Service Life Enhancement Of Hard Coatings For Wear Applications

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Certificate

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DEDICATION

The family and friends are one of nature's masterpieces.

~George Santayana

We would like to dedicate our project to our beloved parents who never stop giving of themselves in countless manners, our siblings whose encouragement made sure that we give in all it takes to finish what we have started and our friends, who motivated us throughout the process.

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ABSTRACT

Chromium hard coatings used in wear resistance applications have an average hardness of 900 Hv. To increase the service life of any application, the wear resistance of its surface should be increased which primarily depends on hardness. This project includes the study of two possible surface coatings having a superior hardness and wear resistant properties in order to replace the conventionally used Cr coating. This includes the formation of Chromium Nitride, through nitridation of Cr coating, formation of Nano Cobalt Phosphorus alloy coating, through electroplating.

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List of Abbreviations

Cr: Chromium

CrN: Chromium Nitride

Co: Cobalt

P: Phosphorus

Co-P: Cobalt Phosphorus

FCC: Face Centered Cubic

nCoP: Nano-Structured Cobalt Phosphorus Alloy Coating

Cr(VI): Hexavalent Chromium i.e. Hard Chrome

EHC: Electro Hard Chrome Coating

Mn: Manganese

HSS: High Speed Steel

CrN: Chromium Nitride

Nitriding: Process of formation of nitride

XRD: X-Ray Diffraction

SEM: Scanning Electron Microscopy

EDS: Energy Dispersive Scattering

POF: Pakistan Ordinance Factories

PSM: Peoples Steel Mills

Billet: length of **metal** that has a round or square cross-section, with an area less than 36 in^2 (230 cm^2)

µm: Micrometer i.e. 10^{-6}m

Cathode: Negative Electrode

Anode: Positive Electrode

DC: Direct Current

AC: Alternating Current

^{o}C: Degrees centigrade

N$_2$: Nitrogen Gass

NH_3: Ammonia gass

": Inches

Hrs: Hours

Torr: Unit of pressure

sccm: Standard cubic centimeter flow rate

N/A: Not Applicable

Micron: Micrometer i.e. 10^{-6} m

Flushing: purging i.e. flowing gas through a chamber for elongated period of time

LOS: Line of Sight channel

NLOS: Non Line of Sight

Nm: nano meter i.e. 10^{-9}m

OSHA: Occupational Safety and Health Administration

g/l: Grams/Litre

ml: millilitre

l: Litre

ml/l: millilitres/litre

Hz: Hertz

V: Volts

HV: Hardness Vickers

d= Arithmetic mean of the two diagonals

F= Load in kgf

d= spacing between the planes

n= integer representing order of diffraction

θ= diffraction angle

λ= wavelength of X-rays

Chapter 1: Introduction

1.1. Background

A coating is a covering of the surface of an object known as substrate. Coating can be an optical or a protective coating. A protective coating is applied to enhance the wear resistant properties and machining performance by acting as a thermal barrier. Coatings are divided into two main categories i.e. soft and hard coatings on the basis of their temperature stability, transmitted wavefront error, cost, life and manufacturing repeatability. Hard coatings are referred to those coatings which have the properties like high hardness, high wear resistance, corrosion resistant at elevated temperatures and fatigue endurance. These coatings are used in Oil & Gas, Automotive, Aerospace, Power Generation, Firearms and many other industrial applications. Coatings can be done on a variety of metals as well as on composites, ceramics, wood, glass and plastics. Different coatings such as carbides, metal oxides, several metals and some plastics can be used to enhance the properties of hardness and wear resistance. [1]

Chromium plating also known as chrome plating is the electroplating of a thin layer of chromium onto a metal object. The chromium layer can provide corrosion resistance, ease cleaning procedures, decorative or increase surface hardness. One type of chrome is decorative chrome which is designed to be aesthetically durable and pleasing having a thicknesses range from 0.05 to 0.5 µm. Hard chrome also referred to as engineered chrome or industrial chrome is a type of chrome coating used to reduce friction, expand chemical inertness, and improve durability through wear resistance and abrasion tolerance. It is very hard, having a hardness value ranging between 65 and 69 HRC (832 and 1044 HV). Hard chrome is thicker than decorative chrome with standard thicknesses ranging from 0.2 to 0.6 mm (200 to 600 µm). For applications where extreme wear resistance is required, the thickness of 1 mm (1,000 µm) or even more provides optimal results. Different applications of industrial hard chrome are:

- Firearms: Interior of gun barrels
- Aerospace: Landing gear components, Aluminum piston heads, actuator components.
- Automotive: parts that see high cycles over long periods of time, shock absorbers, gears, pistons.
- Machine Tools: Tapes, dies, drills, extrusion screws and rolls.

1.1.1. Hexavalent Chromium

Hexavalent chromium plating, also known as chrome (VI) plating or hex-chrome, Cr^{+6}, uses chromium trioxide (chromic anhydride) as the main ingredient. It is used for hard coating and decorative along with bright dipping of anodizing, chromic acid, copper alloys, and chromate conversion coating. [2]

The process of hexavalent chromium plating is as follow:

1. Activation bath
2. Chromium bath
3. Rinse

The tank of chromic acid is used as an activation bath through which a reverse current flows. This etches the surface of work-piece and removes any scale on it. In some cases, the step of activation is done in the bath of chromium. It is a mixture of chromium trioxide (CrO_3) and sulfuric acid (sulfate, SO_4) whose ratio varies greatly between 75:1 to 250:1 by weight. This results in an extremely acidic bath (pH 0). The current density and temperature in the bath has a great effect on the final coverage and brightness. The temperature for decorative coating ranges from 35 to 45 °C but for hard coating it ranges from 50 to

65 °C. Temperature is dependent on the current density and is directly related i.e higher the current density, higher will be the temperature. After which the whole bath is agitated in order to achieve a uniform deposition and also to keep the temperature constant.

One disadvantage of hexavalent chromium plating is its low efficiency of cathode which results in bad throwing power. So, a non-uniform coating is formed with more on edges and less in inside the corners and holes of a substrate. The solution of this problem is that the auxiliary anodes may be used around those areas which are hard to plate or the part may be over-plated and then ground to size. Moreover, hex-chrome is the most toxic form of Chromium.

1.1.2. Trivalent Chromium

Trivalent chromium plating also called chrome (III) plating or tri-chrome, Cr^{+3} uses chromium chloride or chromium sulfate as the main ingredient. The process of trivalent chrome plating is similar to the process of hexavalent chrome plating, except for the anode composition and bath chemistry. Three types of trivalent chromium (Cr) bath configurations are as under: [2]

1. Chloride or sulfate based electrolyte bath – composite or graphite anodes, plus additives are used to prevent the oxidation of chrome (III) to the anodes.
2. Sulfate based bath – insoluble catalytic anodes are used which maintains an electrode potential which prevents oxidation.
3. Sulfate based bath – lead anodes are used surrounded by boxes filled with H_2SO_4 which keeps tri-chrome from oxidizing at the anodes.

Better throwing power and Higher cathode efficiency are the functional advantages of trivalent chromium. Lower current densities are required so the required energy in case of chrome (III) is also less. Moreover, the process of trivalent chromium is more robust as compared to hexavalent chromium as it can withstand interruptions in current. Tri-chrome is less toxic than hex-chrome.

One of the disadvantages of using tri-chrome is that the corrosion resistance of thicker coatings is not as good as it is in case of hexavalent chromium in hard coating applications. In general, the process of trivalent chrome must be controlled appropriately and more closely as compared to hexavalent chrome plating, specifically with respect to metallic impurities which means that those processes which are hard to control e.g barrel plating use hexavalent chromium plating instead of trivalent chromium plating.

1.1.3. Gun Barrels

Chrome plating of gun barrel is one of the main and essential feature in the manufacturing of conventional ammunition. It increases the service life of the barrel multifold. A suitable layer of hard chrome is deposited on the inner side of barrel cylinder. The geometry of the object and the control on coating thickness requires a well specialized systematic approach. The length and diameter of the barrel are very critical factors in determining the design of the plating system. [3,4]

The major steps involved in most of the firearm plating process include: [5]

i. Polishing of parts in order to ensure that the surfaces are free of imperfections which can become visible after plating.
ii. Cleaning of parts with detergent to remove oil, grease and other debris of the surface which can prevent the formation of uniform coating.
iii. Rinsing of cleaned parts thoroughly with water for removal of remaining surface contaminants and debris.
iv. Coating of part with the catalyst to produce the required metal deposition.
v. Immersing of parts in electrolyte solution which contains dissolved ions of metal (electroplating) and or electro-less solution (electro-less plating).

vi. Monitoring of the process during mixing or agitation in order to detect and clear all the gas bubbles that are sticking to the surface which can prevent proper deposition of coating.

vii. Removing of the parts from the plating bath to dry which is followed by oiling.

viii. Reinstalling after reassembling of the parts onto the weapon.

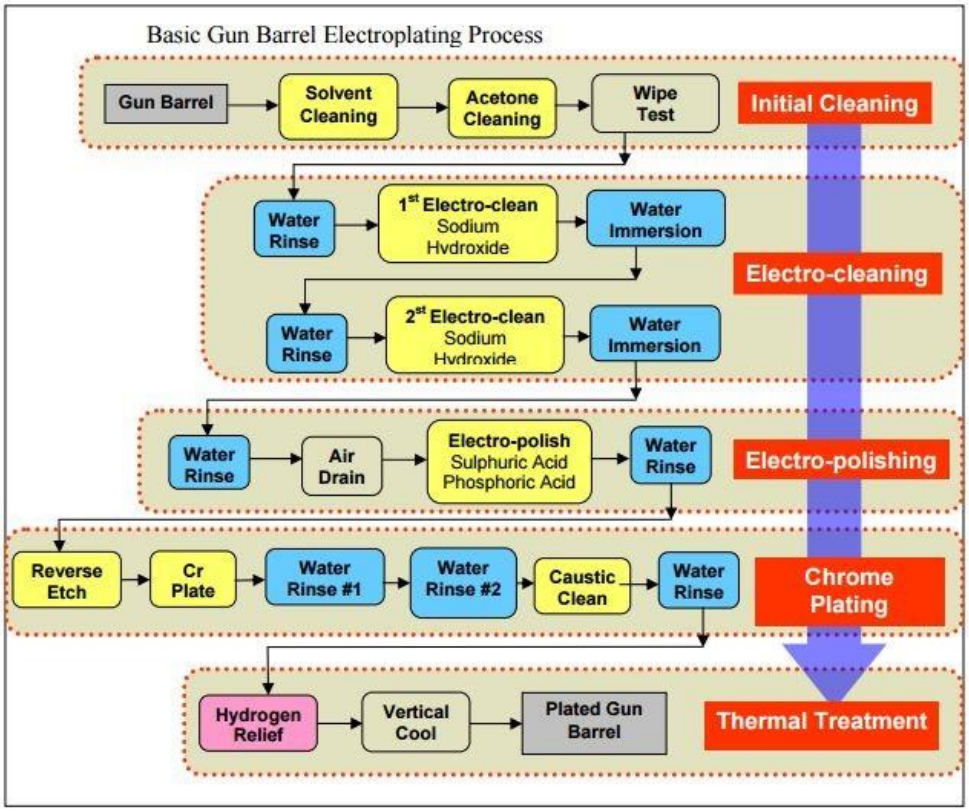


Figure 1.1 Gun Barrel Electroplating Process

The most important element of consideration in plating process of any firearm is to ensure the required level of thickness is attained or not, especially with those weapons which are closely fitted.

