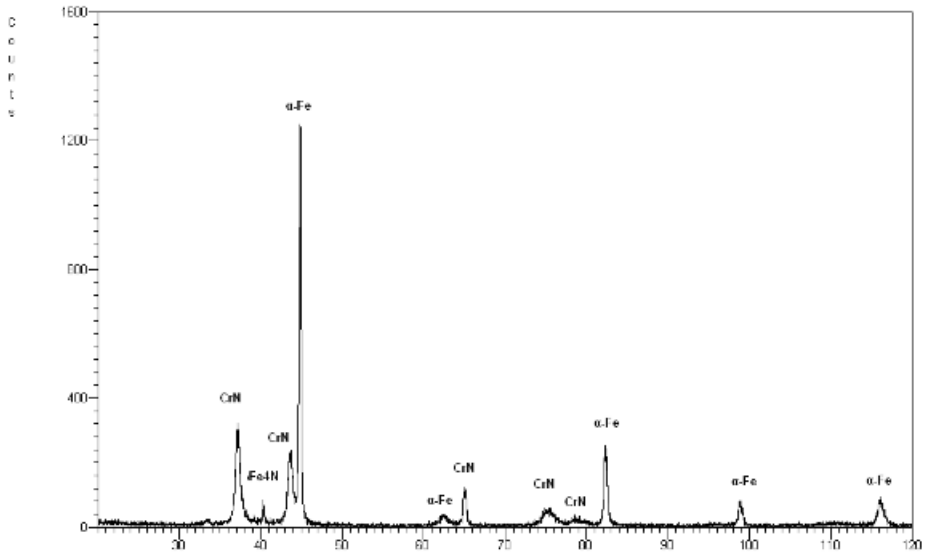
c) 

Fig. A.3) a) Bulk hardened+thin film coated b) Bulk hardened+nitrided c) Bulk hardened +nitrided+thin film coated

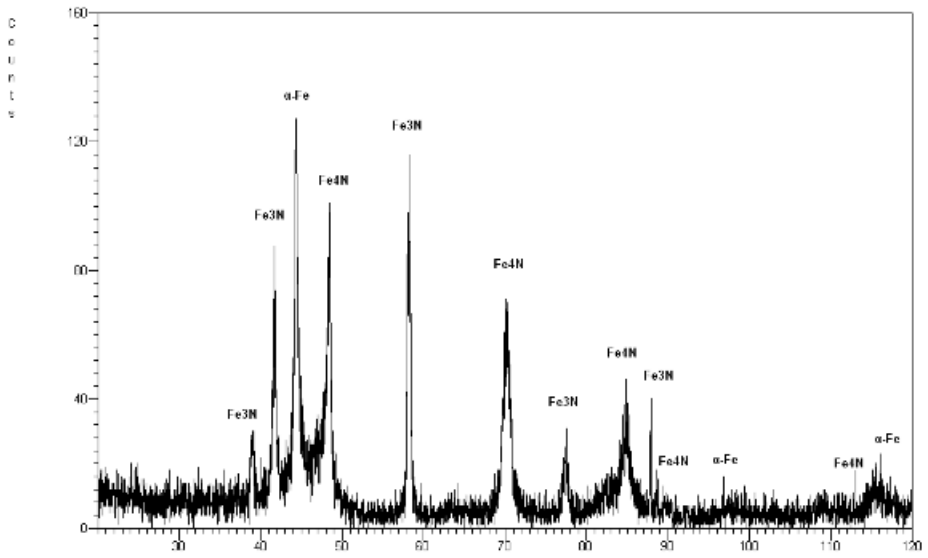
APPENDIX A.4 : XRD pattern of 1.8550 steel in BH state



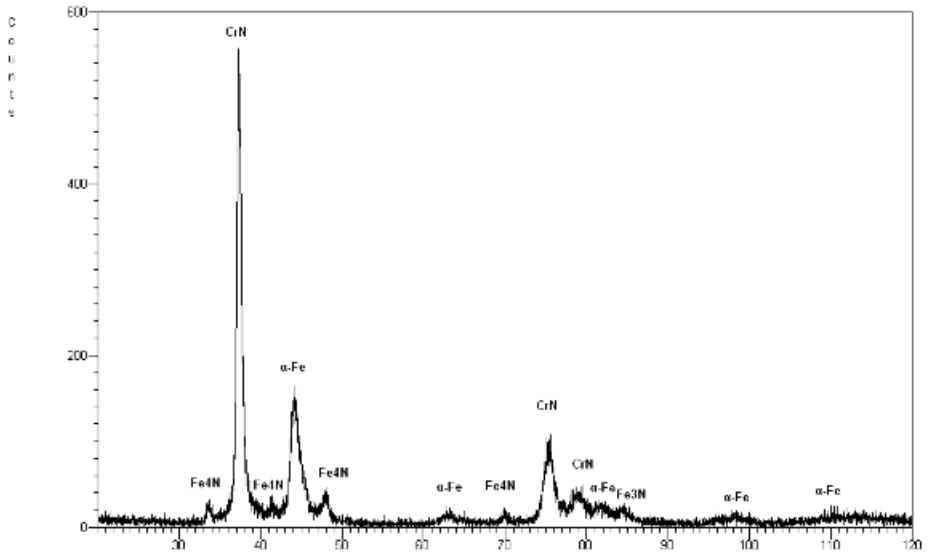
APPENDIX A.5 : XRD pattern of 1.8550 steel in BH + PVD state



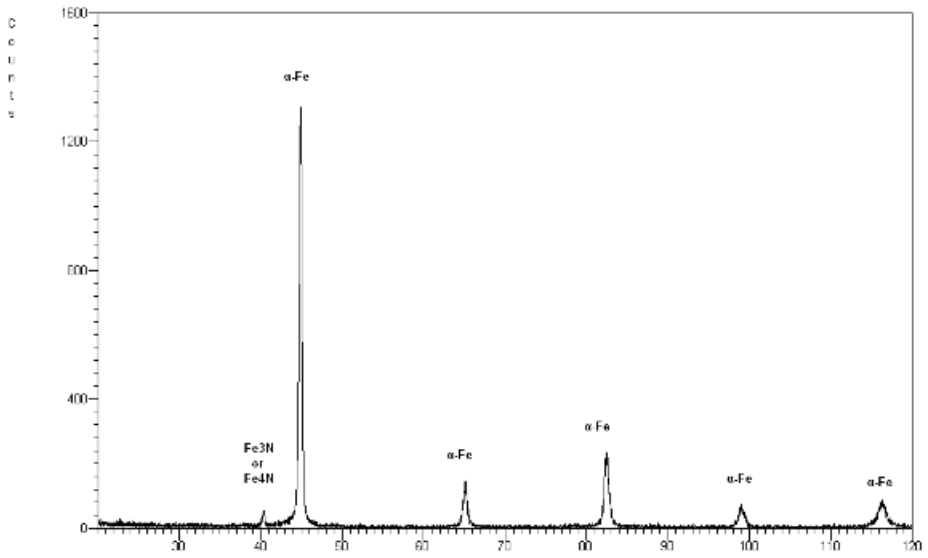
APPENDIX A.6 : XRD pattern of 1.8550 steel in BH + N state



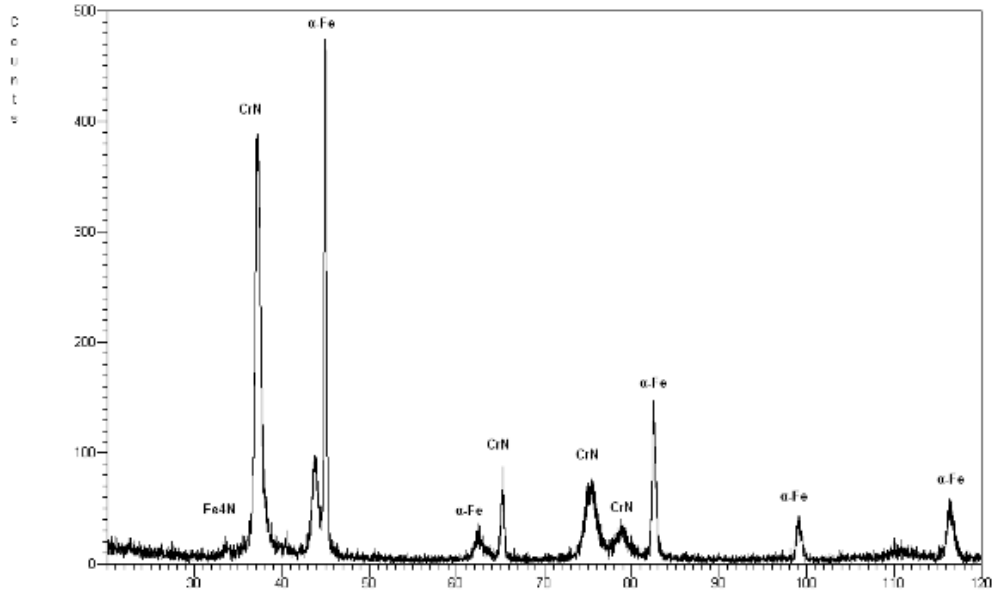
APPENDIX A.7 : XRD pattern of 1.8550 steel in BH + N + PVD state



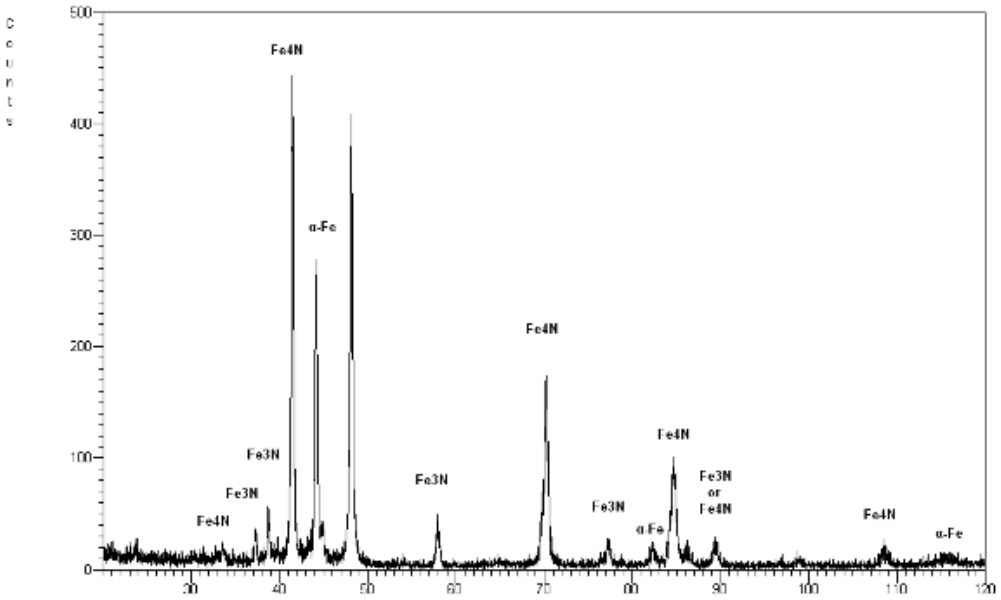
APPENDIX A.8 : XRD pattern of 1.7225 steel in BH state



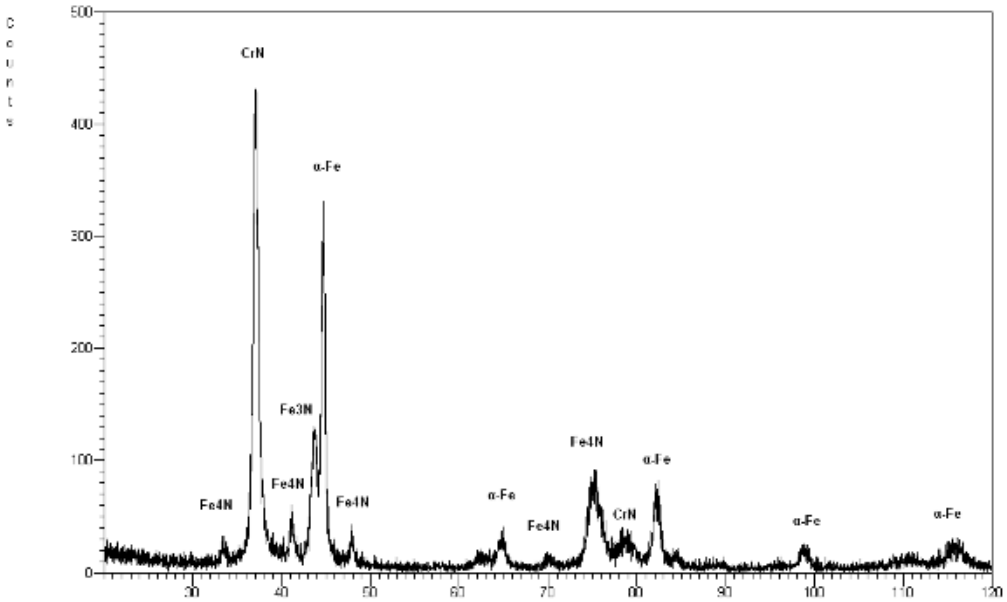
APPENDIX A.9 : XRD pattern of 1.7225 steel in BH + PVD state



