Synthesis and Characterization of Metallic Coating by Pulsed DC

A REPORT SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENT FOR THE DEGREE OF

BACHELOR OF TECHNOLOGY

IN

METALLURGICAL AND MATERIALS ENGINEERING

By

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CERTIFICATE

This is to certify that the thesis entitled, *"SYNTHESIS AND CHARACTERISATION OF METALLIC COATING BY PULSED DC"* submitted by *Miss. ANSHIKA SRIVASTAVA and Miss. PRIYA SINGH* in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by them, under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other Institute or University for any Degree or Diploma.

DATE: **PROF. A. BASU**

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ABSTRACT

Metallic coating is given to provide a layer of protection to metals or other types of materials that are subjected to various harsh operating conditions like high temperature, contact surfaces, corrosive media, high stress and other surface degrading conditions. These coatings help to enhance the reliability and performance of industrial. These coatings are used in industries such as aerospace, defense, military and automotive. Some of the most common metallic coatings that can be applied to substrate are Zn, Cu, Cd, Ni, Zn and Au. In this project Nickel coating was given to mild steel substrate as Nickel gives a anti corrosive coating to the steel surface and also enhances the hardness value of the surface. Nickel is now extensively used in industrial applications for Decorative as well as Engineering purposes because of its bright appearance and resistance to corrosion property. Nickel deposition was carried out using Watts Bath and deposition was carried out by electrodeposition method. Electrodeposition is the fastest and simplest method of providing coating to any substance. Deposit characteristic can be modified by changing various operating parameters like current density, temperature and pH of the solution. Use of pulse DC gives more control over the microstructure and morphology of deposit. Ten different samples were given coating, one used as reference sample was given coating in presence of DC and others using pulsed DC. In case of pulse DC three different parameters can be varied to give different features to deposit namely peak current, T_{ON} and $T_{OFF.}$ Finer grains can be obtained using pulse DC. After the deposition completed, the coating was characterizes by XRD, SEM and hardness measurement.

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CHAPTER 1

INTRODUCTION

From the moment any material is released from the point of production, it get subjected to some form of materials degradation although such degradation may not be instantaneously observed or measured. Materials degradation can be estimated in terms of loss of performance of an engineering system. The rapid rusting of freshly machined steel surfaces is one common example of immediate materials degradation. A simple definition of materials degradation is that it is the result of a wide range of physical processes; it is almost universal in occurrence and is a major engineering problem. Such kind of damage continues throughout the lifetime and materials degradation of any component becomes a limiting factor for the component. There are three main categories of materials degradation which are physical, chemical or biological in origin. Physical origin mostly refers to the effect of force, heat and radiation. Chemical origin refers to destructive reactions between the material and chemicals that contact it. Biological origin involves all interactions between life forms and engineering materials.

Materials degradation is an uncontrolled process without any restriction on interactions between seemingly unrelated events. Surface engineering is a comparatively recent term that refers to control of problems originating from the surface of engineering components. The objective of surface engineering is to ensure that performance of component remains far above the critical level for the entire service lifetime of a system. It is generally observed that the surface of a component is much more vulnerable to damage than the interior of the component and that

surface originated damage will eventually destroy the component. Most types of materials degradation such as, wear, corrosion and fracture are usually found at the surface of a component. As a result of this concentration of damage processes at the surface of a component, surface engineering is essential to control these damage processes. The range of techniques available to prevent materials degradation by shielding has expanded enormously in recent years. Shielding is usually achieved by coating the material with another substance or by generating a surface modified layer, which is more durable than the original material. Material coating can be provided by electrodepositing a metallic layer on the substrate. The metallic layer may enhance the property of the surfaces as corrosion resistance and hardness.

A definition of surface engineering is an informed selection of the appropriate coating or surface modification technology and its effective application to prevent or delay one or more forms of materials degradation thereby improving the performance of components and devices. The technique of coating is however widely used. There are various processes of synthesis of metallic coating viz. electroplating, spraying, hot dipping, chemical vapor deposition and ion vapor deposition. Among these electroplating is cheaper and faster process. Steels are the most versatile engineering materials and are most commonly used metals. Base metals, such as steels are often coated with more corrosion resistant metals such as Zn, Ni, Cd, Cu, Au, Ag, etc. but among the listed examples and others some are expensive while some are hazardous to the environment. Nickel is a metal that has good corrosion and abrasion resistant properties and provides a good appearance of the surface. It is widely used coating material. Steels are used with Ni as a coating. These find application in industries such as aerospace, defense, military and automotive. Mechanical and functional properties of such coatings depend highly on the chemistry and structure of the same. Depending on the texture developed the material properties

are highly anisotropic. The effect of coating conditions on the texture and other structural properties such as grain size of deposit which in turn affect the macroscopic properties of the specimen is a matter of consideration. Also the increased usage of pulse DC in compare to DC is increased now a day due to its inevitable advantages over DC. Pulse DC enables us to have more control over the morphology and microstructure of the coating. In this project, different parameters were varied to observe its effect on the grain size and texture property. Two parameters namely frequency and duty cycle were varied to study the effects. XRD, SEM and hardness measurements revealed some trends depending upon the deposition conditions.