1.1.4. Chrome Firearm Plating

Hard chromium plating was invented in 1920s and were improved and perfected during 1940s and 1950s. Hard chrome coating develops a tough coating that gives an excellent resistance against corrosion and also an enhanced lubricity. An important advantage of using hard chrome is that it has good protection against the propellant gasses which can cause wear inside the gun barrel because of the repeated firing. Hard chrome is also known for producing an extremely durable coating which is hard to scratch or damage. [2]

1.2. Problem Statement

Current weapon systems contain gun tubes which use electrodeposited chromium as a protective finish which protects the interior surface of the bore. The coating protects the surface of the bore against the mechanical effects of projectile and hot propellant gases. Chromium is a heavy metal and is deposited using aqueous liquid electro-deposition onto the surface of the tube. Chromic acid is used in the deposition process which is a hazardous substance and is harmful to health because it contains hexavalent chromium. Hex-chrome in aqueous liquid and misting forms also known as carcinogen and is very much expensive to dispose of because it is toxic in nature. It is a major issue when it comes to the pollution of the environment.

Wear and erosion of the bore leads to a shorter service life of a gun barrel. [1] The principle requirement for performance of the coating inside a gun barrel is to avoid erosion and premature wear of the gun barrel. After the plating of a gun barrel, it is exposed to hydrogen bake-plating process. The liberation of H_2 and other non-chromium contaminants causes a reduction in volume of the chromium layer. Tensile stresses are also builded up during the post-hydrogen relief and cool-down period because the coating volume tries to contract. [5] Some of these stresses are relieved through the development of micro-cracks in the chromium coating. These micro-cracks provide path for the propellant gasses to attack the steel substrate. When the gases reach the substrate, the oxides and carbides are produced underneath the chromium layer which further reduces the melting temperature of the steel and allows the metal to be removed through the action of gas wash. Increase in the unprotected substrate greatly increases the process of wear and erosion. The roughened surface appeared through the erosion causes a boost in heat transfer coefficient which allows even larger heat load to the gun barrel. [2] The thermal cycling inside the gun barrel results in further cracking of the chrome coating. During firing, within few milliseconds, the temperature of the surface of the gun barrel reaches upto 1400ºC. A steep thermal gradient is made which results in excessive shear stresses at the interface of coating and substrate. Due to the development of these stresses, the removal process of chromium is increased even more. [6]

1.3. Purpose of the Study

The present work focuses on the service life enhancement of hard coatings. The service life can be increased by increasing the hardness of a surface. Hardness is mostly used as criteria for judging coatings, castings, overlays, hardfacing and alloys, Harder the surface, greater will be its wear resistance. The hexavalent chromium used inside the bores of gun barrel has an average hardness value of 906 HV. The anti-aircraft machine gun undergoes 3500 rounds before the coating erodes. The main aim of the study is to increase the hardness either by modifying the coating or by replacing chromium coating with some other material having comparable hardness value which will result in a better service life.

The study was supported through different series of phase characterization which includes X-Ray Diffraction (XRD) and Energy Dispersive X-Ray Spectroscopy (EDS). Microstructural analysis was done using Optical Microscopy and Scanning Electron Microscopy while hardness testing were carried out by using Microvicker Hardness and Rockwell Hardness Tester.

The conventially used chromium coated gun barrels have many health hazards. The study aims to make a coating which has no health hazards and is environmentally friendly. It also aims that the coating must be easily applicable in the industry and should be economically feasible.

Chapter 2: Literature Review

2.1. Chromium Nitride

Chromium is a transition element and its nitrides retain many excellent properties, such as thermal and chemical stability at elevated temperature, extreme hardness, good electrical and optical properties and high corrosion resistance. Due to such remarkable properties, these nitrides are extensively used in engineering technology fields such as electronic industries, metallurgy, high-temperature structural ceramics, and wear resistant coatings etc. [7]

Chromium Nitride (CrN) has a Face Centered Cubic (FCC) structure [8] with a hardness value of 1800 Hv [9]. This higher hardness makes CrN a very excellent wear resistant and tough material.

2.1.1. Formation of Chromium Nitride coating

Chromium Nitride coating is formed by nitriding Chromium coating which is deposited by electrode-less plating.

Nitridation of Chromium coating can be done using ammonia or nitrogen gas. Difference between both these gases is that ammonia gas cracks at 700-900^{o}C while nitrogen gas cracks at 1100-1200^{o}C. Moreover ammonia gas is poisonous that is why it is recommended to use nitrogen in the absence of a proper exhaust. [10, 11]

While nitridation, atomic nitrogen diffuse into the chromium coating and set at the interstitial sites of chromium to form Chromium Nitride. A small amount of nitrogen diffuse deeper and form Cr_2N which is a nitrogen deficient phase. This Cr_2N phase is comparatively a softer phase which imparts toughness to CrN coating.

2.1.2. Factors affecting Nitridation

There are different factors which affect the formation of Chromium Nitrides, some of these factors are discussed below:

2.1.2.1. Holding Time

As we increase the holding time, the weight change increases which means that the thickness of the coating will increase. Also as we increase the time the nitrogen will diffuse into more depth. The effect of holding time can be seen in **figure. 2.1.** In this figure, weight change means that its percentage increases with time. [9]

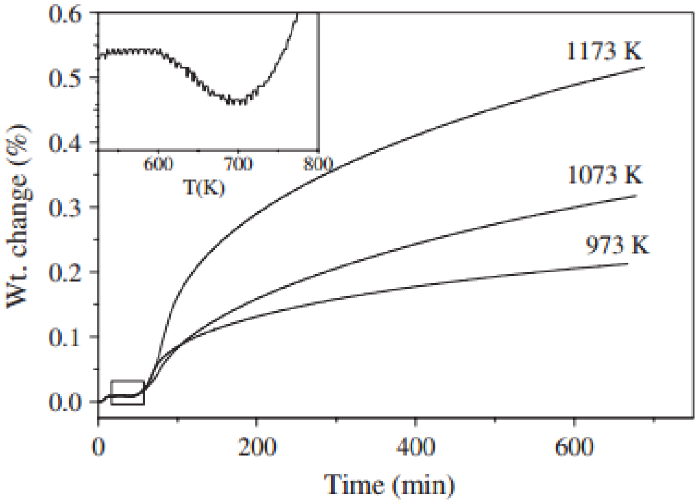


Figure 2.1 Effect of time and temperature on CrN coating

2.1.2.2. Holding Temperature

Temperature increases the mobility of the particles and eventually the diffusion rate of nitrogen atoms. So, as the temperature is higher the reaction rate will be accelerated and more depth can be achieved in the same time as shown in **figure 2.1.** this graph shows the comparison of reaction carried out at three different temperatures and as the temperature increases, the rate of weight change increases. **Figure 2.2.** shows that CrN is not stable at every temperature and pressure range, means that a specific temperature and pressure is required to make a stable CrN phase. [9, 11]

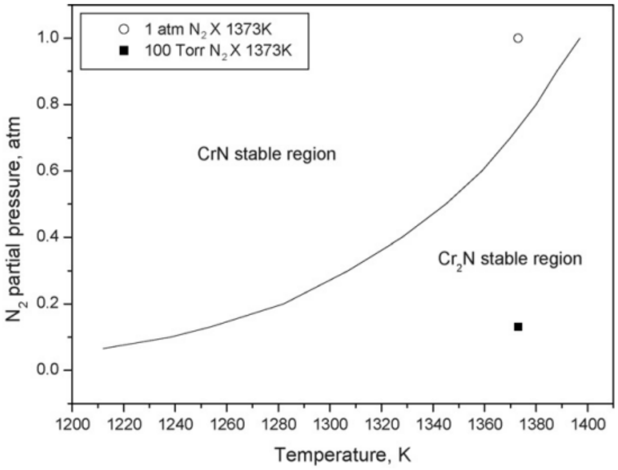


Figure 2.2 Effect of temperature and partial pressure of N2 on CrN

2.1.2.3. Flow rate of Nitrogen

Flow rate of nitrogen is the most important parameter as it is the source of reactive gas. As we have discussed earlier that due to less diffusion of nitrogen atom a nitrogen deficient phase Cr_2N will be formed, similarly due to less flow rate or less supply of nitrogen Cr_2N will be deposit instead of CrN. **Figure 2.2.** shows a specific boundary of CrN and Cr_2N stable pressure range at different temperatures. [11]

2.1.2.4. Impurity Content

Chromium is a highly reactive transition element. It forms oxides very readily even at room temperatures, so impurity of oxygen in the system can be extremely harmful for the formation of Chromium Nitride. A study has shown that the rate of oxygen diffusion in chromium is 3 times higher than nitrogen diffusion, so there is always a probability of formation of oxide even at ppm oxygen content. [12]

2.1.2.5. Thermal Coefficient of Expansion

Another factor which affects the stability or formation of chromium nitride is thermal coefficient of expansion. Chromium nitride and the substrate steel (Manganese steel) has a higher difference in this coefficient due to which at temperature increase due to expansion difference the coating gets chipped off. To avoid the chipping off the coating, a thermally graded layer is formed i.e chromium should act as a middle layer in between Chromium Nitride and substrate to decrease this affect. [9, 12]

2.2. Nano Structured Cobalt Phosphorus Alloy Coating

The second alternative proposed by us in order to replace Hexavalent Chromium is the synthesis of nano-structured Cobalt Phosphorus alloy coating. The recent studies on this coating suggests that the properties exhibited by nCoP are comparable to that of Cr(VI). The development of this system also eliminates the safety concerns associated with Cr(VI) and reduces life cycle costs. Few similarities among both these systems include similar deposition techniques and both are applicable to all conducting materials. Benefit of nCoP over Cr(VI) is that the throughput is very high in nCoP, however nCoP utilizes an advance plating technology i.e. pulsed plating technology to deposit dense, nano-structured deposits.