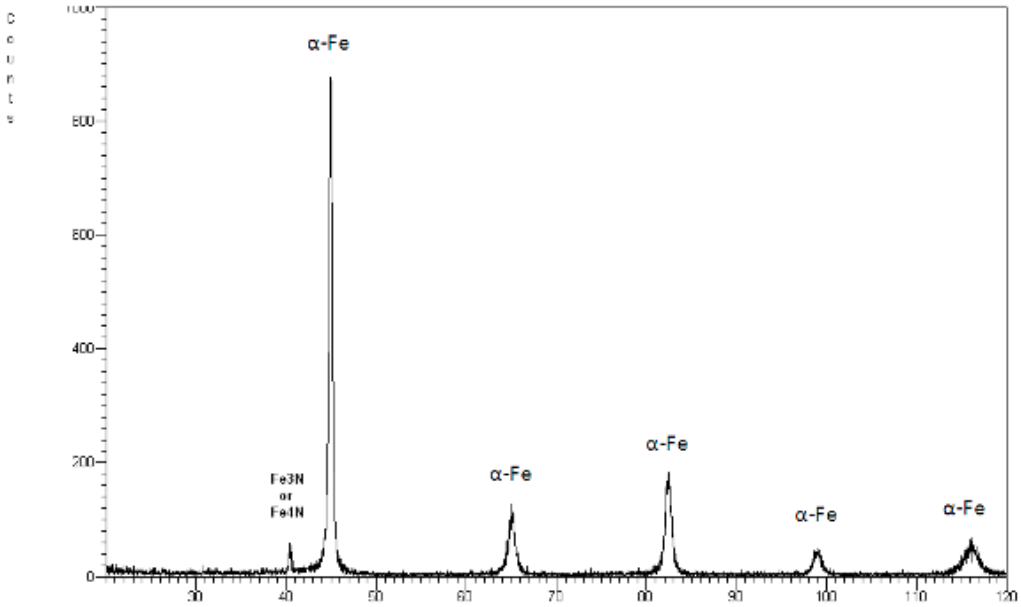
APPENDIX A.10 : XRD pattern of 1.7225 steel in BH + N state



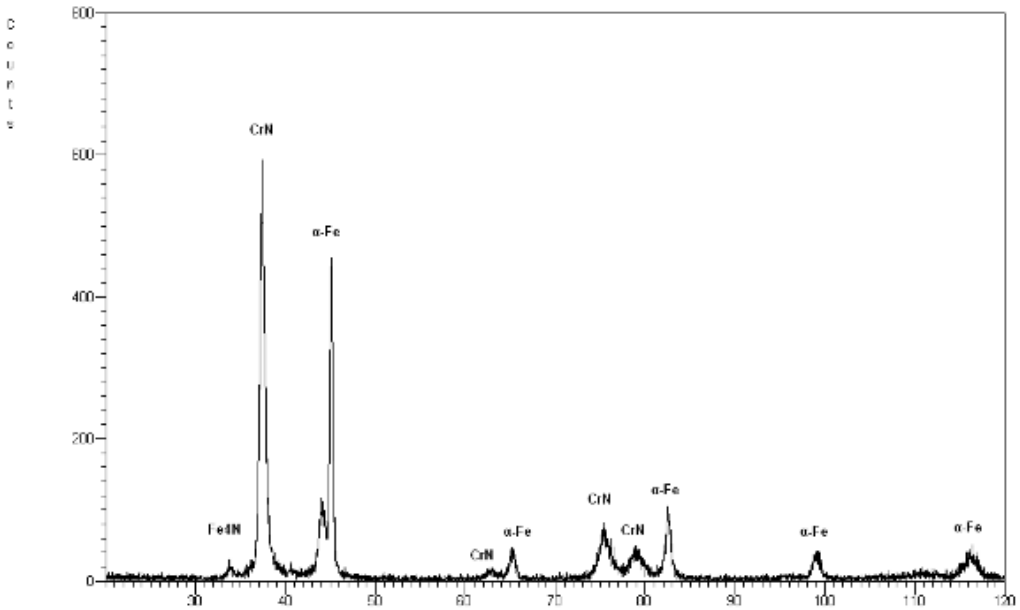
APPENDIX A.11 : XRD pattern of 1.7225 steel in BH + N + PVD state



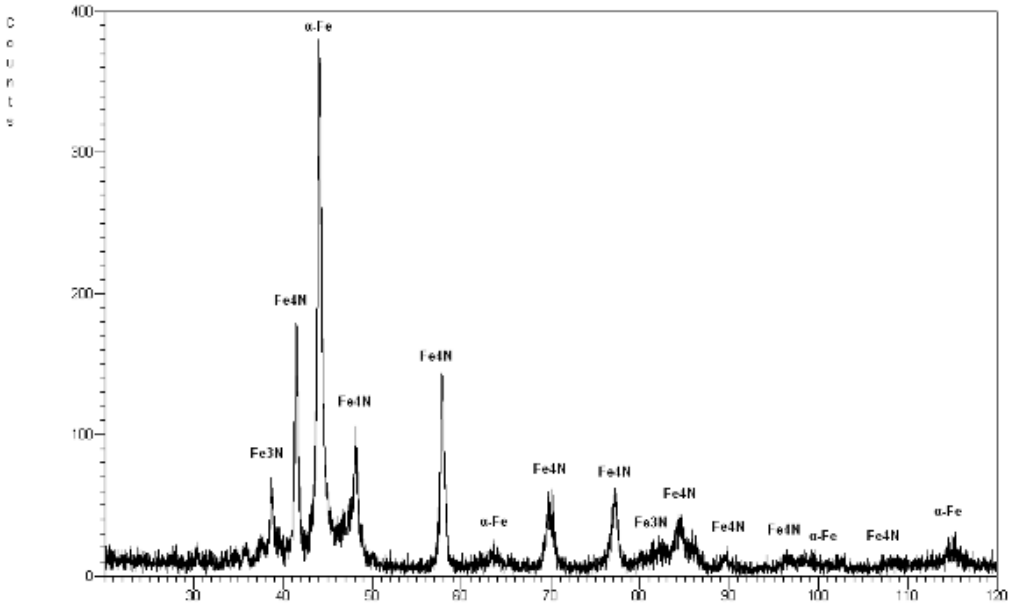
APPENDIX A.12 : XRD pattern of 1.2344 steel in BH state



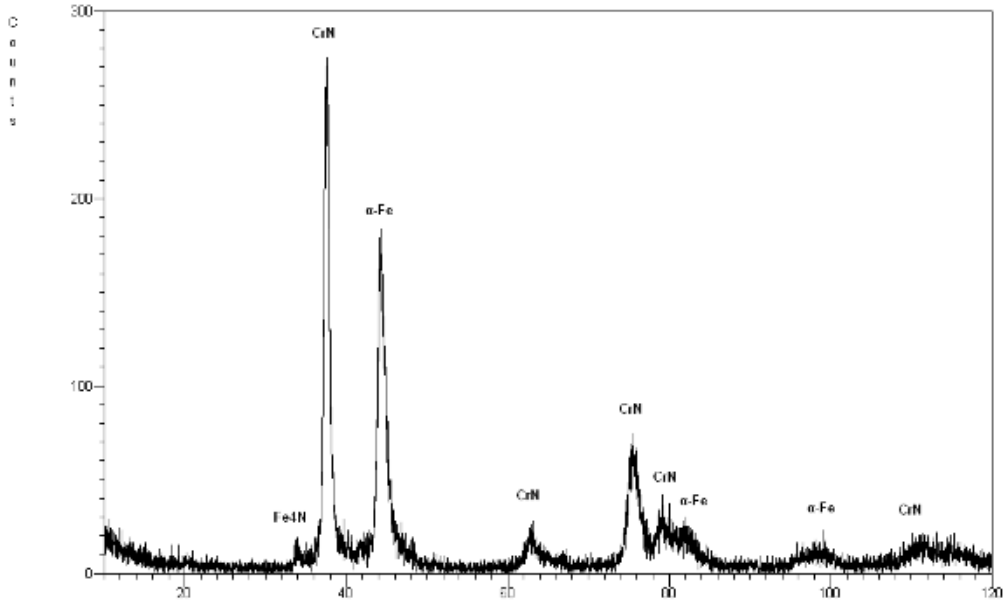
APPENDIX A.13 : XRD pattern of 1.2344 steel in BH + PVD state



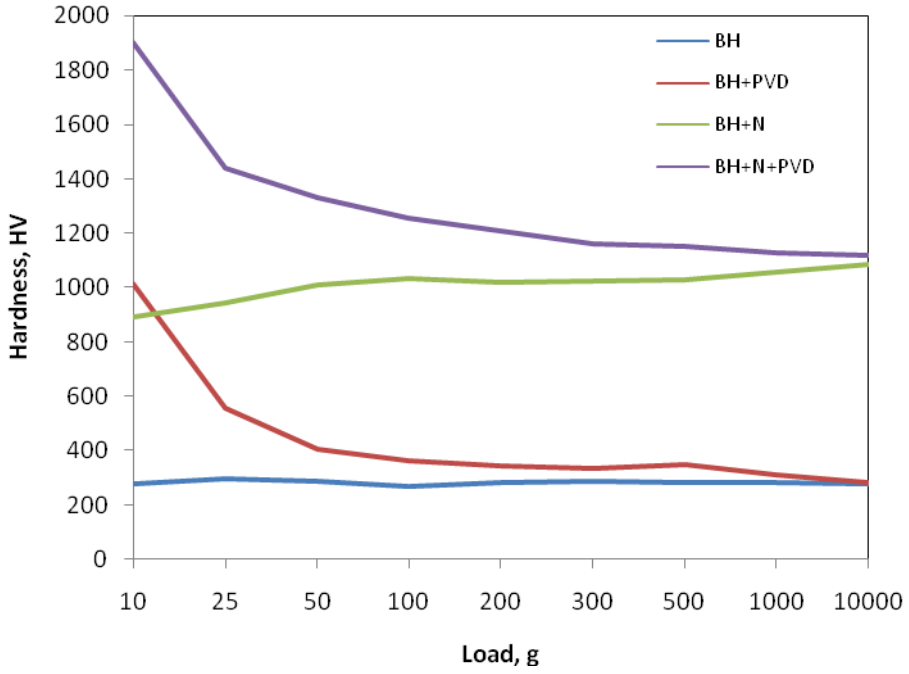
APPENDIX A.14 : XRD pattern of 1.2344 steel in BH + N state



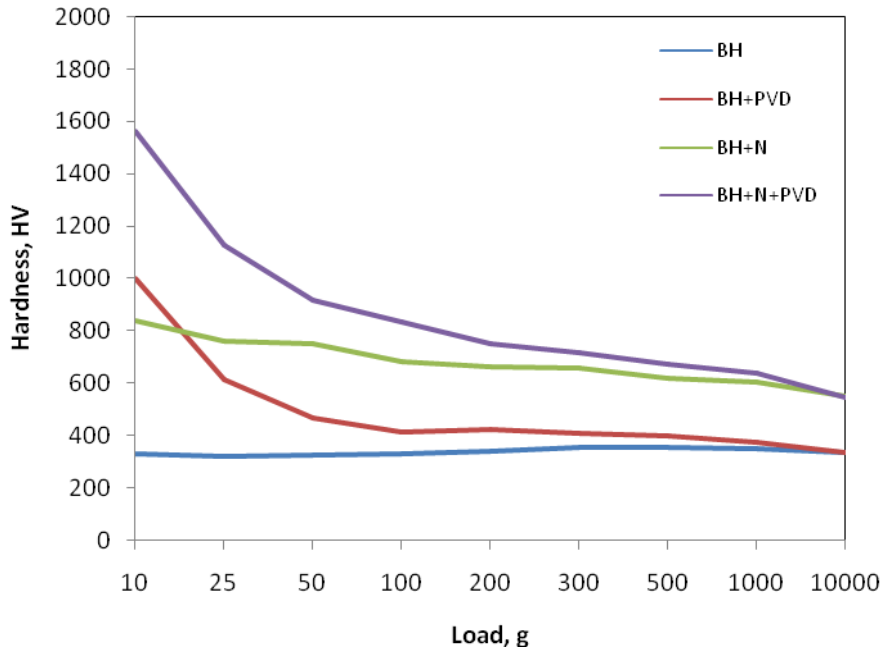
APPENDIX A.15 : XRD pattern of 1.2344 steel in BH + N + PVD state



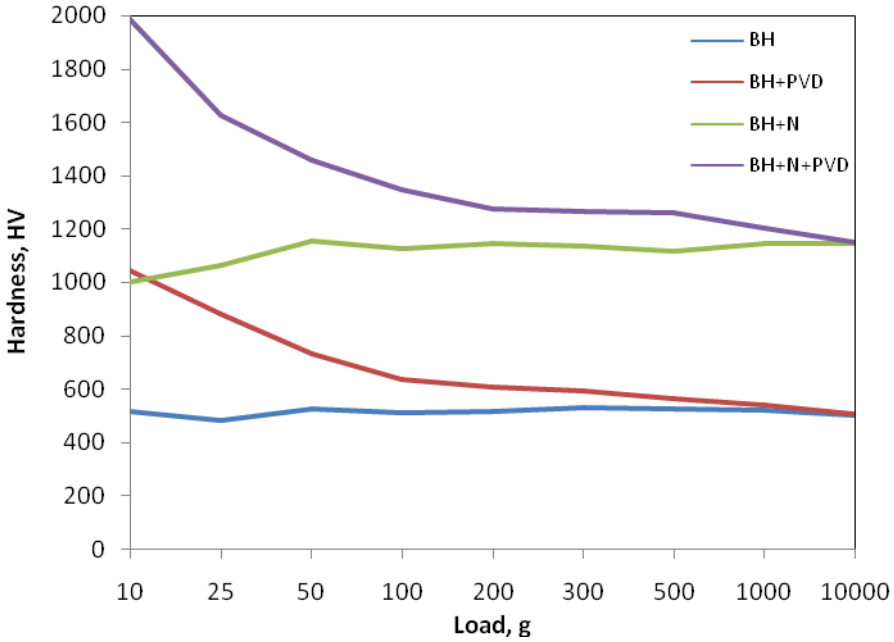
APPENDIX A.16 : Change in hardness with respect to load for 1.8550 steel