2.2.1. Crystal Structure of CoP

The crystal structure of the alloy depends directly on the quantity of Phosphorus present in the lattice. According to Kosta et al in their research the microstructure was a mix of nano crystalline structure and amorphous structure for alloy deposits containing low phosphorus concentrations. A shift in microstructure was observed by the authors from nano crystalline to amorphous when the concentration of phosphorus was increased. It was observed that the microstructure completely became amorphous when the phosphorus concentration was in range of 5-6%. The alloy deposit with low phosphorus concentration can be considered as a replacement of hexavalent chromium. [13]

2.2.2. Microstructure

There is a significant difference in the interface and the cross section morphology of Hexavalent chromium and nCoP deposit. R.A Prado et al concluded from their study that micro cracks were present in the electrodeposited Cr(VI)coating whereas the nCoP deposit was free of such cracks as shown in **figure 2.3.** [14]

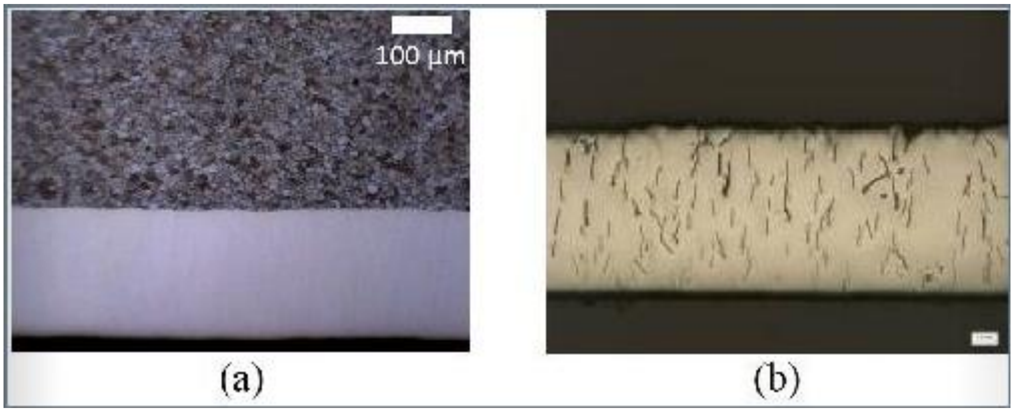


Figure 2.3 (a) Cross Section of nCoP, (b) Cross Section of Cr(VI)

2.2.3. Synthesis

The synthesis route for nCoP is similar to that of Cr(VI) i.e. both are deposited by electroplating, so the infrastructure and apparatus used to deposit Cr(VI) can easily be opted for nCoP. The benefit of nCoP over Cr(VI) is in terms of deposition efficiency and deposition rates due to the usage of pulsed DC current in case of nCoP. The pulsed DC is the form of DC current in which no output signal is obtained for the negative half cycle of AC current (also known as half wave rectification) as shown in **figure 2.4.**

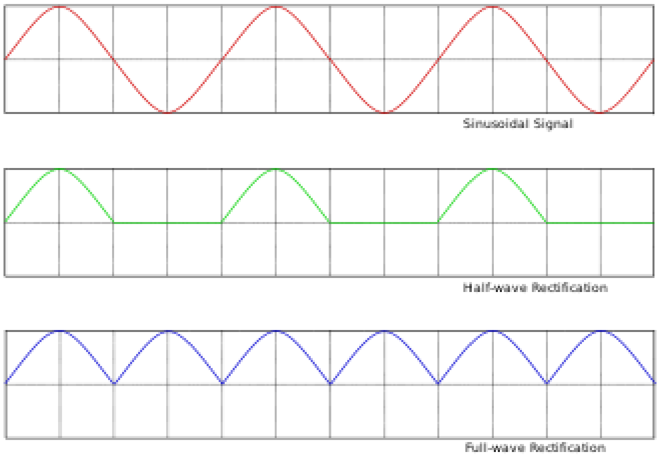


Figure 2.4 Comparision between full wave and half wave rectification

Pulsed DC current also increases the deposit density because of its pulsing nature and on the same time increases the throughput of deposition.

Table 2-1 Comparison of Processes of Cr(VI) and nCoP

	Cr(VI)	**nCoP**
Method	Electrodeposition (Simple DC)	Electrodeposition (Pulsed DC)
Deposition Rate	Up to 0.0010 in/hr	Up to 0.004 in/hr
Efficiency	Up to 35%	Up to 95%

2.2.4. Wear Resistance

R.A. Prado et al used pin on disc method to determine sliding wear resistance comparison among nCoP and Cr(VI). They concluded that Cr(VI) exhibits more loss due to wear as compared to nCoP. The reason mentioned by them was that the co-efficient of friction for nCoP is around 0.4 whereas Cr(VI) has co-efficient of friction of 0.7. Due to high value of co-efficient of friction the wear loss in hexavalent chromium is more as compared to nCoP system.

2.2.5. Hydrogen Embrittlement

The temperatures and atmosphere in which we aim to utilize our nCoP coating is very prone to hydrogen embrittlement (due to presence of high temperatures and hydrogen within a barrel). Now in case of nCoP coating higher deposition efficiencies mean less development of hydrogen bubbles on the cathode in comparison with Cr(VI) deposition. Less generation of hydrogen lowers the chances of hydrogen uptake by the substrate which in turn lowers the chances of hydrogen embrittlement.

The literature survey done by us clearly indicated that nCoP is superior to Cr(VI) coating so it was decided by us to start our experimentation for the development of the system to deposit nCoP whose details are mentioned in the coming section.

Chapter 3: Experimental Methodology

3.1. Introduction

As discussed in chapter one, the motive of our project is to enhance the service life of hard coatings by modifying their morphology. Therefore the samples used were of two types, manganese steel and hexavalent chromium(Cr-VI) coated on manganese steel, as hexavalent chromium coating is already characterized as a hard coating because of its high hardness (750-950 HV). The chromium coated samples were prepared by electroplating Cr-VI on Mn steel substrate. The substrates were in the shape of coin with diameter 2" which were then cut in to smaller specimens first by using HSS blade hacksaw which was then replaced by slow speed diamond cutter because the cutting with hack saw affected the coating homogeneity on the cross section which in turn affected the quality of micrographs. Afterwards, the Cr-VI plated samples were gas nitrided by using nitrogen and ammonia as nitriding media. Nitrogen based nitriding was performed in a tube furnace at 1100^oC for two hours in two different configurations, with and without vacuum pump. Whereas the ammonia based nitriding was performed in a well type carbo-nitrding furnace at 550^oC for 12 hours. The uncoated Mn-Steel samples were used for electroplating of nano structured cobalt-phosphorus alloy coating at 60^oC for two hours. The samples before and after surface treatment were characterized on the basis of surface morphology and hardness. The hardness values were determined by micro-Vickers Hardness tester on hardness vicker scale, whereas the surface morphology and composition was determined using X-ray diffraction(XRD) and scanning electron microscopy(SEM) and energy dispersive scattering(EDS). The results obtained from XRD and SEM were then analysed by the help of X'Pert HighScore, Image J and Origin. The experimental procedures, methodologies and the equipment used have been discussed in detail for both nitriding and Co-P electroplating in the coming sections.

3.2. Processing history of received samples

As stated previously, two types of samples were used for our study, uncoated and Cr coated Mn-steel samples and both were obtained from Pakistan Ordinance Factories (POF). The billets of Mn-steel substrates are being manufactured Peoples Steel Mills (PSM), Karachi in traditional induction furnace, the billets are then processed in different manners by POF to form gun barrels of various pistols and guns for example ST9, G6, G3, Anti Air craft HMG, etc. The samples we used were processed by POF in order to match the specifications and conditions of the materials used in anti-aircraft heavy machine gun barrels.

The samples used for deposition of nCo-P coating were Mn-steel whereas the samples used for nitriding were Cr coated. The Cr coating thickness used in the barrel is up to 200µm but in order to broaden the scope of our study, three different set of samples were prepared by POF (depending upon coating thickness). The specifications of them were:

1) Average Cr coating thickness of 1.25µm
2) Average Cr coating thickness of 61 µm
3) A gun barrel with average coating thickness of 200µm

3.2.1. Electroplating

The process used for preparation of Cr coated sample was electroplating. Electroplating is basically a metal deposition process in which external current is used to extract metal ions from metal salt solution and deposit them on an electrode. [15] Word electrode was coined by Michael Farady and is derived from two Greek words *electron* meaning amber and *hodos* meaning a path, so electrode can be considered as a conductor which provides path for the flow of electrons. There are two types of electrodes in an electroplating cell i.e. an anode and a cathode. Loss of electrons occurs at anode whereas gain of electron occurs at cathode. Another component of electroplating cell is the electrolyte which can be understood as a solution of metal ions that are to be deposited on the cathode. The electroplating theory is based on [16] Faraday's Law of electrolysis i.e. mass of the material deposited is directly proportional to the amount of current applied through the electroplating cell. Mathematically it can be stated as:

$$\boxed{\text{Mass} = \frac{(\text{Current})*(\text{Time})*(\text{Atomic Mass})}{(\text{Faraday's Const.})*(\text{Ionic Charge})}}$$

3.2.1.1. Processing conditions

The electroplating cell being used by POF for chromium coating utilizes chromic acid as electrolyte, Mn-steel as cathode, lead as anode and DC power source. The cell is operated at 60^{o}C with current input of upto 80A/dm^3 which yields deposition rates of 0.6 microns per hour. The Mn-steel barrels (cathode) are dipped in the electrolyte such that the barrels are dipped in the electrolyte completely. The lead anode in the form of a wire is inserted in the barrel such that the optimum distance between the anode and the cathode is achieved because this distance affects the efficiency of electroplating. Now when DC current is passed through the system the Cr starts to deposit on the inner surface of the barrel.

The samples we used for nitriding were prepared in similar conditions in which the cathode was in the shape of Mn-steel coin of diameter 2" and the rest of the conditions were same. The maximum Cr coating thickness achieved on the coin shaped cathode were up to 50 microns and the reason mentioned by the POF officials was the increased distance between anode and the cathode as their system was designed for Cr coating on the inner side of barrels.

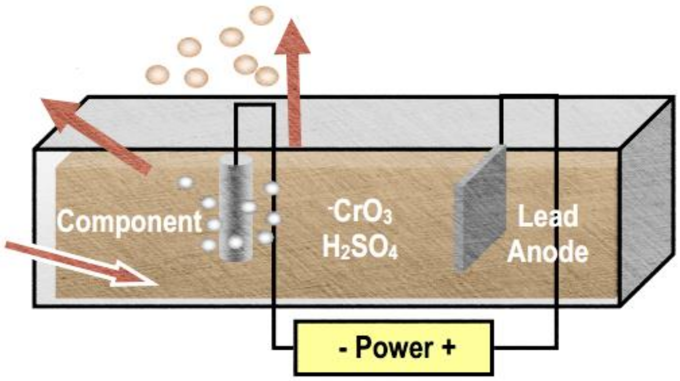


Figure 3.1 Schematic showing electroplating of Cr

3.3. Nitridation

In order to enhance the service life of hard coatings the treatment finalized by us was to synthesize functionally graded nitridation because such treatment imparts combination of high hardness and toughness to the surface. Specifically gas nitridation was shortlisted to achieve the target because of the following reasons:

1. The precursor gasses i.e. N_2 and NH_3 are easily available and are cheap.
2. Gas nitriding can easily be performed on inner surface of gun barrels.
3. Gas nitridation of Cr yields functionally graded coating with two different phases i.e. hard CrN layer on the surface and a subsurface tough layer of Cr_2N phase.

As mentioned previously, we did nitridation using two precursor gasses i.e. by nitrogen and ammonia. Both processes involved different process cycles and equipment which are discussed separately below.

3.3.1. Nitridation by Nitrogen

Nitridation by nitrogen was performed in a tube furnace in two configurations i.e. with and without vacuum pump. The reasons we selected tube furnace in order to nitride our samples were:

1. Temperatures up to 1400°C can be achieved because of the molybdenum carbide type of heating element as for nitridation by nitrogen temperature of 1100°C is required.
2. Inert atmosphere can easily be created without leakage.
3. Gas flow can easily be controlled.
4. Gas wastage is very low in case of tube furnace.
5. Tube furnace can easily be utilized to nitride the inner side of barrels.