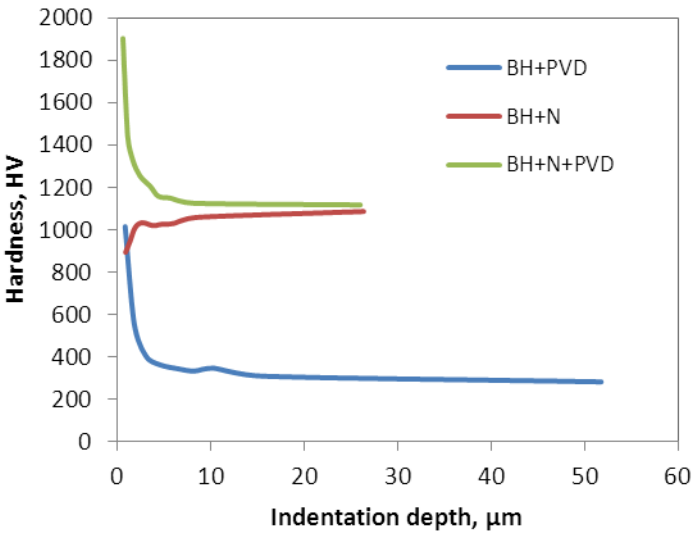
APPENDIX A.17 : Change in hardness with respect to load for 1.7225 steel



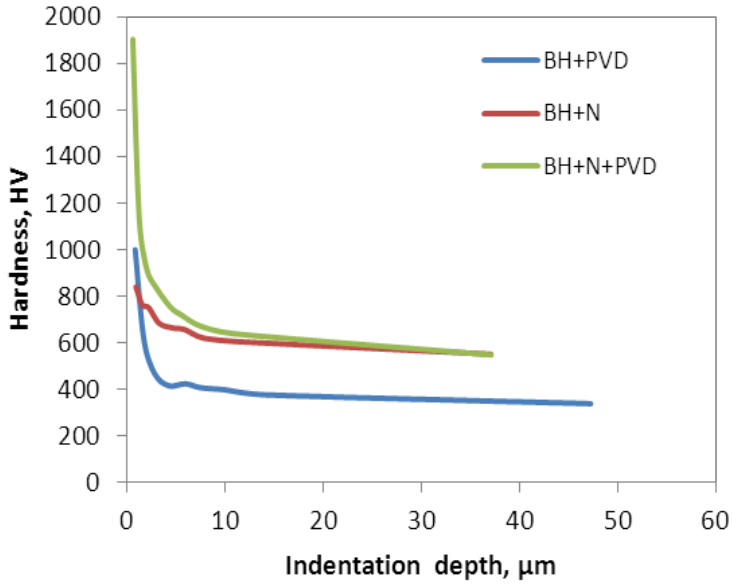
APPENDIX A.18 : Change in hardness with respect to load for 1.2344 steel



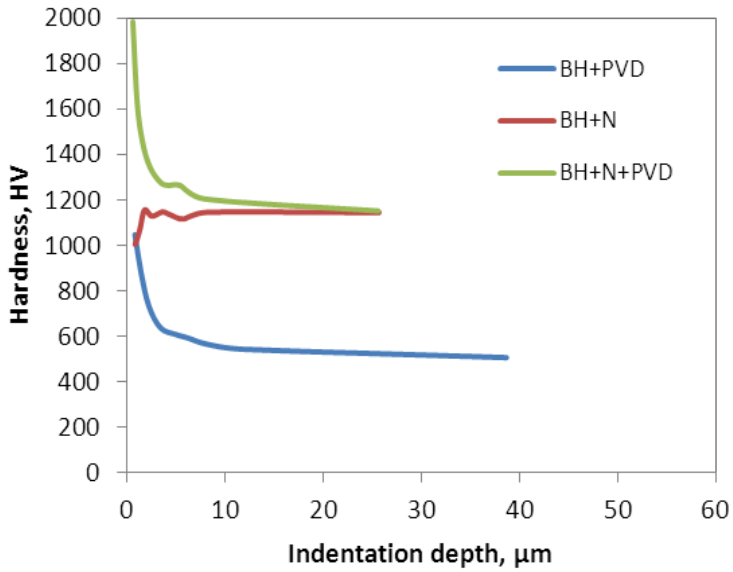
APPENDIX A.19 : Variation of indentation depth with respect to applied load for 1.8550 steel



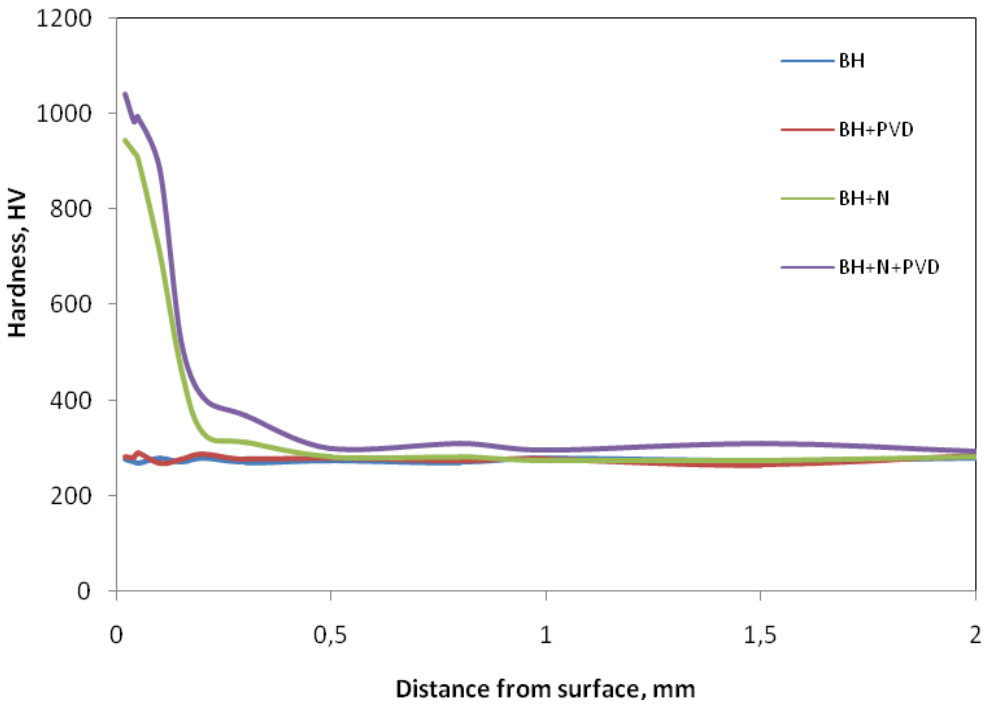
APPENDIX A.20 : Variation of indentation depth with respect to applied load for 1.7225 steel



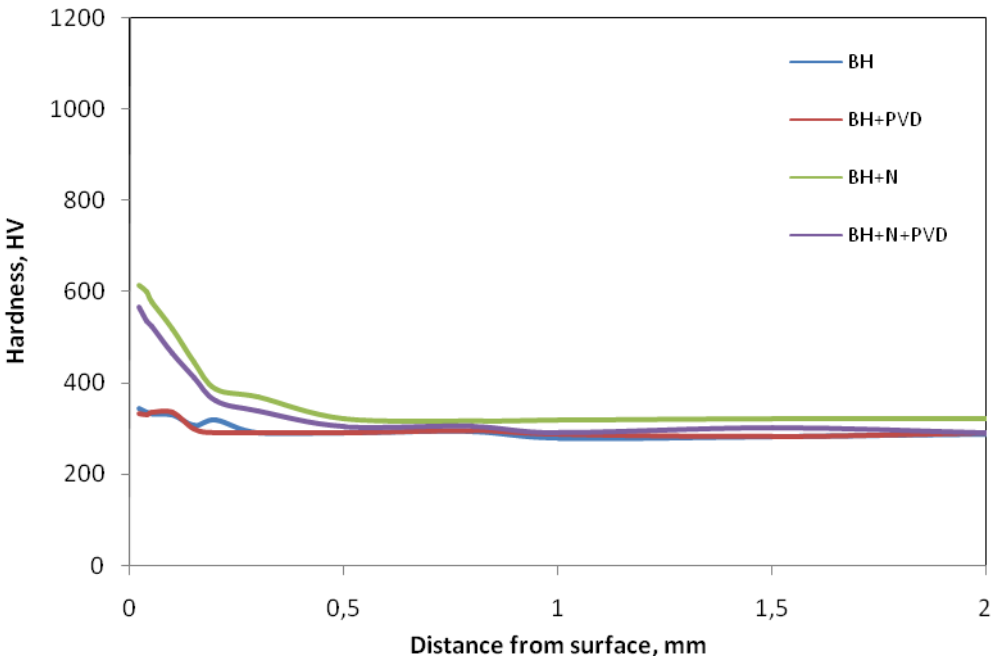
APPENDIX A.21 : Variation of indentation depth with respect to applied load for 1.2344 steel



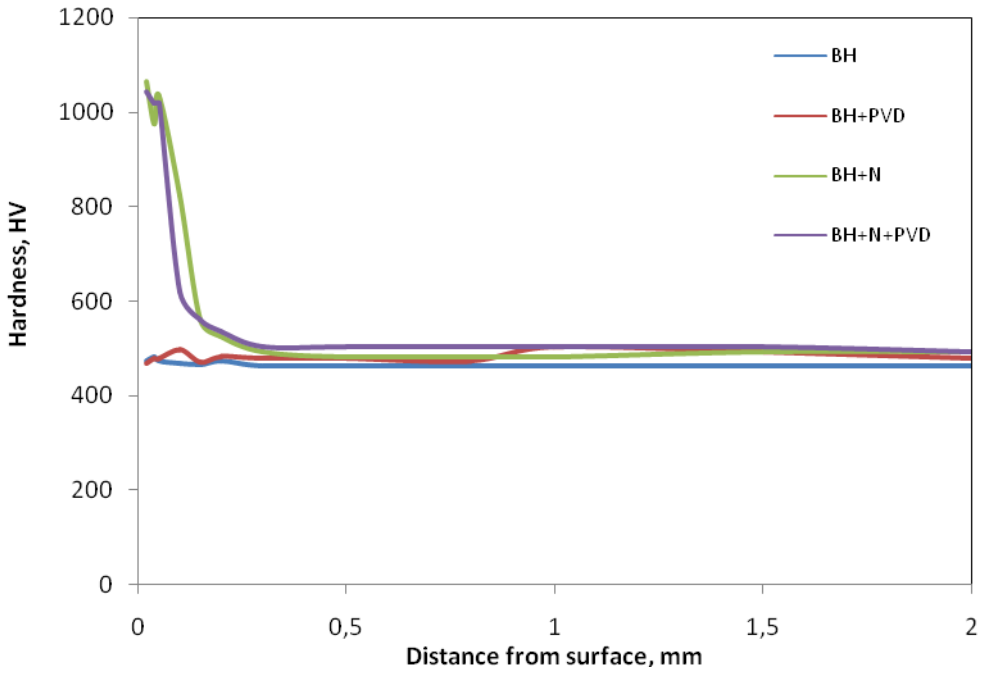
APPENDIX A.22 : Change in microhardness along cross section from surface to core in 1.8550 steel



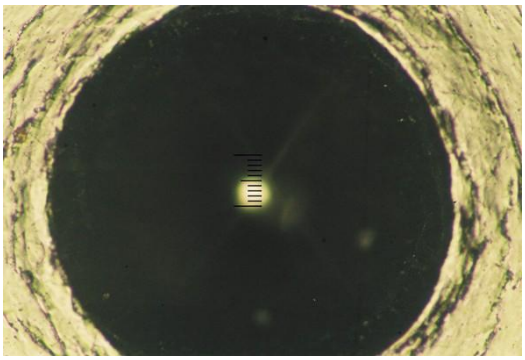
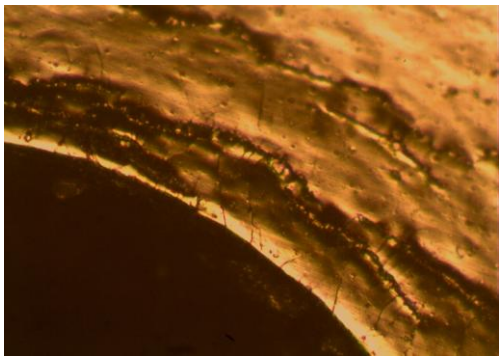
APPENDIX A.23: Change in microhardness along cross section from surface to core in 1.7225 steel

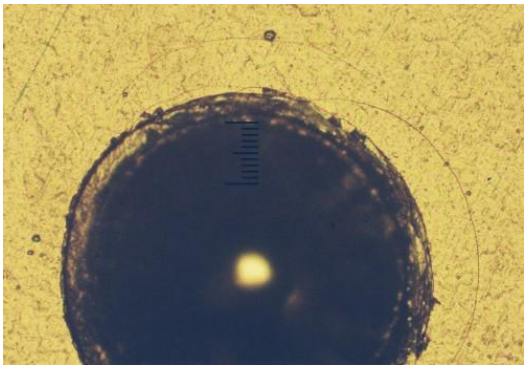
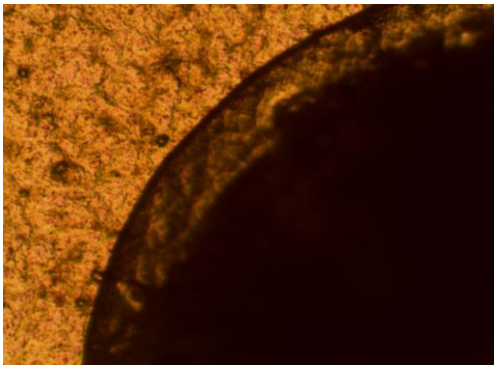