Quartz tube of 0.75" diameter was used by us at 1100°C for two hours in order to nitride our sample. After setting up the apparatus it was purged with nitrogen for one hour so that atmospheric air was replaced with nitrogen. Once purging was complete, heating was started at the rate of 10°C/minute up to final temperature of 1100°C. Once final temperature was achieved the apparatus was held at that temperature for different time periods (maximum holding time for experiment was 2 hours). Complete heating cycle is shown in **figure 3.2.**

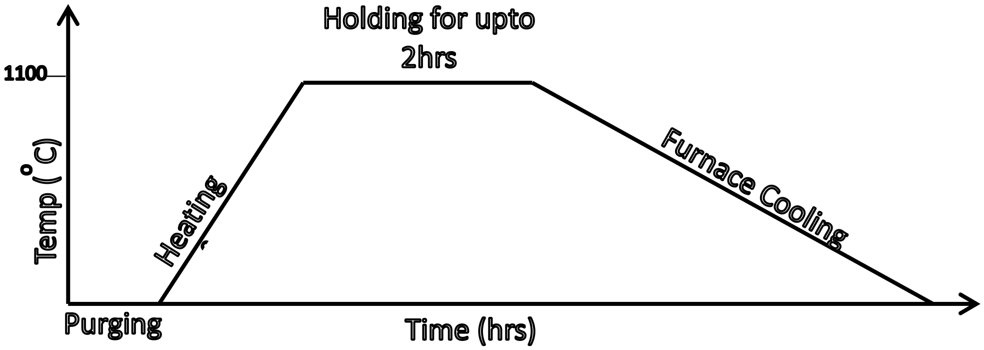


Figure 3.2 Nitridation heating cycle

Now in order to achieve the optimum conditions for nitriding in tube furnace series of experiments were performed which are discussed separately below. In first four experiments

3.3.1.1. First experiment

In first attempt the experimental conditions were same to as described below but the flow rate during the four stages of our experiment i.e. during purging, heating, holding and cooling was measured by the bubble method. As the pipeline outlet taking gas away from the tube was merged in a water container. Now when gas flows through the apparatus bubbles were generated in water and we estimated the gas flow in terms of bubbles per minute.

Purging was done for one hour and the holding time at 1100^{o}C was 2 hours. As a result of this experiment chromium oxide was formed instead of chromium nitride which is thoroughly discussed in chapter 4. The reason for this oxide formation was found out to be high osmotic vapour pressure due to usage of water at the pipeline outlet.

3.3.1.2. Second Experiment

In this experiment modifications were made in the experimental setup to control gas flow rate and high osmotic pressure on the pipeline outlet. Gas flow was controlled by introduction of gas flow meter at the point where gas enters our system and the osmotic pressure problem was removed by using oil at the pipeline outlet, as vapour pressure of oil at room temperature is lower as compared to vapour pressure of water at room temperature i.e. vapour pressure of oil is 0.01 [17] torr at 100^{o}C whereas the vapour pressure of water at room temperature is 31.8 torr.

Purging of gas was done for one hour, at 60sccm flowrate and rest of the parameters of the experiment were same to previous experiment. Now as a result of modifications in the apparatus, few peaks of chromium nitride were present along with major peaks of chromium oxide in the XRD pattern of the sample which is discussed in chapter 4.

3.3.1.3. Third Experiment

Results of second experiment indicated the presence of nitride phase in the system but the results were not significant to conceive the surface morphology of sample as the quantity of the nitride phase was small. Now in order to increase the quantity of nitride phase it was finalized that purging time had to be increased so that all of the oxygen is removed from the system. Removing oxygen from our system will diminish the chances of formation of chromium oxide.

Apart from purging time, rest of the experimental conditions was identical to the second experiment. The results of this experiment were identical to that of previous experiment as no significant change in amount of nitride phase was indicated by the XRD of the specimen.

3.3.1.4. Fourth Experiment

After discussion with the supervisor and the faculty members the reason for no significant increment in nitride quantity after experiment four was turned out to be the high partial pressure of nitrogen in the atmosphere as 79% of the atmosphere comprise of nitrogen so in order to remove oxygen from our experimental apparatus by flushing nitrogen will require excessive amount of nitrogen gas which is not economical. So it was finalized that we will use a vacuum pump to minimize oxide formation. The reason for not using vacuum pump in the first place was its unavailability in the department.

Now to achieve the desired goal a two staged rotary vane pump was introduced in the system. This time the system was first evacuated for 10-20 minutes, then purged with nitrogen at 60 sccm flowrate for one hour. Once the purging was complete the furnace was heated to 1100^{o}C at the rate of 10^{o}C per min and then temperature was holed at 1100^{o}C for two hours.

As a result of this experiment we were able to increase the quantity of chromium nitride as grey patches of nitride were present in significantly large amount as compared to green patches of chromium oxide on the sample (determined by the appearance of the chipped of coating as it was grey in color) but it was chipped off from the substrate. The reason for this chipping off was determined to be high holding time due to which all of the Cr coating was nitride and due to this reason it chipped off as Cr coating act as an intermediate layer between substrate and the nitrided surface which is necessary to absorb the stresses on the surface. The presence of the experiment was considered due to the leakages present in the system because of the minor leakages in the joints of the pipeline, flanges and the corks of the tube. Leakages were determined by the soap bubble test on all the joints as very small bubbles were formed on the joints during the gas flow.

3.3.1.5. Fifth Experiment

Now to run the final experiment all of the pipelines were replaced with 12mm high pressure polyurethane pipelines and all the joints were properly sealed with epoxy so that no oxygen gas remain in the system. After ensuring zero leakage of the system, it was evacuated two times for twenty minutes with a ten minute interval. After evacuation nitrogen gas was introduced in the apparatus whose flow rate was initially 60sccm but it decreased with time. This decrement of flow rate confirmed the zero leakage in our apparatus. The apparatus was then heated to 1100^{o}C at the rate of 10^{o}C/min but this time the holding time was set to be 30 minutes.

As a result of these final modifications the chipping off problem was catered but the complete of chromium oxide was not achieved. Reason for again formation of oxide after complete evacuation of our apparatus turned out to be impurity of the precursor gas as it was not 5N[1] pure nitrogen.

---

[1] 99.999995% pure nitrogen

Now the overall experimentation associated with nitridation by nitrogen are shown in **table 3.1.**

Table 3-1 Nitrogen nitridation experiments

Exp No.	**Evacuation time (minutes)**	**Purging time (minutes)**	**Heating rate (°C/min)**	**Flow rate (sccm)**	**Cooling rate**
1.	N/A	60 min	10 °C/min	-	Furnace cooled
2.	N/A	60 min	10 °C/min	60 sccm	Furnace cooled
3.	N/A	120 min	10 °C/min	60 sccm	Furnace cooled
4.	10 min	60 min	10 °C/min	60 sccm	Furnace cooled
5.	40 min	60 min	10 °C/min	60-0 sccm	Furnace cooled

Apart from experiments one and two all the experiments were performed on the 50-60micron thick chromium coating. The first two experiments were performed on the 1.26 micron thick coated sample.

3.3.2. Ammonia Nitridation

As discussed previously nitridation by nitrogen resulted in oxide formation so efforts were made to nitride the 50-60 micron chromium coated samples using ammonia gas. The reasons for using ammonia were:

1. It is easy to dissociate oxygen from tube by flushing ammonia through it.
2. Nitridation by ammonia occurs at relatively low temperatures i.e. around 600°C
3. Functionally graded coating can easily be achieved.

The process of ammonia nitridation has critical dis benefits also associated to it including:

1. The process is very slow i.e. it takes more than 24 hours to complete nitridation.
2. Gas consumption is quiet large.
3. Ammonia has health hazards associated to it.
4. Precursor gas is not readily available.

Due to the unavailability of ammonia cylinder in the department, the samples were given to Heavy Industries Taxila for ammonia nitridation. They used Italian made well type carbo-nitriding induction furnace to nitride our samples. The whole nitriding cycle took 24 hours to complete.

The first step of the process was to heat the furnace up to 150^{o}C and then purge the crucible with ammonia for 2 hours. The pressure of ammonia is maintained between 80-90mmHg during the whole cycle. As the second step furnace is heated to 400^{o}C and maintained at this temperature for 2 hours while the flushing of ammonia is occurring at constant pressure.

Once the two staged purging of the ammonia was complete, the furnace was heated to 510^{o}C and maintained at that temperature for 12 hours, this was the first stage of nitridation. After completing the first stage, the furnace is heated to 550^{o}C and then again this temperature was maintained for 12 hours this was the second stage of nitridation. The samples were then furnace cooled to room temperature after the completion of two staged nitridation. The whole nitridation process opted at HIT is shown in **figure 3.3.**

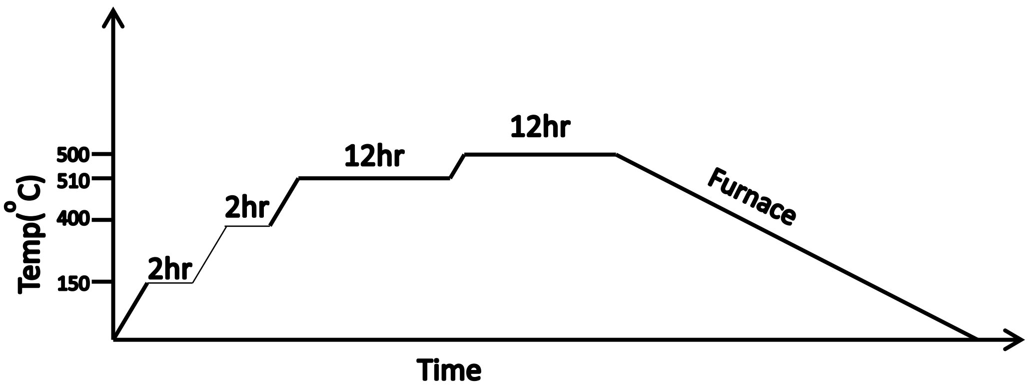


Figure 3.3 Ammonia experiment heating curve

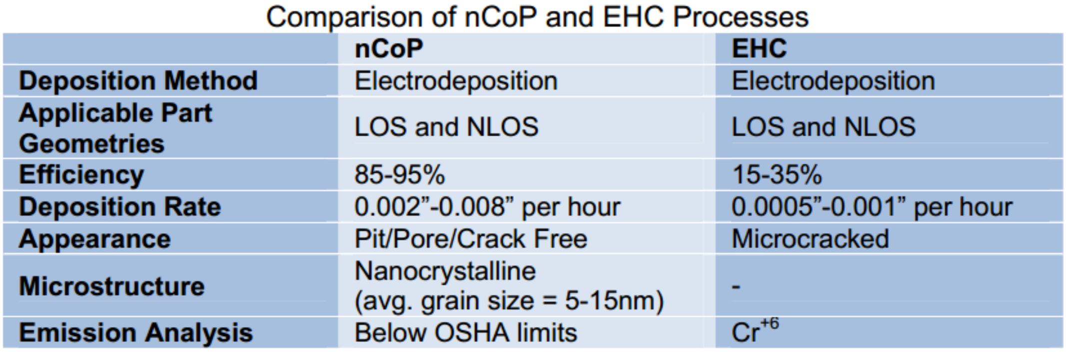
The results of ammonia nitridation are discussed thoroughly in the Results and Discussion chapter of the thesis.