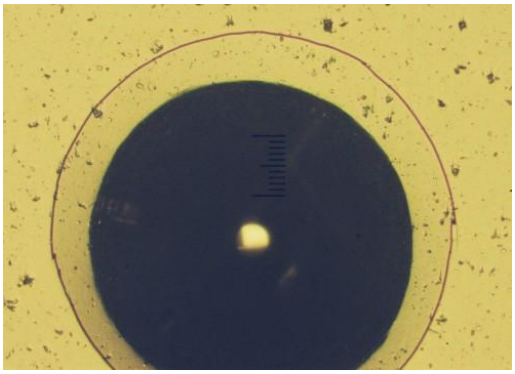
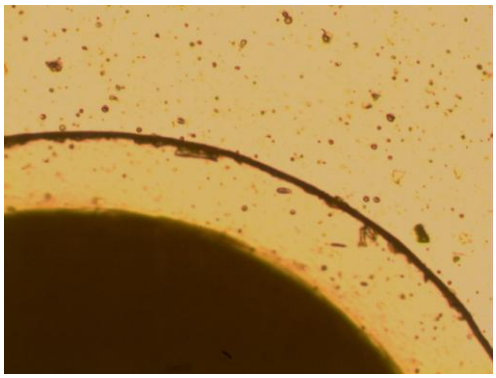
APPENDIX A.24: Change in microhardness along cross section from surface to core in 1.2344 steel



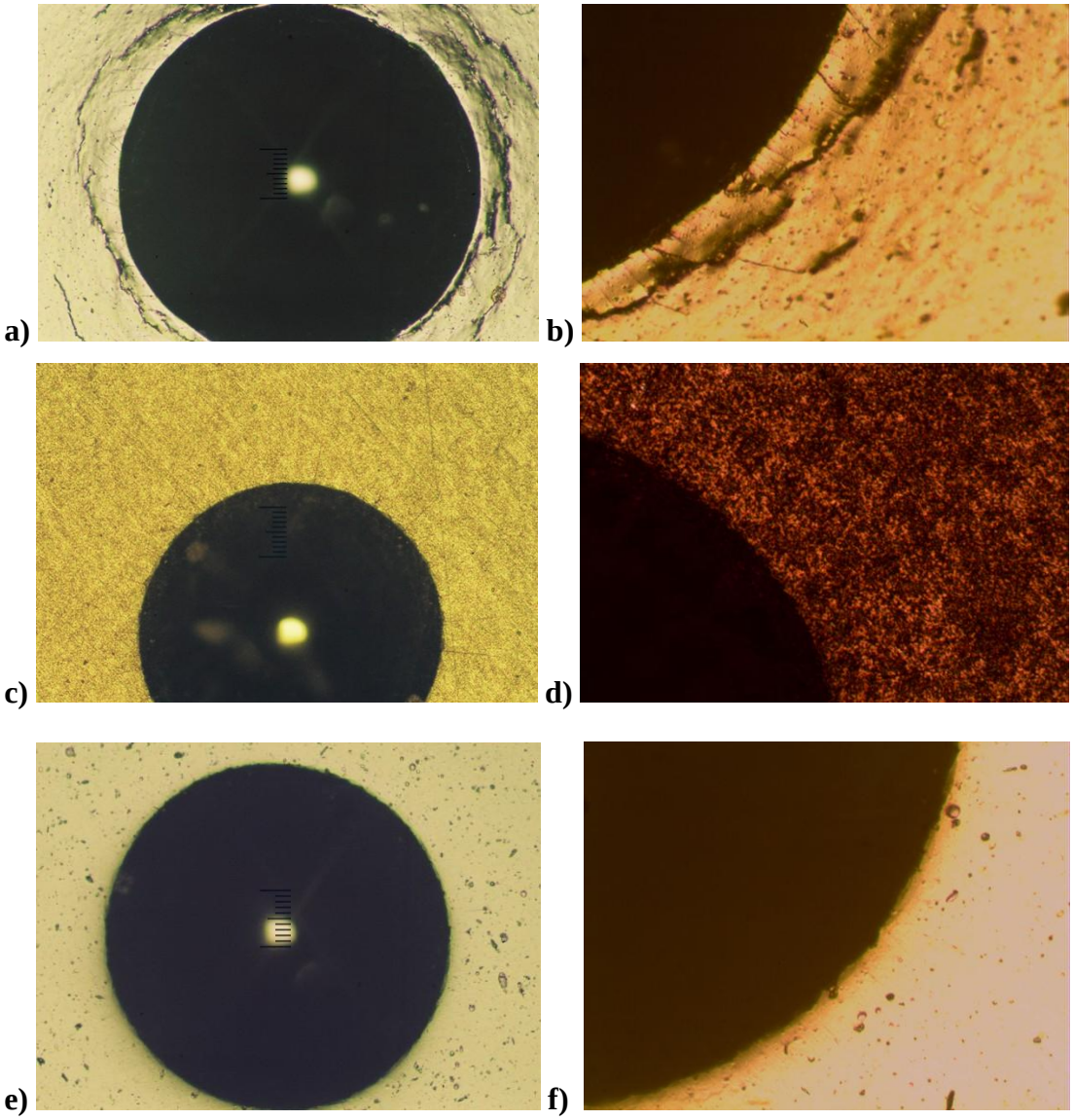
APPENDIX A.25 : Rockwell C indents on 1.8550 steel at 100x and 200x magnification a), b) BH+PVD c),d) BH+N e), f) BH+N+PVD

a)  b) 

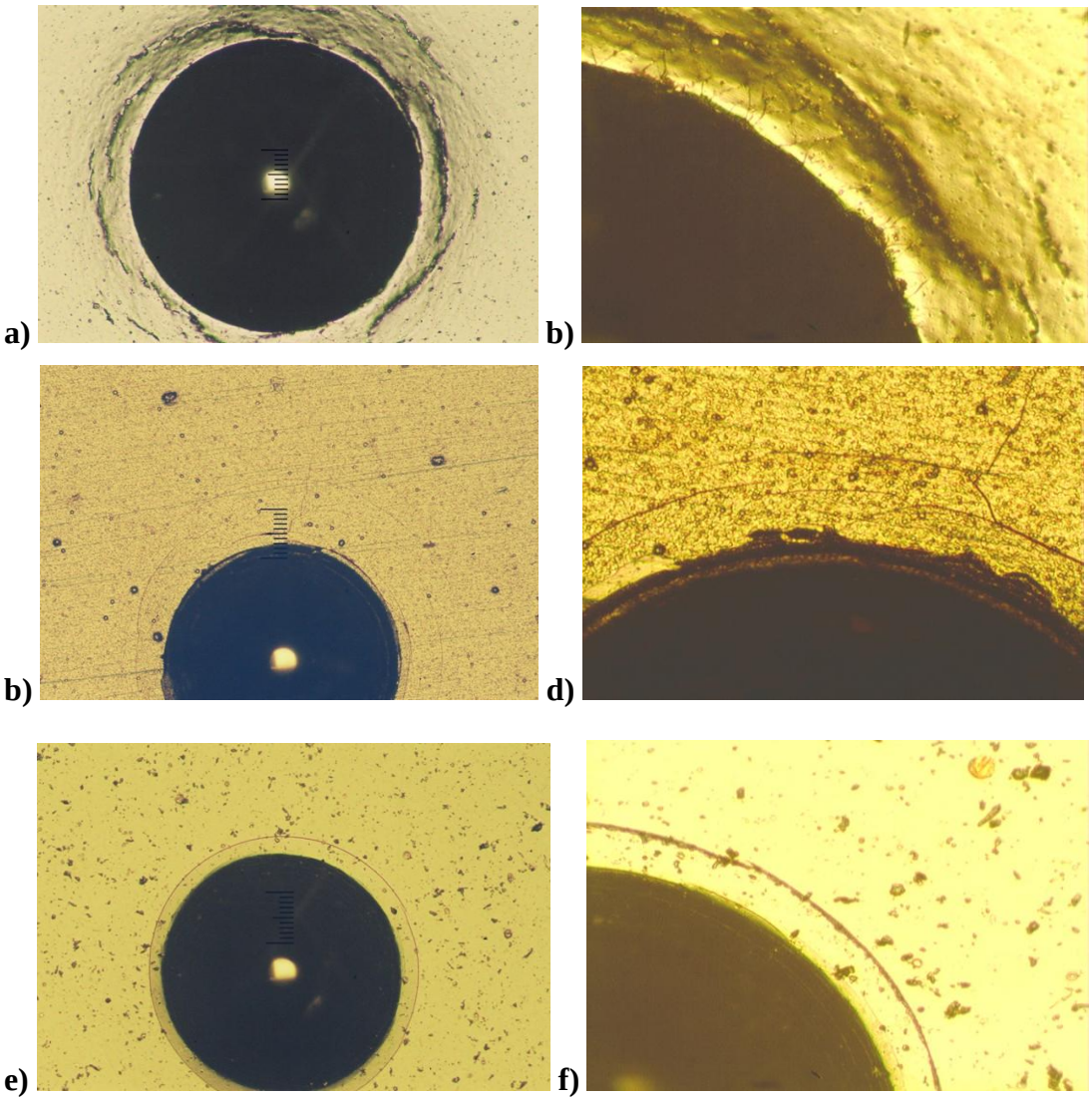
c)  d) 

e)  f) 

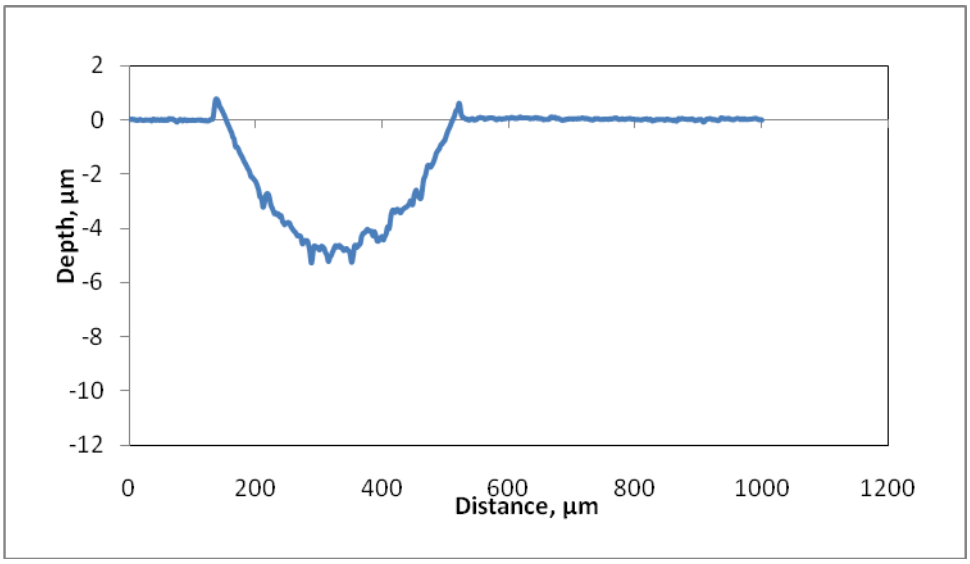
APPENDIX A.26 : Rockwell C indents on 1.7225 steel at 100x and 200x magnification a), b) BH+PVD c),d) BH+N e), f) BH+N+PVD



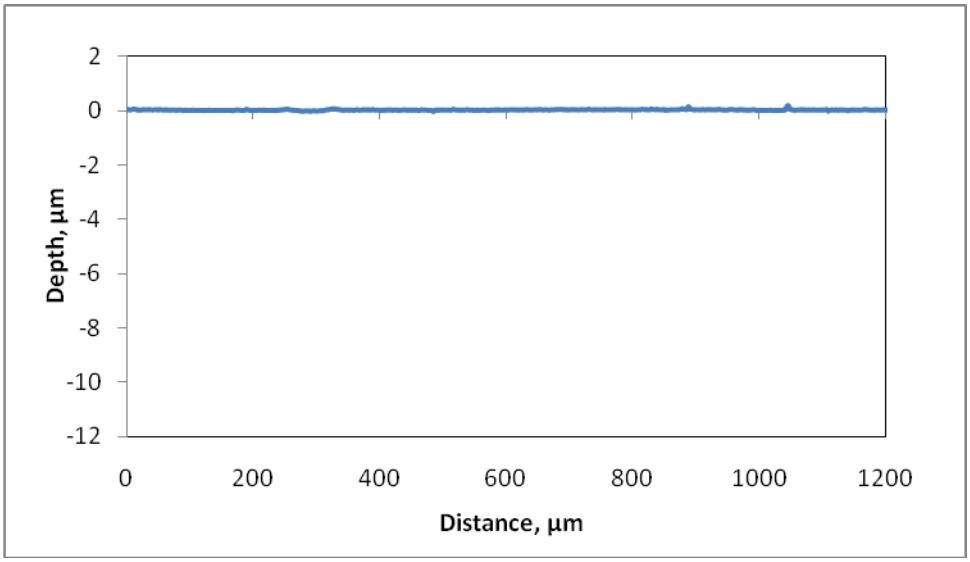
APPENDIX A.27 : Rockwell C indents on 1.2344 steel at 100x and 200x magnification a), b) BH+PVD c),d) BH+N e), f) BH+N+PVD