3.4. Nano Structured Cobalt-Phosphorus alloy Coating

The second solution proposed to achieve our desired goal is the electrodeposition of nano structured cobalt-phosphorus alloy. This system was selected by us because of following benefits associated to it:

1. Improved wear resistance as compared to Cr.
2. Low co-efficient of friction.
3. High deposition efficiencies.
4. Low health hazards associated to it.
5. High repeatability of the process.

A brief comparison between chromium and nano structured Co-P alloy coating can be tabulated [18] as:



Comparison of nCoP and EHC Processes

	nCoP	EHC
Deposition Method	Electrodeposition	Electrodeposition
Applicable Part Geometries	LOS and NLOS	LOS and NLOS
Efficiency	85-95%	15-35%
Deposition Rate	0.002”-0.008” per hour	0.0005”-0.001” per hour
Appearance	Pit/Pore/Crack Free	Microcracked
Microstructure	Nanocrystalline (avg. grain size = 5-15nm)	-
Emission Analysis	Below OSHA limits	Cr^{+6}

3.4.1. Experimental Procedure

The experimental procedure of deposition of nCo-P alloy coating is similar to that of hard chromium deposition i.e. it is deposited by electroplating. However plating pre-treatment, electrolyte, electrodes and current densities were different as compared to electro hard chrome plating. These parameters are discussed briefly in the coming sections.

3.4.1.1. Electrolyte preparation

Electrolyte was prepared using combination of cobalt chloride, boric acid, phosphoric acid and sodium dodecyl sulfate. Each of the components plays an important role in deposition of cobalt on the substrate. For example, cobalt chloride is the source of cobalt ions and phosphoric acid was the source of phosphorus in the system. Whereas boric acid served as buffer to maintain the pH of the electrolyte and sodium dodecyl sulfate was added so that homogenous deposition is obtained because during deposition gas bubbles generate on the surface which hinder the homogeneity of deposited material. Sodium dodecyl sulfate prohibits the formation of gas bubbles on the surface of the substrate.

The composition of electrolyte mentioned in the literature was in grams per liter but for our experimentation we converted it to grams/500ml as we prepared 500 ml electrolyte. For phosphoric acid the quantity was mentioned in terms of g/l, we converted it to volume/volume by using the formula of density i.e.

Density = mass/volume

Volume = mass/density

The density of phosphoric acid is 1.88g/ml which was then used to convert mass/volume to volume/volume.

Table 3.2. shows both the compositions mentioned in literature and used by us.

Table 3-2 Composition of electrolyte

Sr. No	Component	Quantity mentioned in literature	Quantity Used
1	Cobalt Chloride	25g/l	12.5g/500ml
2	Boric Acid	35g/l	17.5g/500ml
3	Phosphoric acid	30g/l (15.9ml/l)	8ml/500ml
4	Sodium dodecyl sulfate	0.2g/l	0.1g/500ml

As a result of this composition pH of 2 was achieved, this was similar to that mentioned in the literature.

3.4.1.2. Plating pre-treatment

The pre-treatments mentioned in the literature comprised of degreasing and activation of the substrate followed by thorough washing of it with water at room temperature. We did pre-cleaning of the substrate by two methods:

1. Anodic degreasing in NaOH solution.
2. Grinding and polishing for activation of the surface and then

The pretreatments were done in order to activate the surface of the substrate so that a homogenous interface is maintained during the electrodeposition of cobalt ions.

3.2.1.1. Electroplating

After pre cleaning of the specimen it was then electroplated at 50°C. Functional generator was the source of pulsed DC current which was monitored using a cathode ray oscilloscope. Temperature of the system was monitored by a thermocouple and it was maintained by using a hot plate. The frequency of the current was set to 50 Hz and the applied voltage was 2 volts.

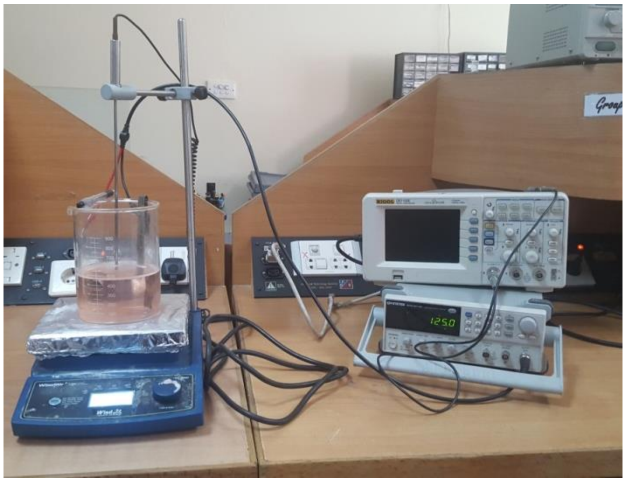


Figure 3.4 Apparatus for electroplating of nCoP

Total of 5 experiments were performed with identical current, voltage and temperature but the plating time was varied. The detail of all the experiments is mentioned in the table below:

Table 03-3 Experimental conditions for CoP

Serial No.	Time (mins)	Temperature (°C)	Voltage (V)
1.	30	50-60	2.5
2.	60	100	2.5
3.	60	50-60	2.5

4.	90	50-60	2.5
5.	120	50-60	2.5

The second experiment was replicated because the plating temperature reached 100^{o}C due to which the deposited coating was burnt as the electrolyte started boiling.

3.3. Characterization:

The characterization techniques used by us in order to analyze the treatments done on our samples were:

1. Optical Microscopy
2. Micro Vickers Hardness
3. X-Ray Diffraction (XRD)
4. Scanning Electron Microscopy (SEM)
5. Energy Dispersive Spectroscopy (EDS)

The working principle, procedure and need for each technique is discussed separately below:

3.3.1. Optical Microscopy

This technique is used to determine the surface morphology, phases present, percentage of phases, coating thickness etc. We used OM to determine surface morphology and coating thickness of our sample for which we used optical microscope. The basic principle of optical microscopy is that light is shined on the cross sectional surface and on the basis of interaction of light with the surface a magnified image of high resolution is obtained.

A light microscope consists of three major parts i.e. an eye piece, objective lens and a light source. Light source is basically the source of light that is shined on the substrate, objective lens makes a real image of the substrate surface whereas the purpose of eye piece is to form an enlarged and virtual image of the object utilizing the real image formed by the objective.

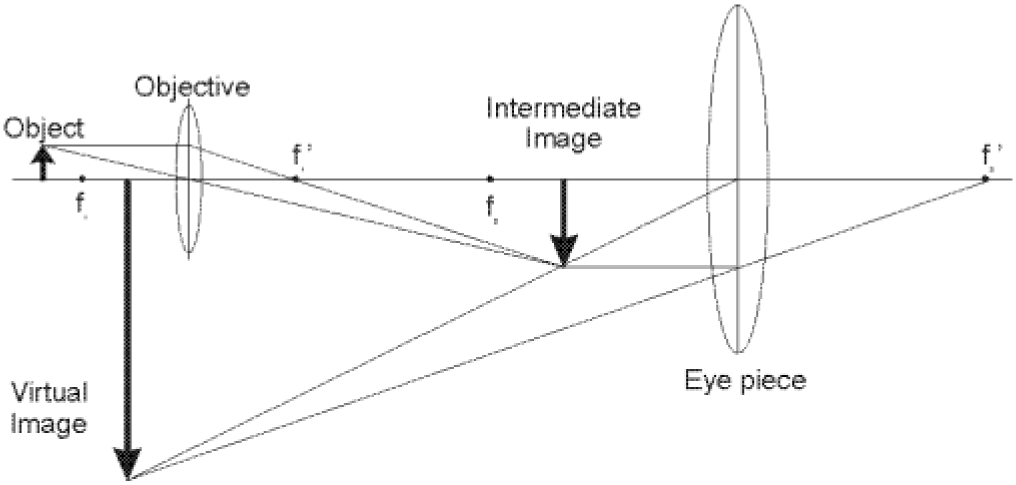


Figure 3.5 Schematic of basic light microscope

The samples we used for microscopy were cut from bulk material using high speed blade hack saw and slow speed diamond cutter. The cross-section was then carefully grinded and polished to even out the irregularities on the surface. The samples were grinded on emery papers of size 120, 240, 400, 800 and lastly 1200. Then the samples were polished using polishing fiber of 1 micron and 5 micron and polishing media used was 0.05 micron and 1 micron alumina powder respectively. After polishing, usually etching of the sample is done using an etchant but in our case no etching of surface was done because we were interested in observing coating thickness and surface morphology whereas etching is done in order to reveal the phases present in the substrate.

3.3.2. Micro-Vickers Hardness

Instead of using Rockwell, Brinnell, Vicker hardness tests, we performed micro-Vickers hardness on the treated and non-treated samples because this technique precisely determines the hardness of the coating whereas other techniques are used to determine the hardness of bulk materials because the working load is very high. The working principle of micro-Vickers technique is similar to that of Rockwell hardness testing i.e. an indent is made on the surface and then the dimensions of this indent are measured to determine the hardness of the surface. The indenter used in micro-Vickers is a diamond tip pyramidal indenter, which is used to make indents on the surface. Now harder the surface, smaller are the dimensions of indent and vice versa. The procedure used to measure hardness of the coating by us was:

a. Sample placement on micro-Vickers hardness tester
b. Setting of the apparatus to zero and image viewing through microscope
c. Application of load
d. Load removal and measurement of the dimensions of indent via optical microscope
e. Calculation of Vickers hardness number

Vickers hardness number is calculated on the basis of dimensions of the indent on the surface using following formula:

$$HV = \frac{2F\sin\frac{136^o}{2}}{d^2} \qquad HV = 1.854\,\frac{F}{d^2}$$

Where:

HV= Vickers Hardness

d= Arithmetic mean of the two diagonals

F= Load in kgf

The schematic of the indenter is shown below in which the depth of the indent is usually 1/7th of diagonal length.

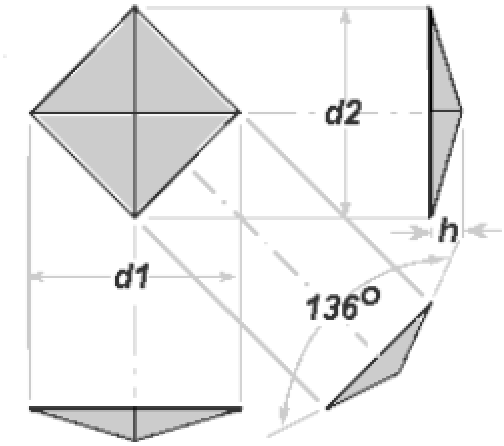


Figure 3.6 Schematic of Indenter

3.3.3. X-Ray Diffraction

XRD was used by us for quantitative analysis of the treated and non-treated samples. Compositional analysis of coating and nitridation was done by XRD because this method can be opted for any phase or a coating whose volume percent is greater than 3 vol%. The principle of XRD is based on the phenomenon of X-ray-matter interaction. When X-rays fall on a surface they interact with the atomic planes in such a way that the scattering of the incident x-rays cancel in some directions and reinforce in others. The scattering will be detectable only when the x-rays are diffracted by same family of planes. The whole process is based on Bragg's Law i.e.

$$n\lambda = 2dSin\Theta$$

Where

d= spacing between the planes

n= integer representing order of diffraction

θ= diffraction angle

λ= wavelength of X-rays

The results of XRD ware obtained in the form of intensity Vs 2□ pattern which was then analyzed Xpert Highscore. Each and every phase has its unique XRD pattern saved in the software, and it matches it with most identical pattern which is discussed in section 4 of this thesis.