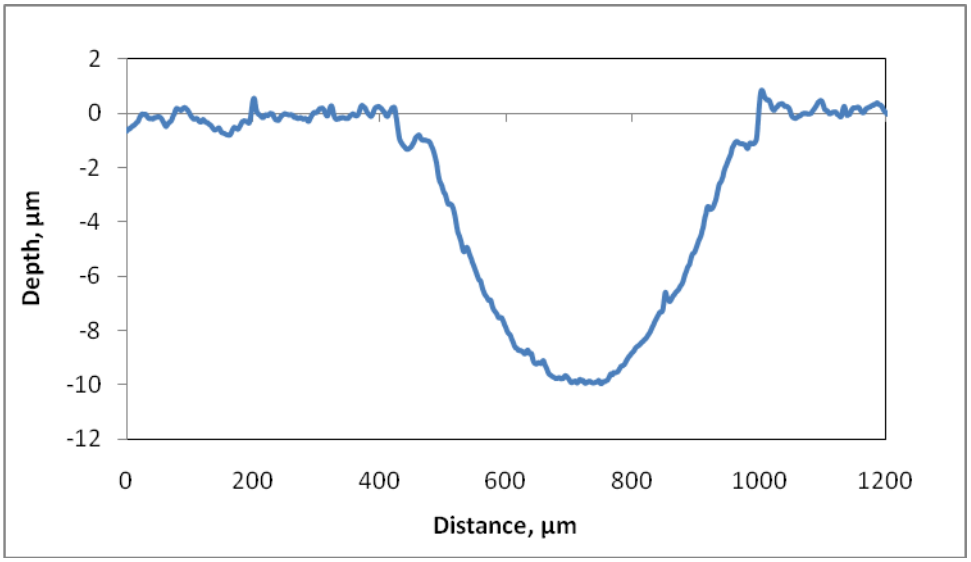
APPENDIX A.28 : The 2D profile of the wear track formed on the surface of the bulk hardened 1.8550 alloy



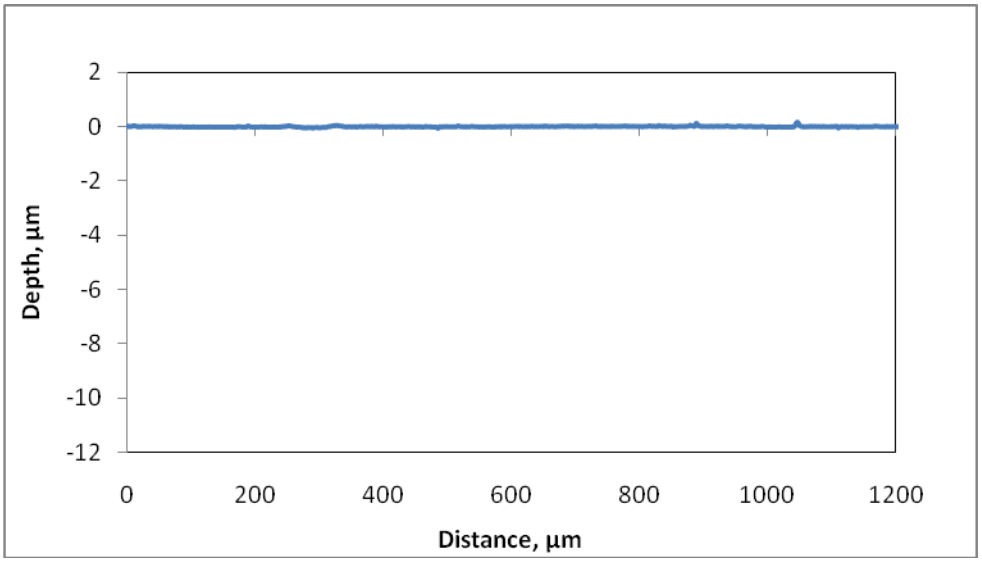
APPENDIX A.29 : The 2D profile of the wear track formed on the surface of the bulk hardened + thin film coated 1.8550 alloy



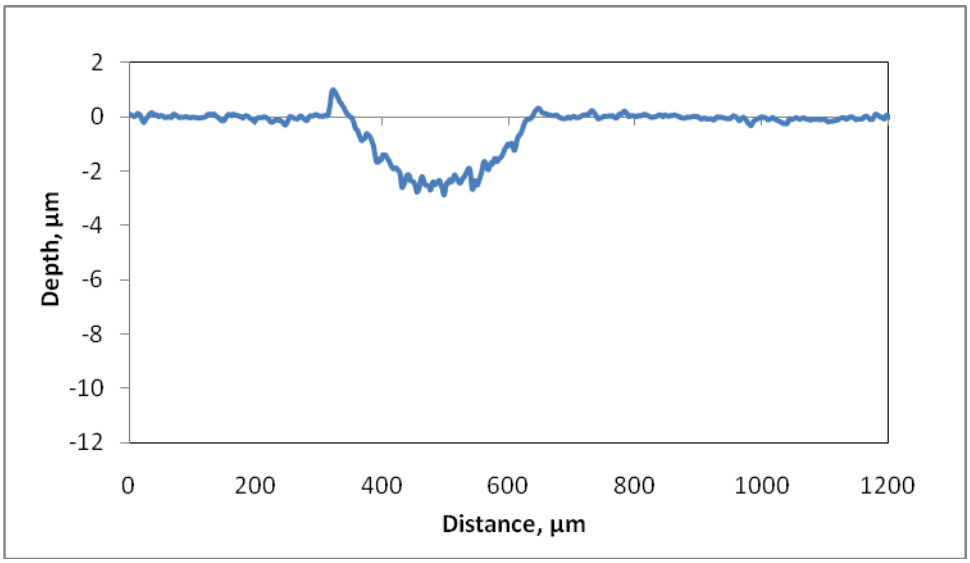
APPENDIX A.30 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided 1.8550 alloy



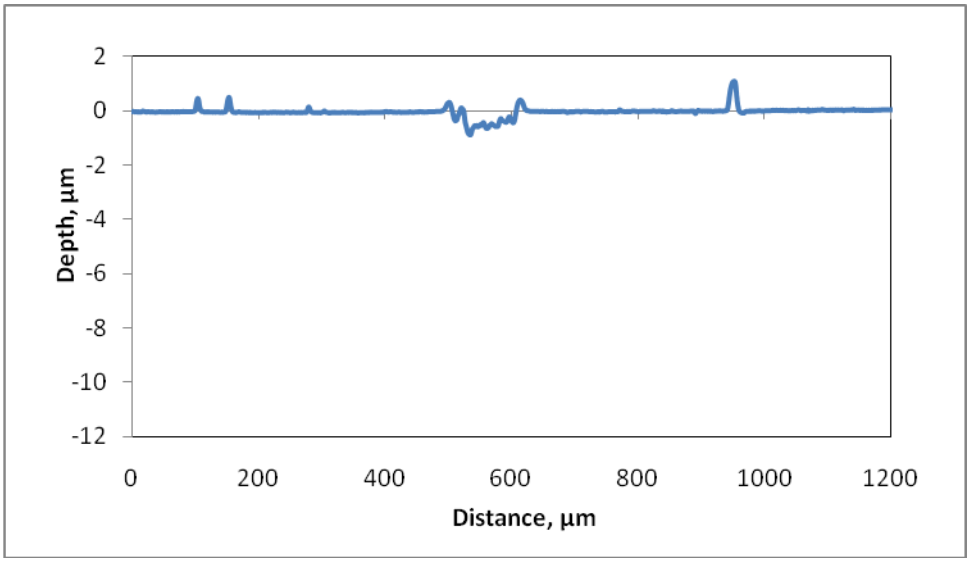
APPENDIX A.31 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided + thin film coated 1.8550 alloy



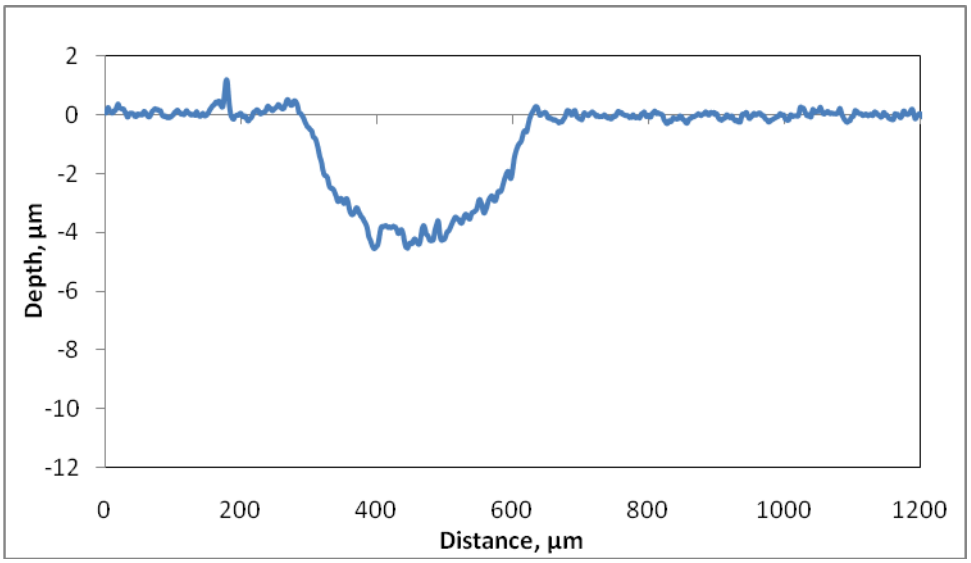
APPENDIX A.32 : The 2D profile of the wear track formed on the surface of the bulk hardened 1.7225 alloy



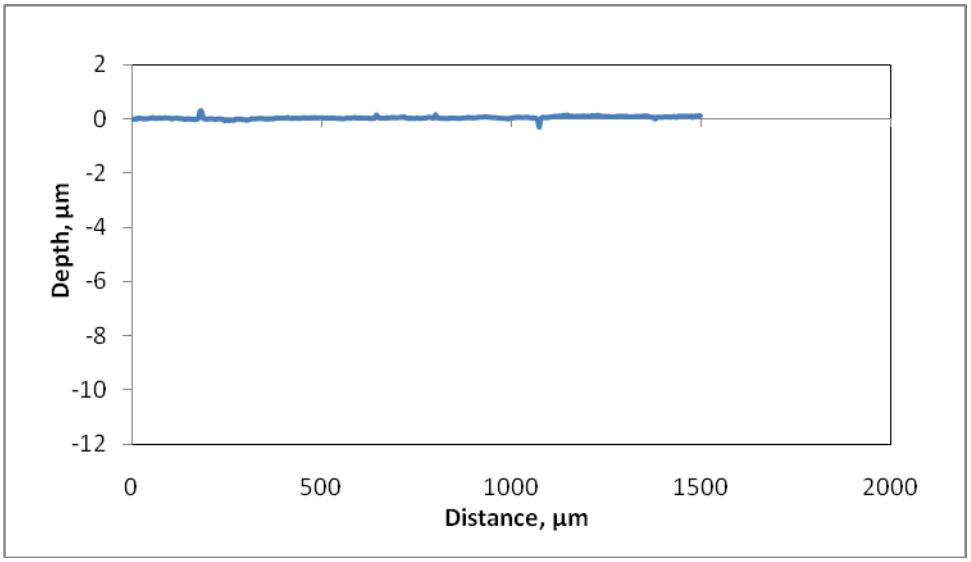
APPENDIX A.33 : The 2D profile of the wear track formed on the surface of the bulk hardened + thin film coated 1.7225 alloy



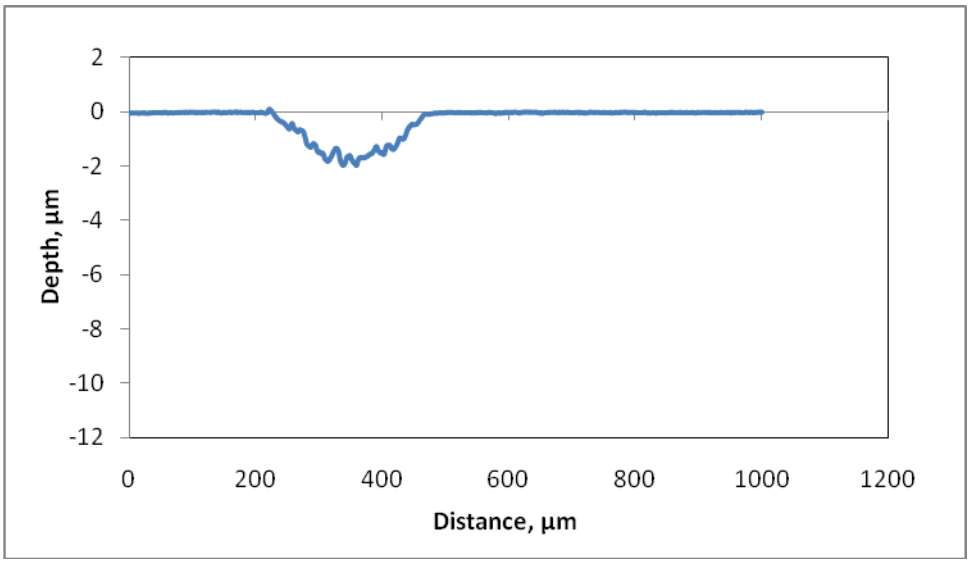
APPENDIX A.34 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided 1.7225 alloy



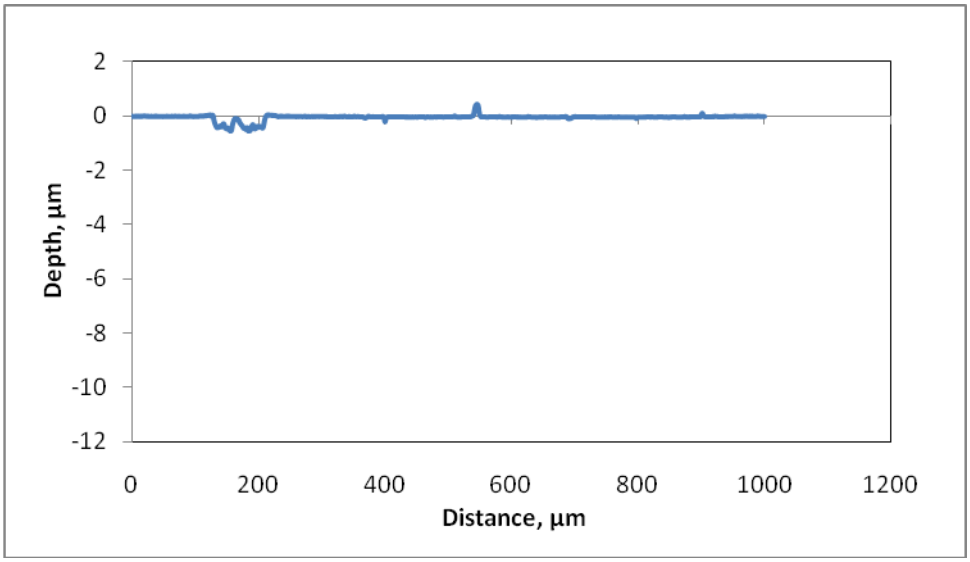
APPENDIX A.35 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided + thin film coated 1.7225 alloy



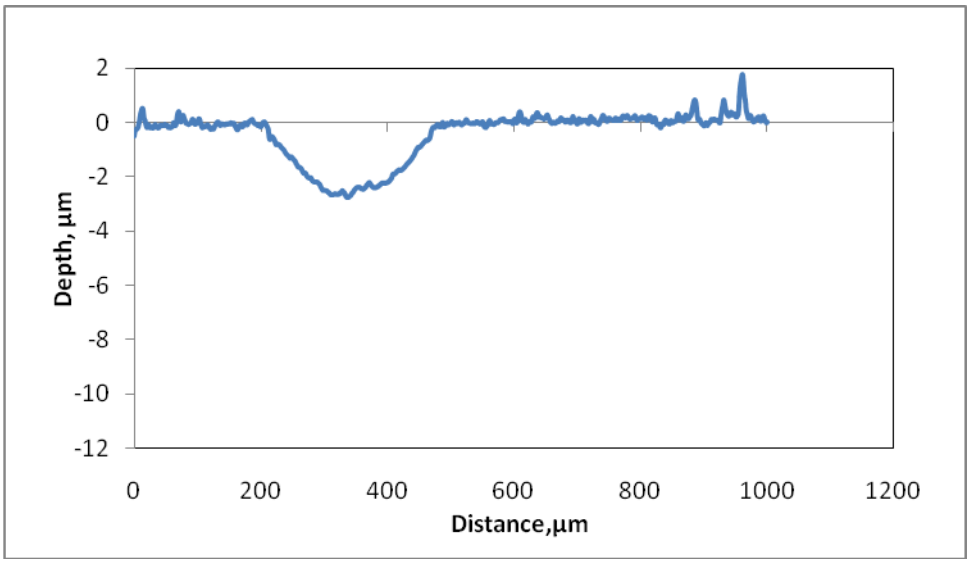
APPENDIX A.36 : The 2D profile of the wear track formed on the surface of the bulk hardened 1.2344 alloy



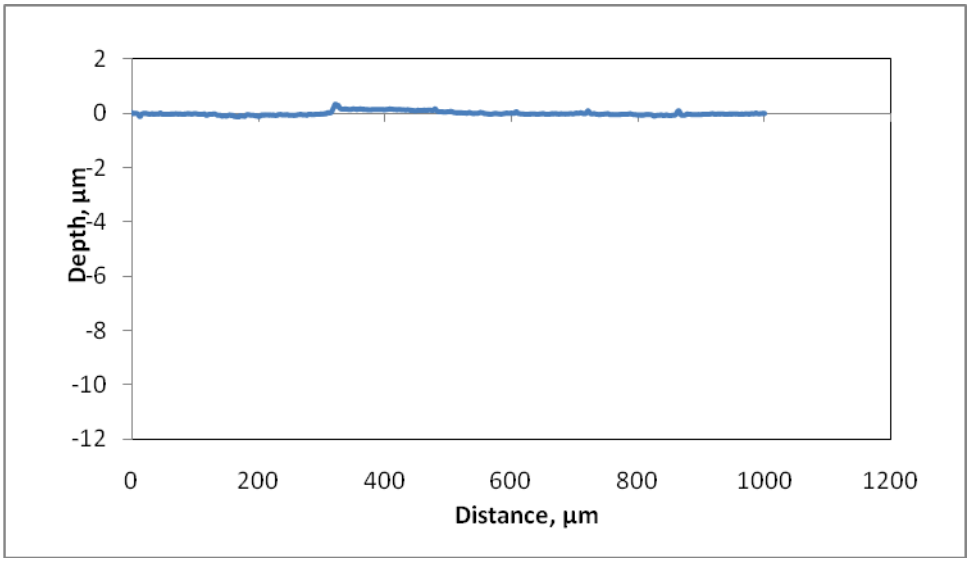
APPENDIX A.37 : The 2D profile of the wear track formed on the surface of the bulk hardened + thin film coated 1.2344 alloy



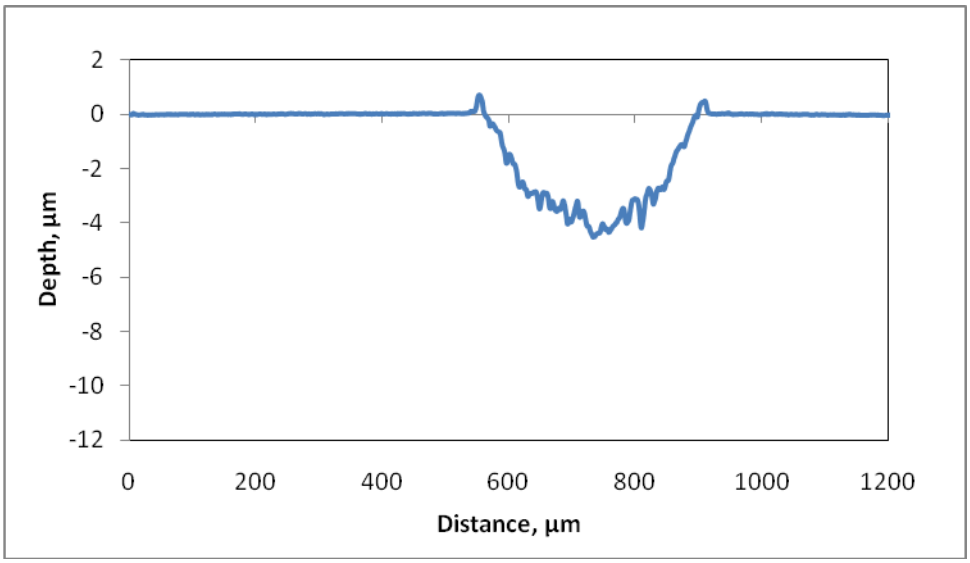
APPENDIX A.38 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided 1.2344 alloy



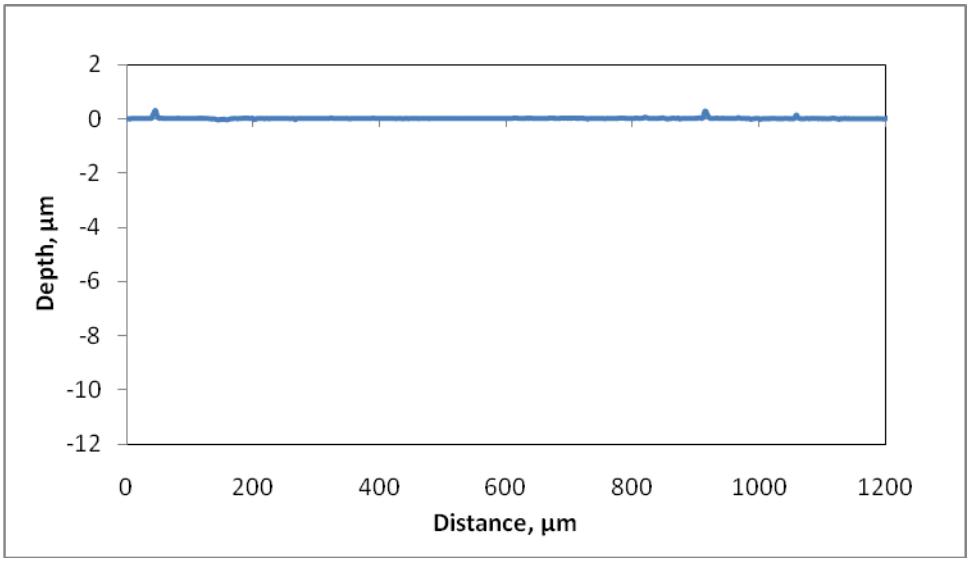
APPENDIX A.39 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided + thin film coated 1.2344 alloy



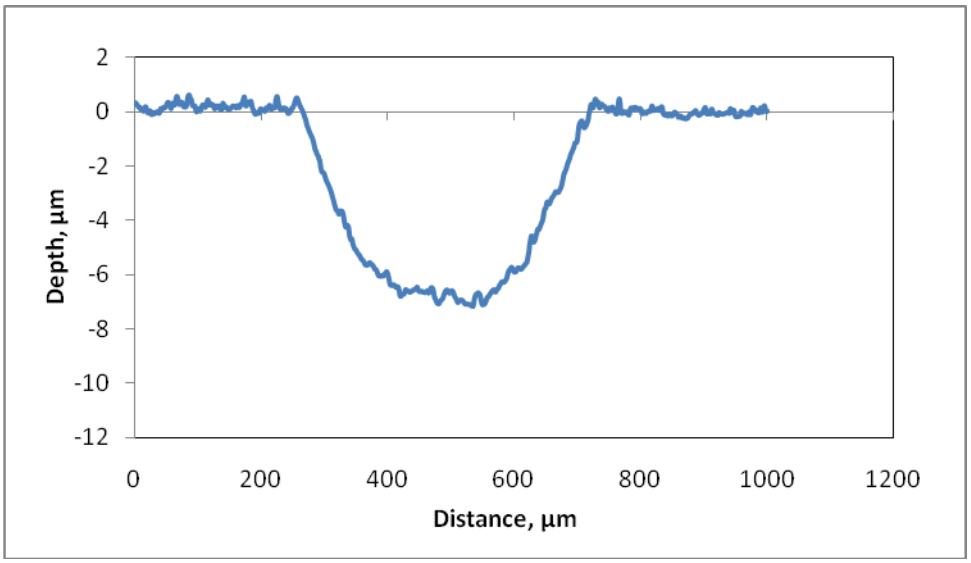
APPENDIX A.40 : The 2D profile of the wear track formed on the surface of the bulk hardened 1.2738 alloy



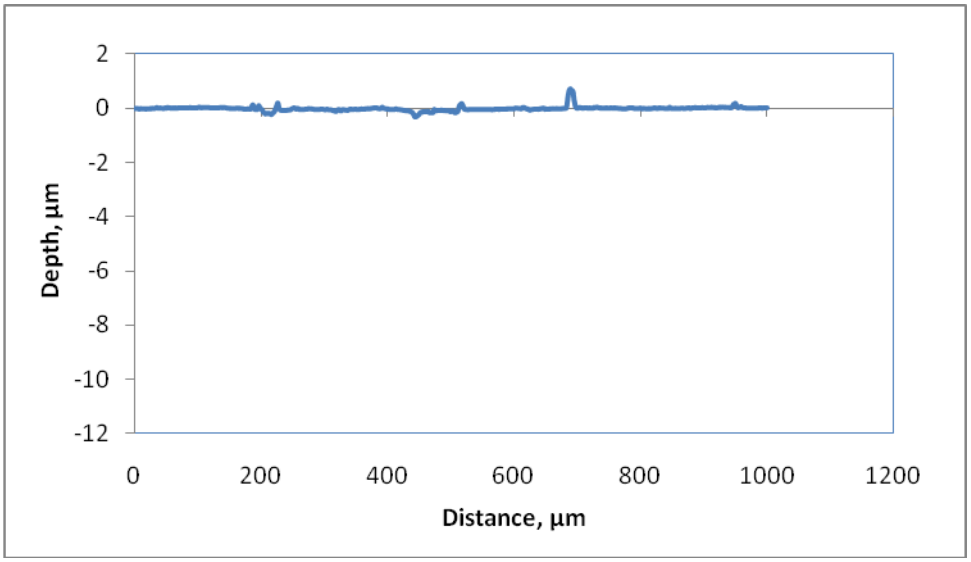
APPENDIX A.41 : The 2D profile of the wear track formed on the surface of the bulk hardened + thin film coated 1.2738 alloy