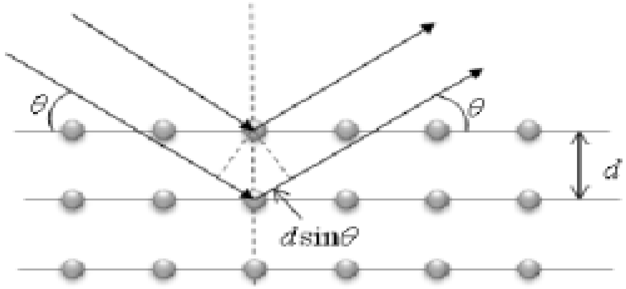


Figure 3.7 Diffraction from atomic planes

3.3.4. Scanning Electron Microscopy

SEM utilizes a beam of electrons in the range of 1eV to 1,000,000eV which is incident on the sample surface. This electron beam interacts in a variety of ways with the specimen surface which are:

1. Back Scattered Electrons
2. Secondary Electrons
3. Augers Electrons
4. Characteristic X-ray

These interactions depend directly on the penetration of the beam as depicted by the fig below:

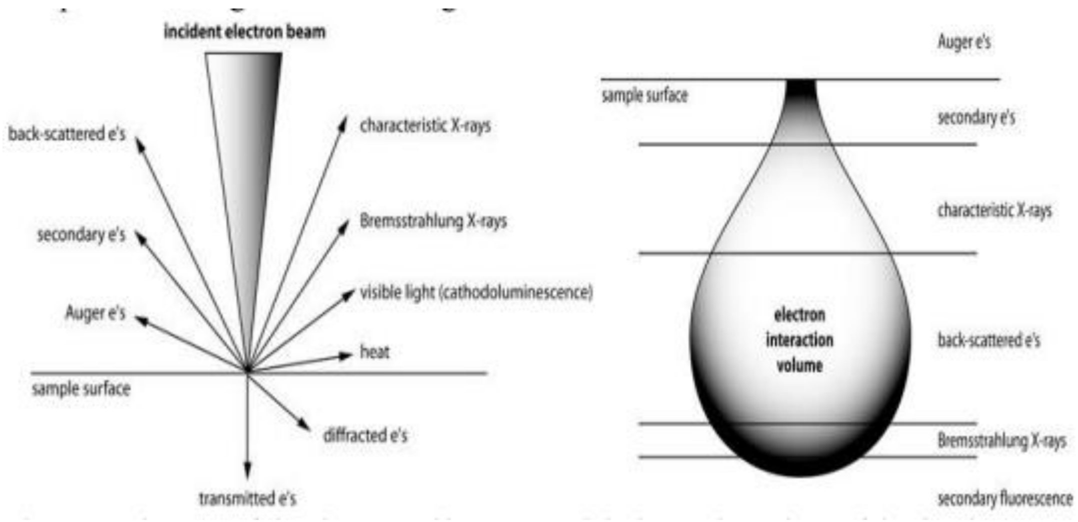


Figure 3.8 Electron Beam Interactions with Surface

For imaging secondary electrons are used in the process, these are generated due to the collision of incident electron beam with the outermost electrons of the surface atoms which are loosely bonded. The energy of secondary electrons depend directly on the energy of the incident beam and the depth range from which these electrons are emitted is between 2-50nm. These electrons are detected by the detector for imaging. The overall schematic of working mechanism of SEM is:

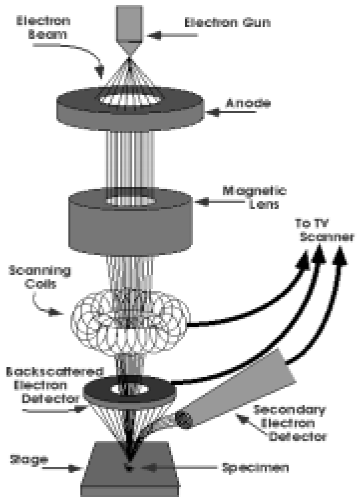


Figure 3.9 Working Mechanism of SEM

3.3.5. Energy Dispersive Scattering

This technique is based on the detection of characteristic X-rays that are generated due to interaction of electron beam with surface. These X-rays are signature of individual atoms which are used to determine the surface composition i.e. which atoms are present on the surface. This technique gives a qualitative analysis of a surface and cannot be used for atoms with valency less than 4 because for those atoms the energy of characteristic x-rays is so low that it cannot be detected by the detector.

Chapter 4: RESULTS AND DISCUSSION

The section discusses results of all the experiments conducted during the project. The discussions assisted in making different conclusion from our study on surface modification. Some on the characterization techniques which were used are tabulated in table. 4.1.

Table 4-1 Characterization techniques

Characterization Technique	Properties
X-Ray Diffraction, XRD	Phase identification
Scanning Electron Microscope, SEM	Coating Thickness
Optical Microscopy, OM	
Energy Dispersive Spectroscopy, EDS	Elemental analysis
Micro-Vickers Hardness Tester, MVHT	Hardness of Coating

4.1. Chromium Coating

Chromium Coatings with three varying thicknesses of 1.26 µm, 40-50µm and 500µm were used in the project. XRD, SEM/OM and MVHT were performed to confirm their presence and other properties. These results are being shown and discussed here:

4.1.1. XRD Results

The XRD patterns of 1.26 and 50 – 60 µm thick samples are shown in **Figure 4.1 (a)** and **(b)** respectively while XRD on 500 µm was not performed as the sample was curved. In both of these figures the major peak of Cr was appeared at 44.6^{o} and Fe peak with a very low intensity appeared at 65.3 ^{o} in **'a'** and not in **'b'**. As we know that the peaks in X-rays appeared when the incident rays interact with the atomic planes. So, as the thickness is increased, the interaction with the substrate (Iron) decreases which indicates the diminishing of substrate peak at 65.3 °.

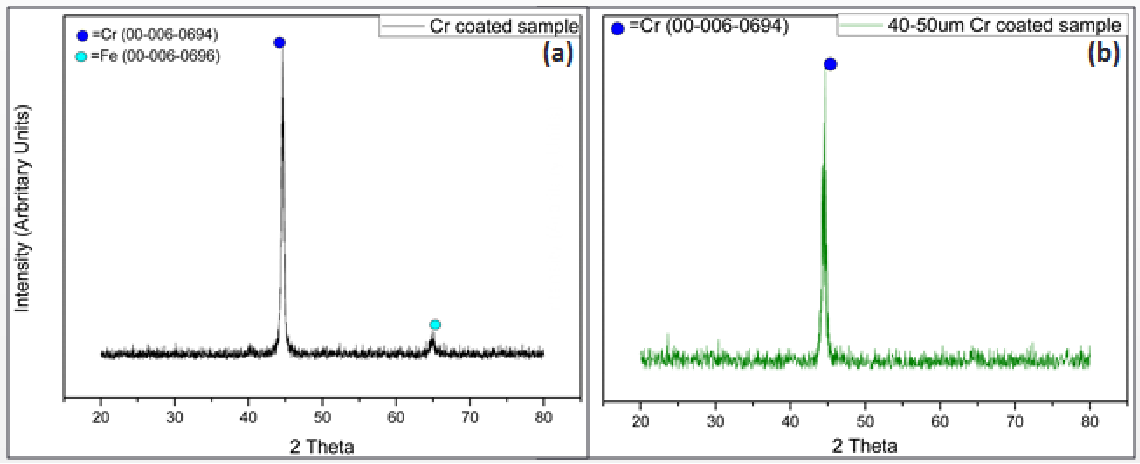


Figure 4.1 XRD patterns of (a) 1.26 and (b) 50 – 60 µm thick samples

4.1.2. SEM/OM Results

SEM and OM was performed on the cross-section of the samples to find out their coating thicknesses. As 1.26 µm was not detected by the OM so SEM was performed on the sample to identify its thickness. OM was used to take cross-sectional images of 40-50 µm samples. **Figure 4.2 (a)** and **(b)** shows the coating thicknesses of Cr 1.26 and 40-50 µm and their average coating thickness was measured to be 1.26 and 61 µm respectively. Furthermore, the thickness of 500 µm Cr coatings was not counter checked because of its curved cross-section.

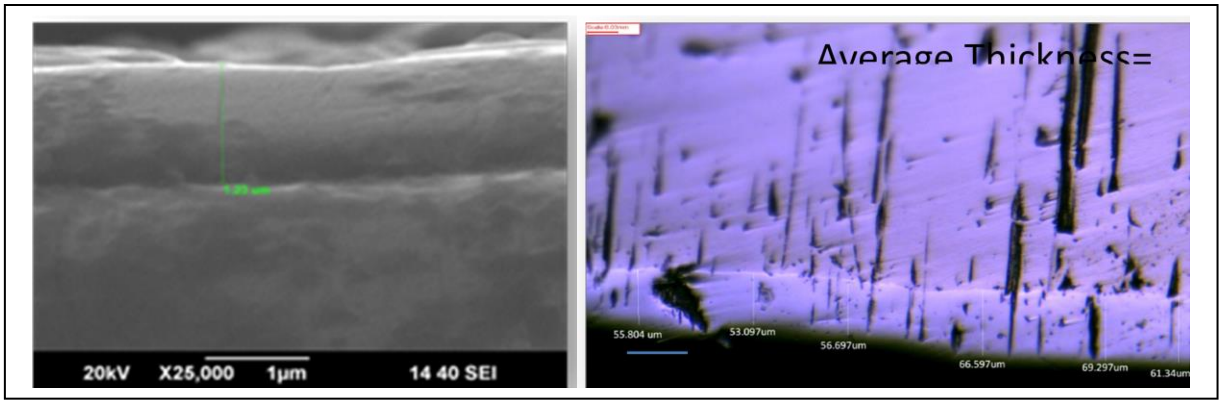


Figure 4.2 Coating thicknesses of (a) Cr 1.26 and (b) Cr 40-50 µm samples

4.1.3. Hardness Results

Hardness of non-coated Manganese steel and all the three Cr coated samples were measured. The trend of their hardness values are shown in **Figure 4.3.** where it is observed that with the increase in coating thickness on the sample, the hardness of Chromium coating decreases. The sample having a thickness of 200 µm had an average hardness of 312 Hv which is even less than the non-coated sample. As we have discussed in section 2 that the increasing plating time increases the coating thickness, but it also decreases the ion concentration in the electrolyte which will decrease the crystallinity of the coating and eventually the hardness decreases. [19]

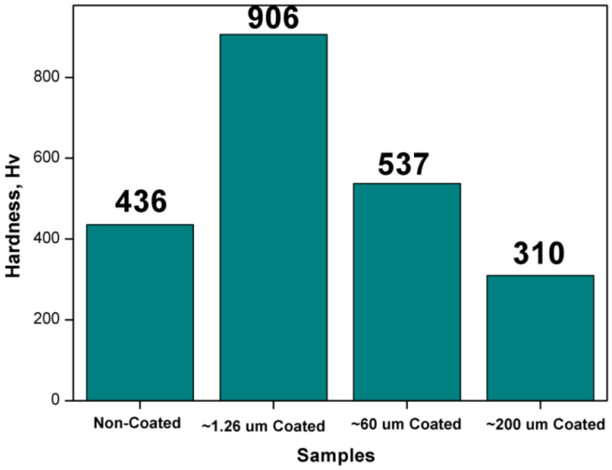


Figure 04.3 Hardness comparison of samples

4.2. Chromium Nitride Coating

4.2.1. XRD Results

This section separately discusses the XRD of different nitrided samples. The results of XRD shows the different phases present in the samples.