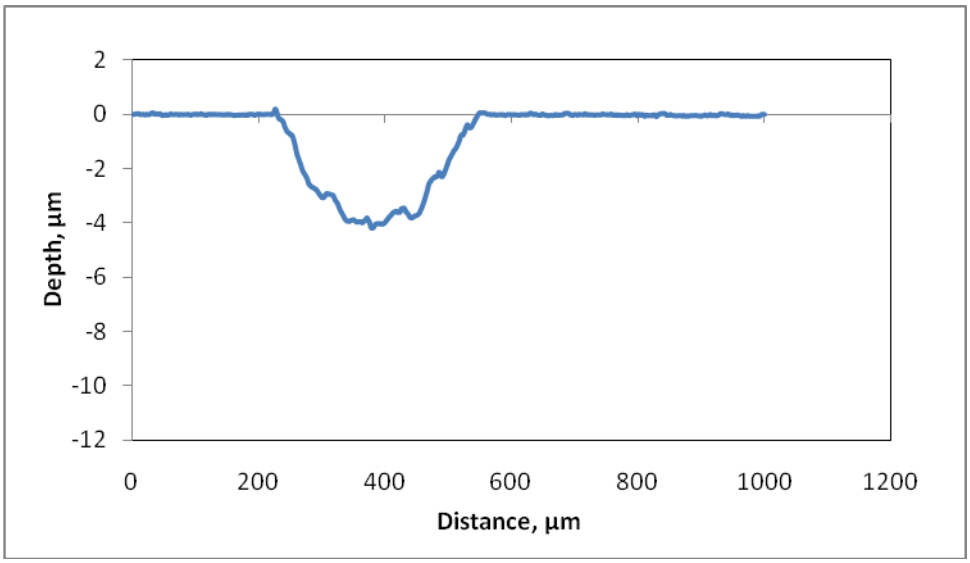
APPENDIX A.42 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided 1.2738 alloy



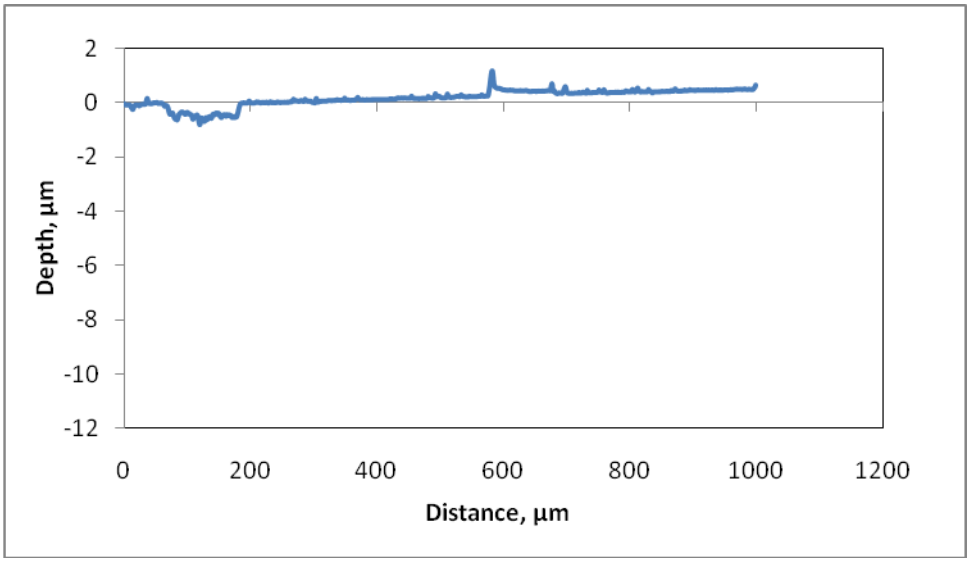
APPENDIX A.43 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided + thin film coated 1.2738 alloy



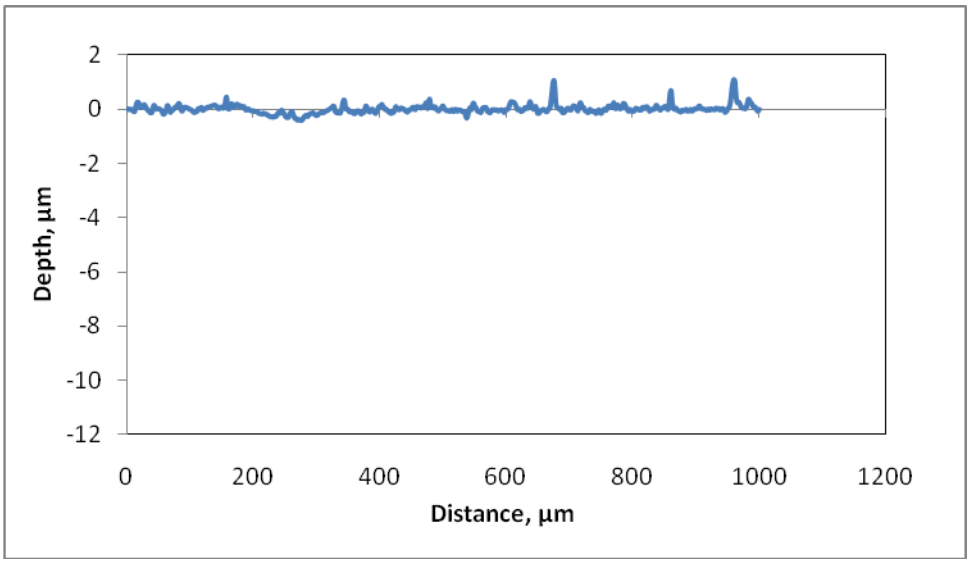
APPENDIX A.44 : The 2D profile of the wear track formed on the surface of the bulk hardened 1.2379 alloy



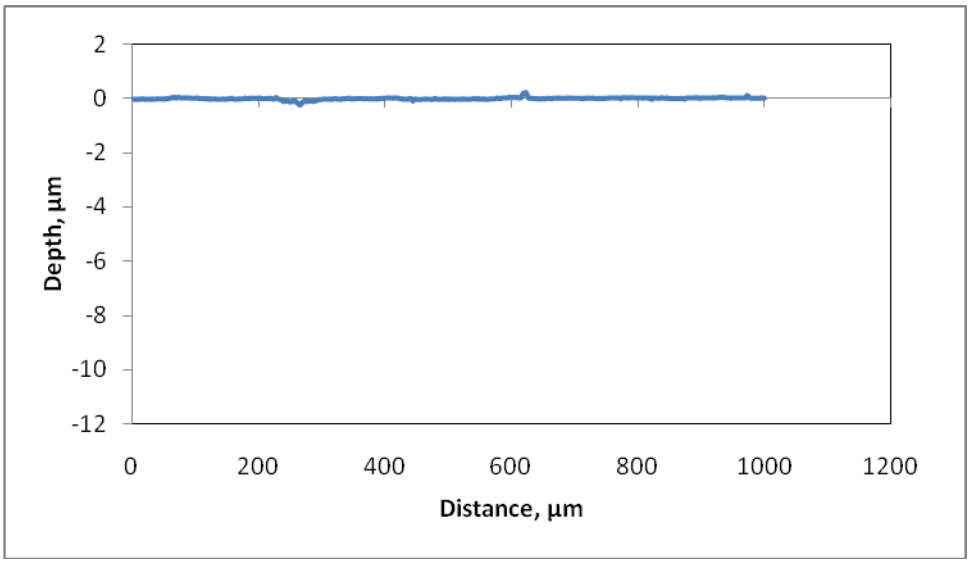
APPENDIX A.45 : The 2D profile of the wear track formed on the surface of the bulk hardened + thin film coated 1.2379 alloy



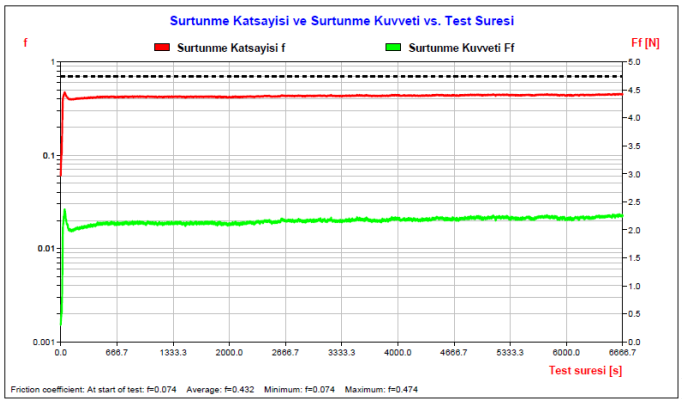
APPENDIX A.46 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided 1.2379 alloy



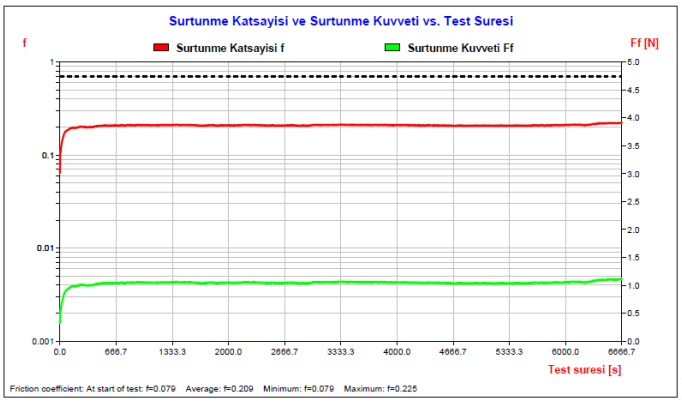
APPENDIX A.47 : The 2D profile of the wear track formed on the surface of the bulk hardened + nitrided + thin film coated 1.2379 alloy



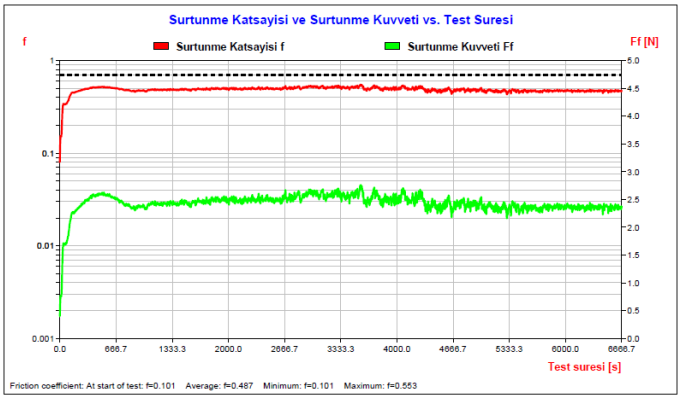
APPENDIX A.48 : Friction curves of 1.8550 alloy



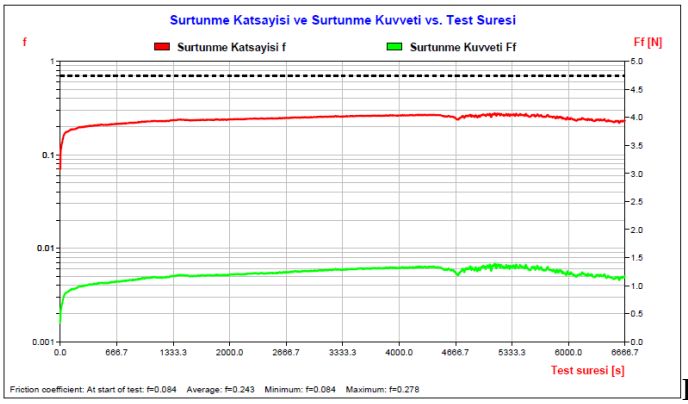
BH



BH+ PVD

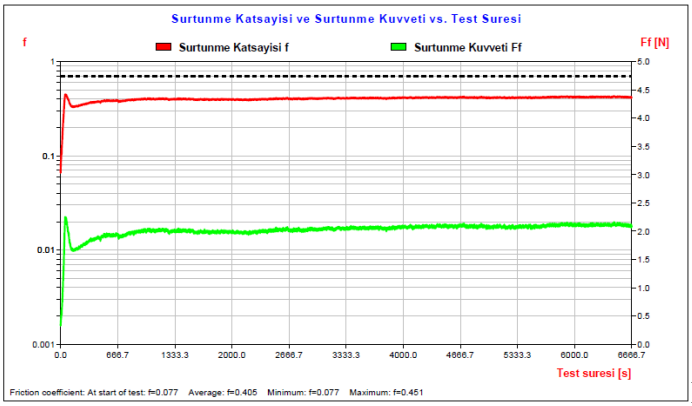


BH+N

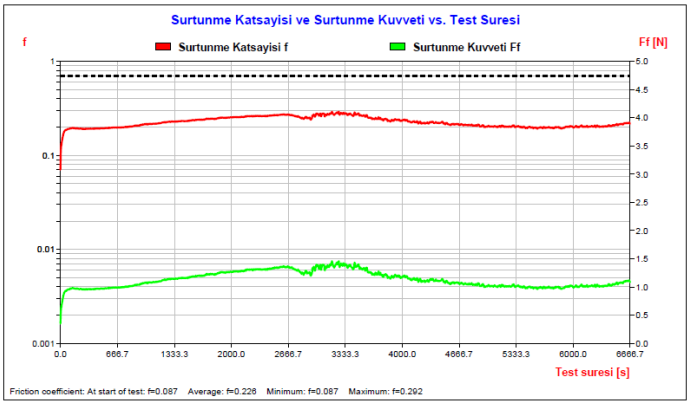


BH + N + PVD

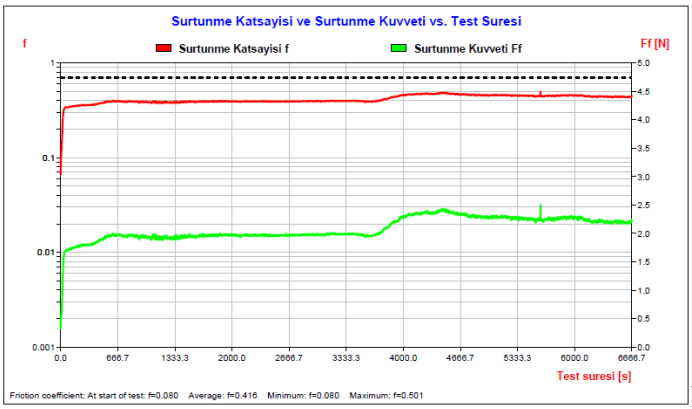
APPENDIX A.49 : Friction curves of 1.7225 alloy