4.2.1.1. First Nitridation

The results of first nitridation are presented in **figure 4.4.** which contains the peaks of chromium oxide that were appeared at 25°, 34°, 36°, 55 ° and 65.5° and only one peak of Cr_2N was obtained at 68°. The reason behind the deposition of oxides instead of Cr_2N is that the water was placed at the outlet of nitrogen gas which causes the water to back flow due to high osmotic pressure [20] which acts as a source of oxygen. Moreover the nitrogen flow rate was 15 sccm which provides insufficient nitrogen to form CrN. As a result Cr_2N was formed instead of CrN. [11]

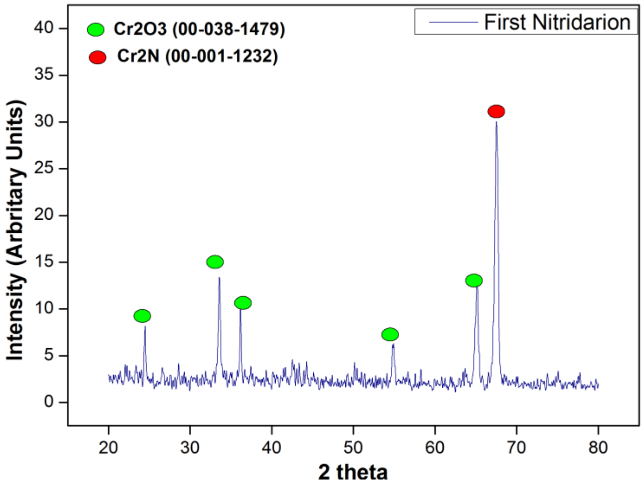


Figure 04.4 XRD result of first nitridation

4.2.1.2. Second Nitridation

The second nitridation was done by improving the system as discussed in section 3. The **figure 4.5.** shows the XRD pattern of this test results. As the flow rate was increased, the number of Cr_2N peaks increases which means that more Cr_2N planes were deposit. The same number of peaks of Chromium oxides can explain that the diffusion of oxygen in chromium is much easier than nitrogen. [12]

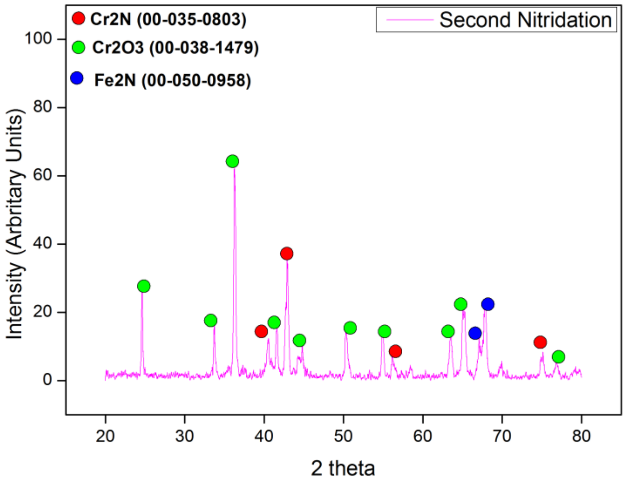


Figure 04.5 XRD result of second nitridation

4.2.1.3. Third Nitridation

The XRD pattern for third nitridation is shown in the **figure 4.6. (a)** and **(b)**. **(a)** shows the pattern of substrate which mainly contains Chromium Oxide peaks at multiple angles and some of the peaks from Cr_2N. **(b)** shows the pattern of that powder coating which was chipped off from this substrate. In this pattern along with some peaks of CrN, same oxide peaks were appeared on the substrate pattern. So this shows that we have deposit CrN but we have to avoid oxide formation and chipping off.

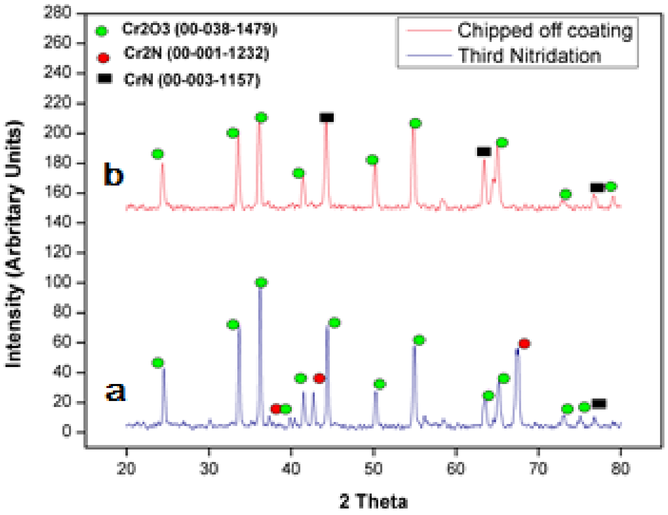


Figure 04.6 XRD result of third nitridation

4.2.1.4. Fourth Nitridation

Figure 4.7. shows the X-ray Diffraction pattern of fourth nitridation, which was performed through creating vacuum in the chamber. This pattern shows only one peak of Chromium Nitride while five other peaks of Chromium oxide. Even after creating vacuum, the formation of oxide was due to the impure supply if nitrogen gas.

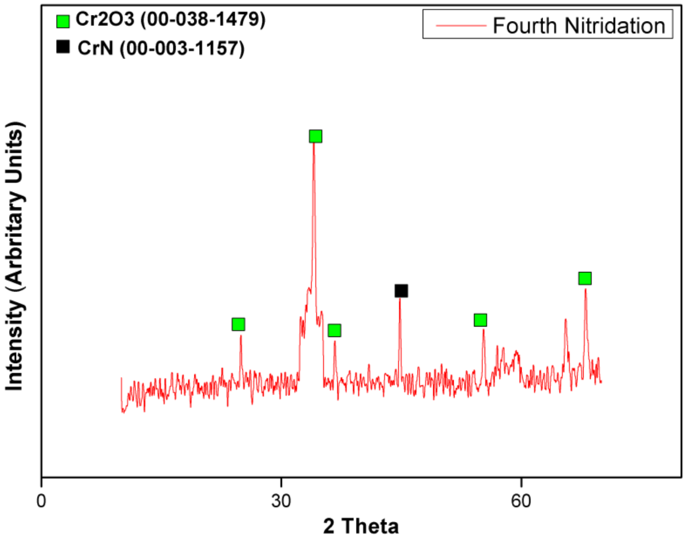


Figure 4.7 XRD result of fourth nitridation

4.2.1.5. Fifth Nitridation

Figure 4.8. shows the X-Ray Diffraction pattern of fifth nitridation, which was also performed by creating vacuum but with the different holding time. This pattern shows only the presence of Chromium oxide, and none of the peak matches nitrides. Even after creating vacuum the formation of oxide can only be explained by the impurity within nitrogen cylinder.

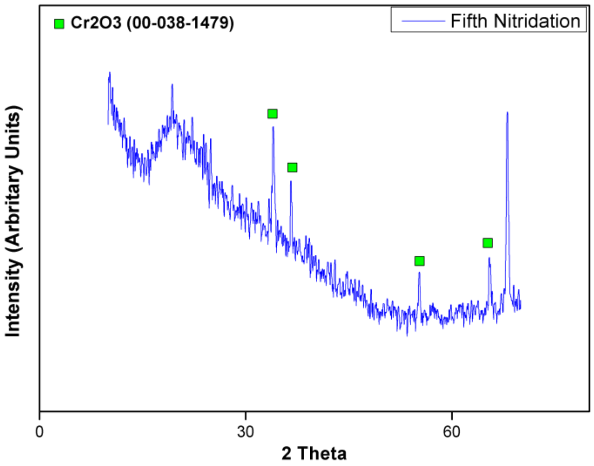


Figure 04.8 XRD result of fifth nitridation

4.2.1.6. Ammonia Nitridation

Figure 4.9. shows the XRD of ammonia nitridation. This pattern gives more intense peaks of Chromium Nitride along with oxygen peaks which have low intensity. Reason for less oxygen and high amount of nitrogen is because ammonia cracking occurs at much lower temperature. Hence, higher amount of atomic nitrogen will be present which will decrease the diffusion of oxygen.

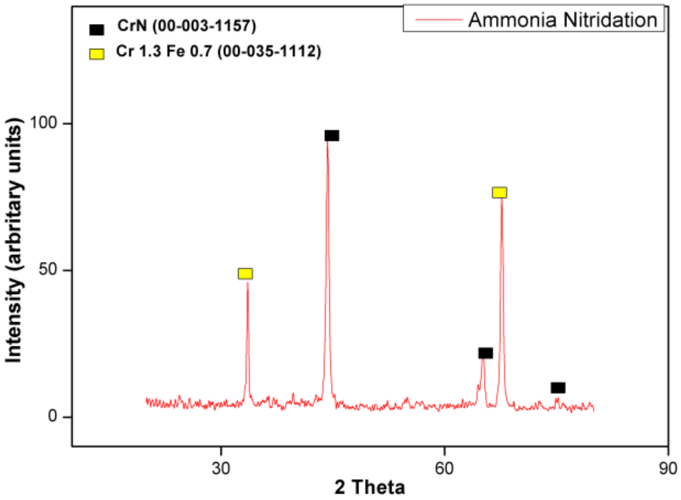


Figure 4.9 XRD result of ammonia nitridation

4.2.2. SEM Results

As all the coatings other than ammonia nitrided samples were either chipped off or only islands were formed, thatswhy the coating thicknesses of those samples were not determined. **Figure 4.10.** shows the cross-sectional image of ammonia nitrided sample. Functionally graded morphology was observed in this SEM image which means that the chromium forms a middle layer in between Chromium Nitride and substratE. Functionally graded CrN avoids the chipping of the coating layer because miss-match of thermal expansion coefficient of CrN and the substrate is eliminated. The thickness of this coating at different points varies drastically from nanometer to micron.

Figure 4.10 Functionally Graded CrN

4.2.3. EDS Results

Elemental analysis through Energy Dispersive Spectroscopy was done on ammonia nitrided sample in order to further confirm the presence of nitrogen which was mainly used to confirm Chromium Nitride, as no peak of other nitrides were present in the XRD pattern. Block EDS analysis was done at the corner of the cross-section of the sample in order to include the coating as well as substrate in the analysis. **Figure 4.11.** shows the cross-section image along with relative amount of elements present. It is cleared from the EDS image that the nitrogen is present in the coating.

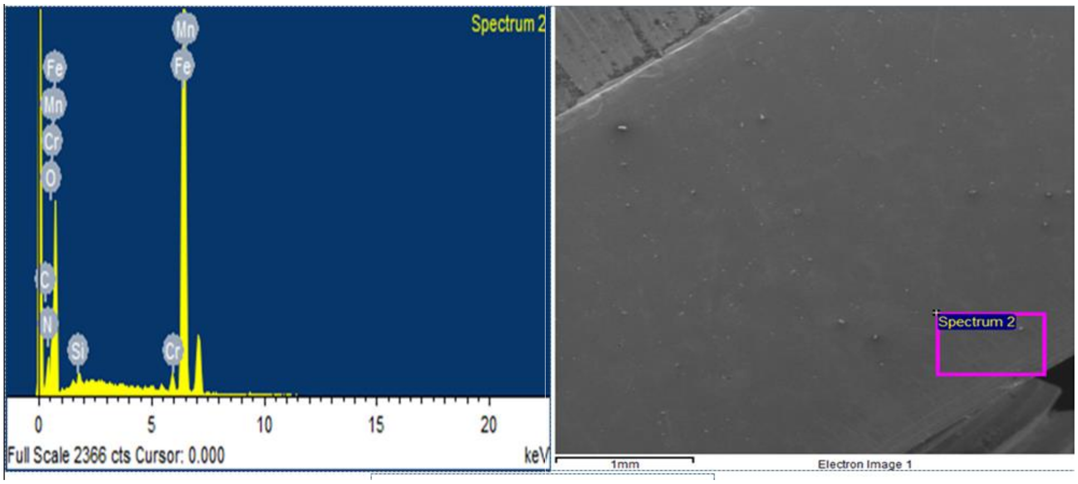


Figure 4.11 EDS result of CrN

4.2.4. Hardness Results

Ammonia nitridation was done on 50 – 60 µm Chromium coated sample so its hardness is compared with other samples having the same coating thickness. **Figure 4.12.** shows the comparison of hardness values of ammonia nitrided sample and Chromium Coated sample. The nitridation done on chromium coated sample resulted in the increase in hardness of about ~100 Hv. Hardness value of Chromium Nitride in literature is around 1500 Hv, while we observed a very low hardness value because of the less crystalline Chromium coating and inclusions present in it, as discussed earlier in 4.1.

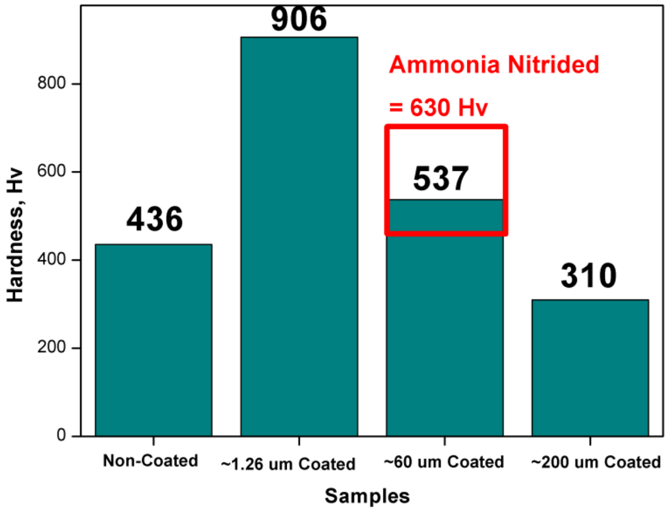


Figure 4.12 Hardness comparison of CrN with Cr

4.3. Nano Crystalline Cobalt Phosphorus Coatings

4.2.1. XRD Results

Figure. 4.13. shows the X-Ray Diffraction results of the Co-P experiments. A single high intense peak at 40^o was obtained from (111) plane. This shows that the nano crystalline Co-P was not deposited and the growth is directional. So, only one plane was deposited.

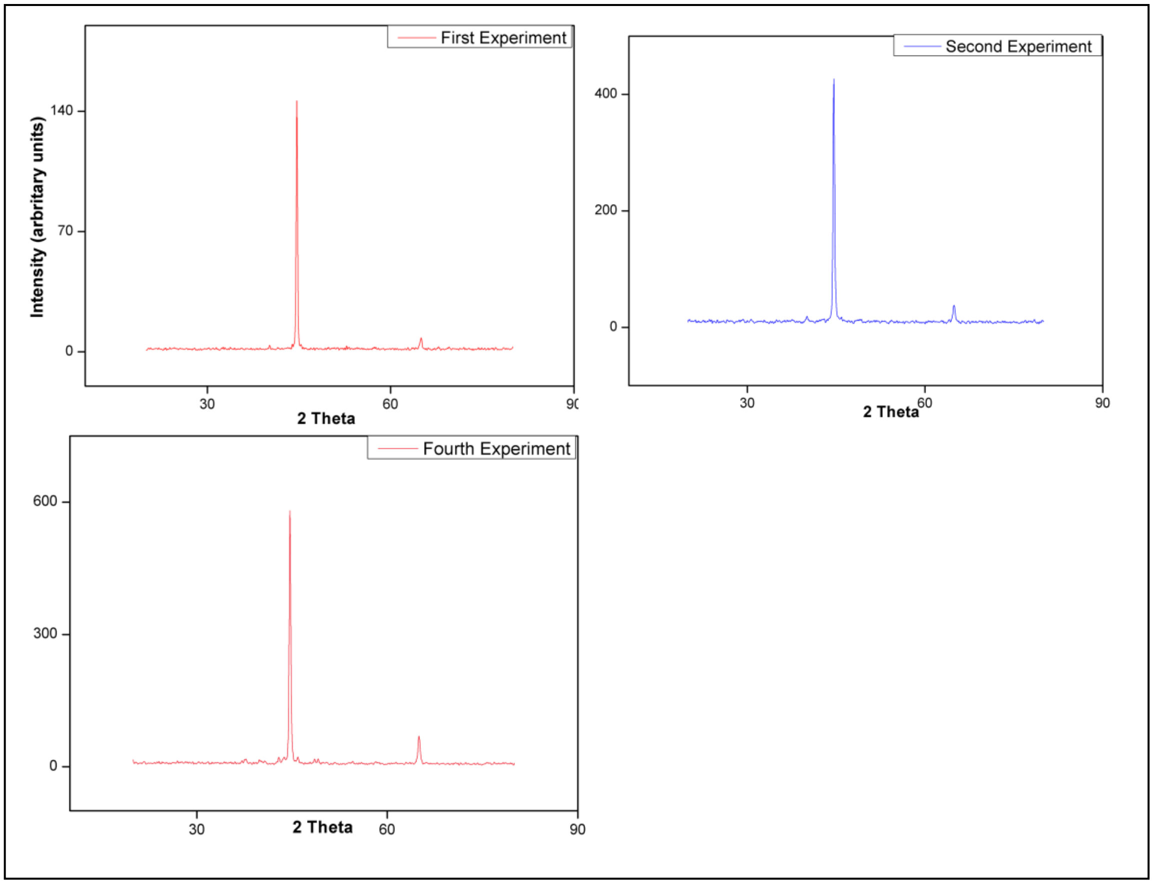


Figure 4.13 XRD results of Co-P

4.2.2. SEM Results

To further investigate Co-P coating, SEM images were used to calculate the coating thickness as shown in **Figure. 4.14**. The coating thicknesses obtained by 60 minutes and 120 minutes of plating time were measured to be 10.26 µm and 34.54 µm respectively. This proves that with the increase in plating time, the coating thickness also increases. [10]

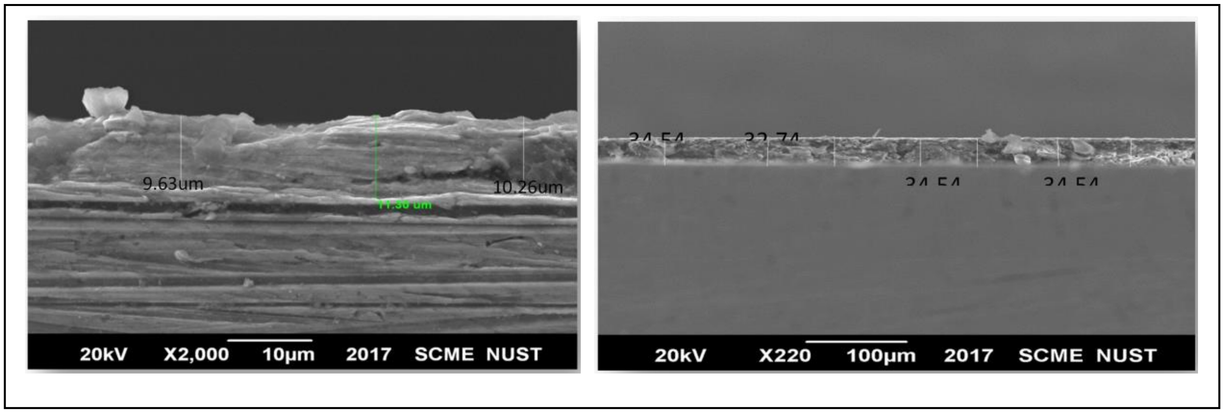


Figure 4.14 SEM results of Co-P

4.2.3. Hardness Results

Figure. 4.15. shows the hardness trend with plating time. As we observed in section 4.1 that with increase in plating time hardness value decreases, the same trend is observed here. [19] However, the hardness value of 30 minutes plating time was observed to be very low. This was due to the fact that the coating thickness was few microns so the hardness of the coating was not measureable instead the hardness of the substrate was being measured. Maximum hardness i.e. 680 Hv hardness is 140 Hv higher then ~60 µm Chromium coating, which means we have increased

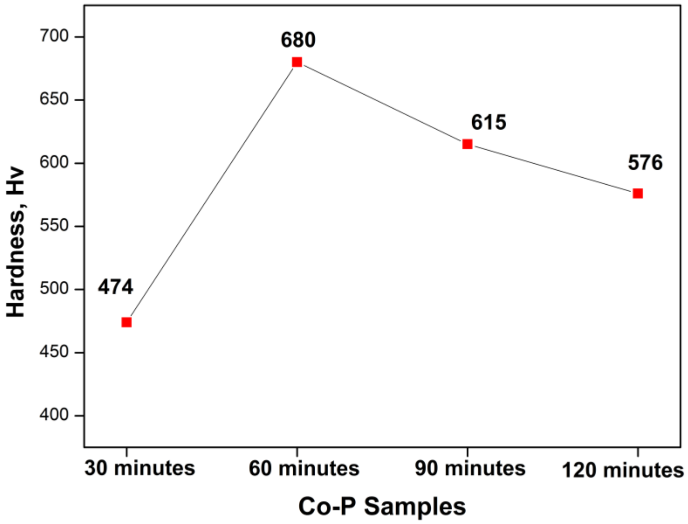


Figure 4.15 Hardness comparison of Co-P samples

Conclusion

Following are the conclusions drawn through this study:

- Increasing holding and plating time increases the thickness of CrN and Co-P coatings respectively.
- Increasing plating time decreases the hardness, so Chromium Coating thickness needs to be optimized for gun barrels
- Oxide is the major product being formed when nitridation is performed without vacuum and with impure cylinder.
- Functionally graded CrN needs to be synthesized to avoid chipping off the coating.

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