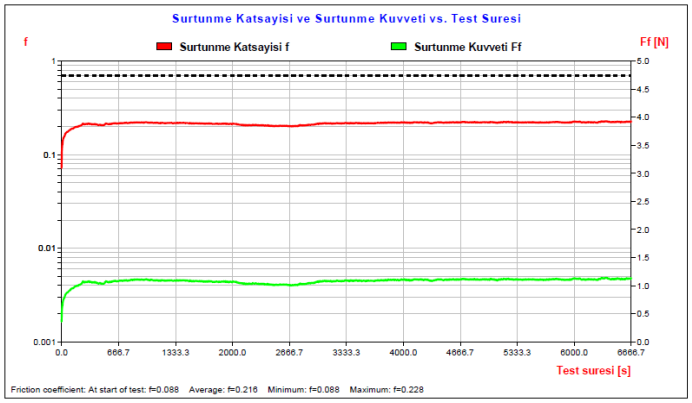
BH



BH +PVD

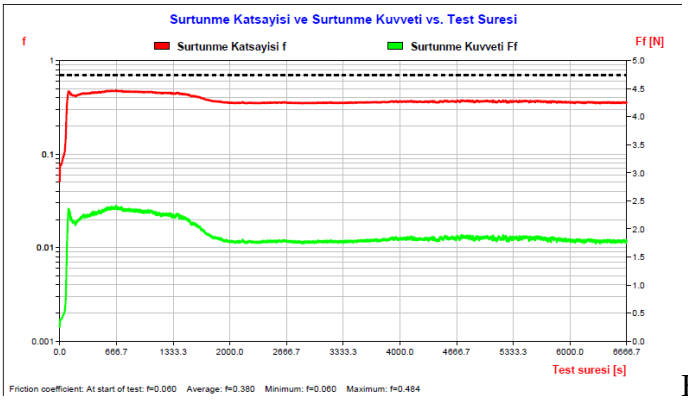


BH+N

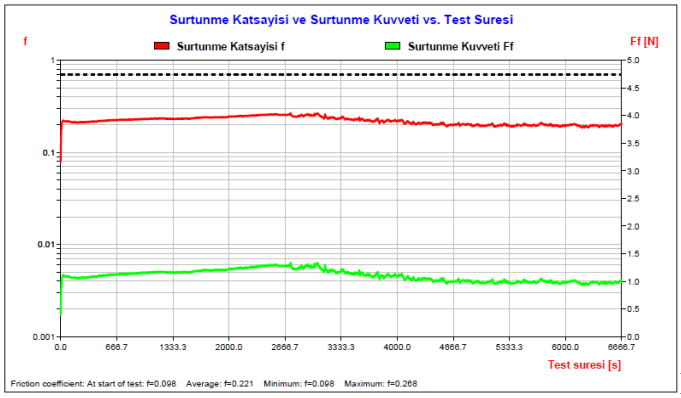


BH + N +PVD

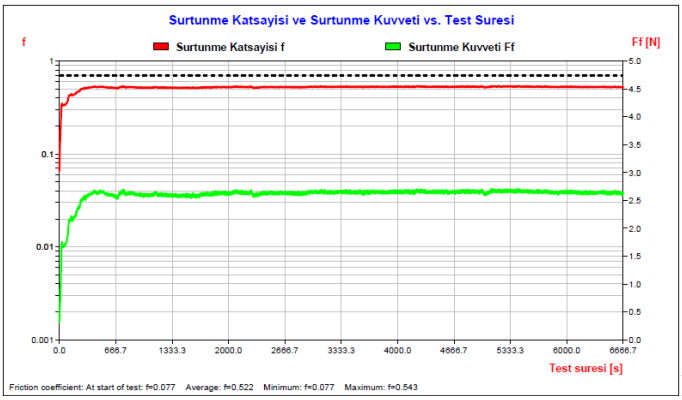
APPENDIX A.50 : Friction curves of 1.2344 alloy



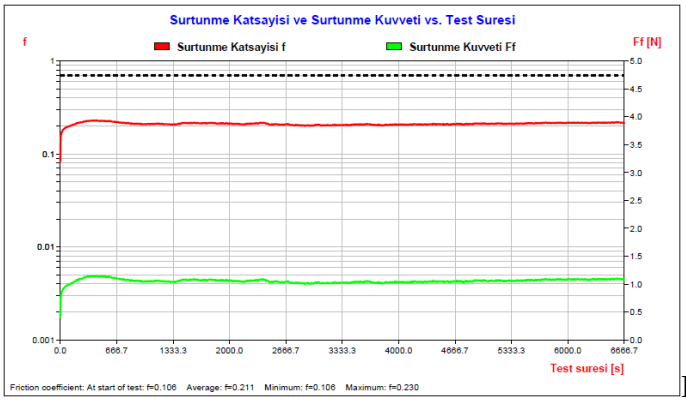
BH



BH + PVD

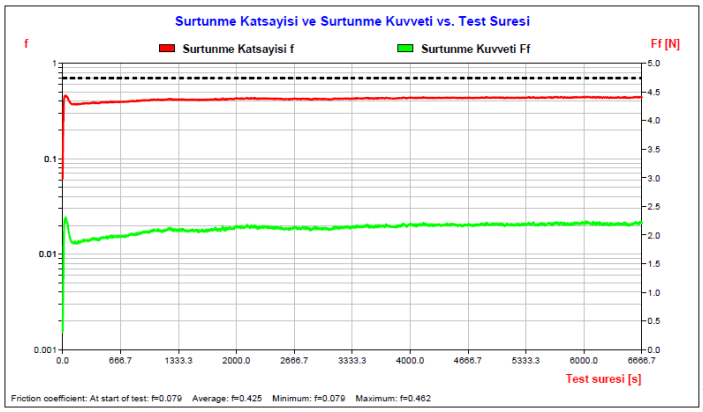


BH + N

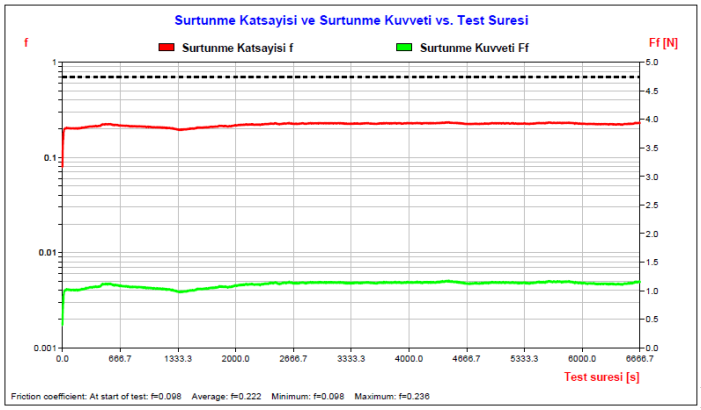


BH + N + PVD

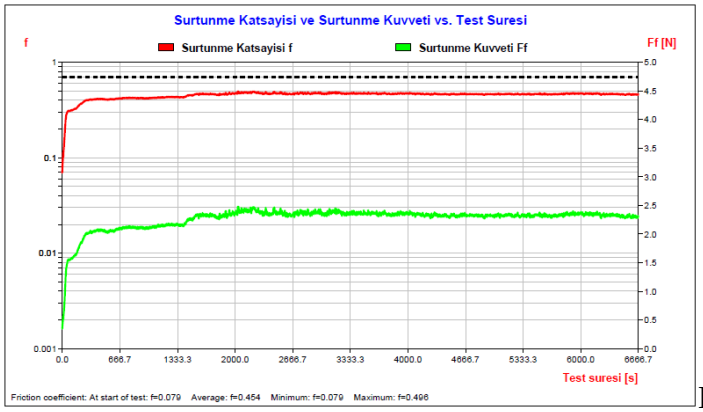
APPENDIX A.51 : Friction curves of 1.2738 alloy



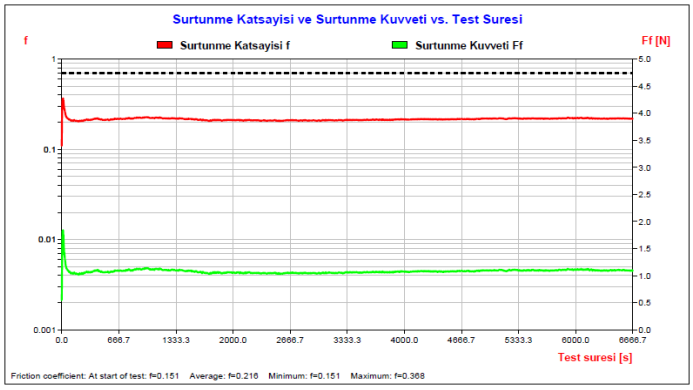
BH



BH + PVD

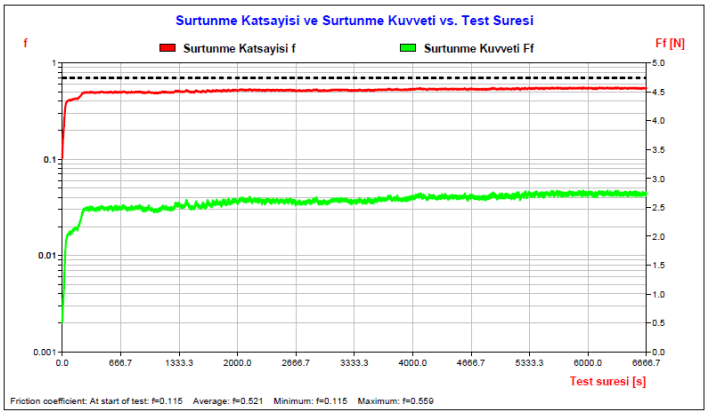


BH + N

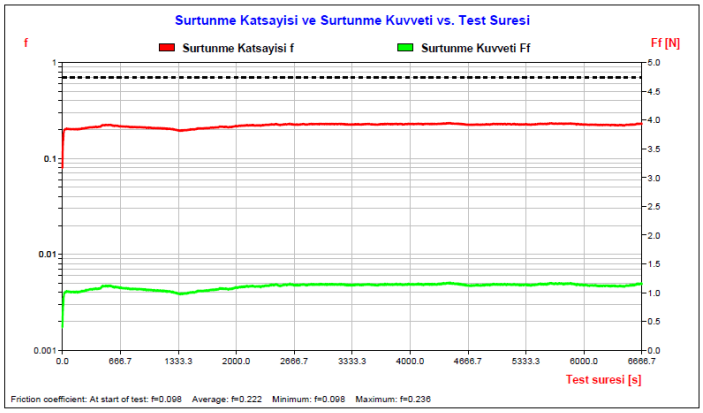


BH + N + PVD

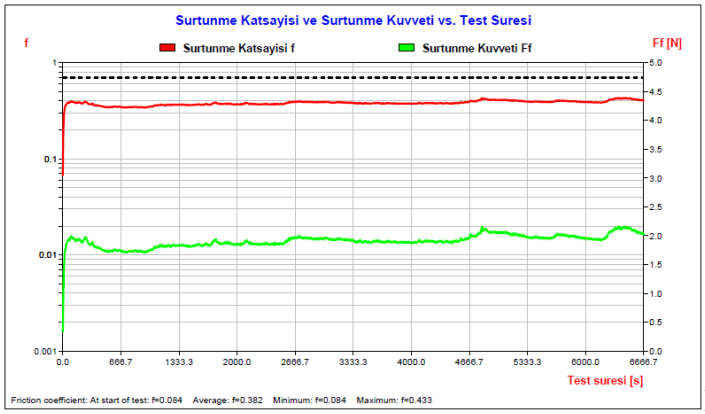
APPENDIX A.52 : Friction curves of 1.2379 alloy



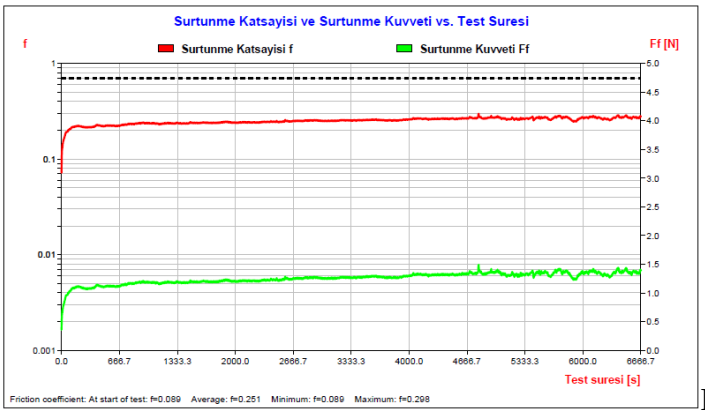
BH



BH + PVD



BH + N



BH + N + PVD

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