KEYWORDS: Surface degradation, Metallic coating, Nickel coating, Electrodeposition, Pulse DC, Texture, Grain size, Hardness.

CHAPTER 2

LITERATURE SURVEY

2.1 Metallic Coating

A substrate is provided with coating for several purposes. The coating layer enhances surface properties and is helpful in various applications. Sometimes coatings help to prevent the changes that are incurred due to changing conditions. Surface coating is a very common technique in order to enhance the reliability and performance of industrial components. There are some components used in industry which are more prone to the surface degradation and sometimes fail to withstand the harsh operating conditions and is a concern in the industrial world. In many cases this surface degradation is basically dedicated to the factors like unfavorable hostile ambience and also the high relative motion between the contacting surfaces, corrosive media, temperature and stress applied.

When a protective coating is given to a material, it acts as a barrier between the surface and the environment that it is exposed to during the operation. The protective layer is preferred as it acts as the primary mechanism of defending the material from external contamination.[1] There are many properties that can be modified using a suitable coating on the material such as mechanical, thermal, electrical, magnetic as well as the appearance of the surface can be improved. This has lead the scope of surface modification by giving it a coating, not only it provides a better solution to some problems but also improves the quality and is a cost effective method. This is a cost effective approach against surface failure.[2]

Several coating methods are successfully applied in industry to protect carious machineries and equipment from surface damage as corrosion, oxidation and wear. Different coatings are provided depending on the required property from the material.

There can be different surface treatments as mentioned below:

1. Overlay Coating:

A material different from that of the bulk material is deposited on the substrate. The coating is different from the substrate and a clear boundary exists at substrate/coating interface.

2. Diffusion Coating:

There exists an interaction between the coating element the substrate chemically by diffusion. New elements get diffused at the surface of substrate generally when temperature is raised. This results in the change of composition and properties of outer layer as compared to that of the bulk.

3. Thermal or Mechanical surface modification:

In this method, the metallurgy of the surface of component is changed by the thermal or mechanical means, generally to increase hardness. The type of coating that has to be given depends on the application required. Some of the techniques involved are electroplating, vapor deposition, thermal spraying etc. The metal coated components finds application in automotive industry, aerospace industry, paper industry and iron & steel industry.

2.2 Surface Engineering

Surface Engineering is an activity that is intended to enhance the properties of the surfaces of components so that their functions and serviceability can be improved. This can also be defined

as the treatment given to the surface to perform functions that are different from the functions that are expected from the bulk of a material.

2.2.1. General requirements from the surface engineered components

General requirements from the surface engineered components are:

- Better corrosion resistance
- Better oxidation resistance
- Enhanced wear resistance
- Enhanced mechanical properties e.g. toughness
- Improved appearance
- Enhanced magnetic and electrical properties

The bulk of the material or substrate can not be totally independent of the surface treatment. Many surface treatment are not only limited to the immediate region of the surface but also it does affect the substrate. **Various surface engineering options include:**

- Change in the surface metallurgy
- Change in the surface chemistry
- Providing a surface layer or coating

To deal with the option of giving a surface coating to the substrate, we have various available methods of adding a surface layer or coating:

- Organic coating like paints and polymeric coating etc.
- Ceramic coating like glass lining and cement lining etc
- Slip or sinter ceramic coatings

- Hot dip galvanizing coating as zinc coating

- Electroless plating

- Mechanical plating

- Thermal spraying

- Chemical Vapor Deposition(CVD)

- Physical vapor Deposition(PVD)

The surface of a metallic material consists of a matrix of individual grains, which may vary in size and bond strength depending on the means by which the material was manufactured and also on the elements that were used to form those grains.

Surface of many components are selected on the basis of their texture and colour but for engineering application, demand is much more than this. Engineering components are required to perform certain functions completely and efficiently under various working conditions. A very good example of a component working in a harsh condition is a cutting tool used for machining application. This experiences high loads, high speeds, friction and high temperature due to friction, providing a surface coating may help in dealing with such circumstances. By improving the tool surface, not only the service life is improved but surface finish is also improved. Understanding the physical and chemical make up of the applied surface is very important.

2.2.2. Solid surfaces

A clean looking and polished surface need not to be a smooth surface microscopically. Depending upon the manufacturing processes used a zone of work hardened material will be at the base of these additional layers. Above this worked layer, there is an amorphous or microcrystalline structure, called the *Beilby* layer, which results from melting and surface flow during machining of a molecular layer. There is an oxide layer above the beilby layer due to the

presence of oxygen from the external environment. The outer region consists of adsorbed gases and water vapor.
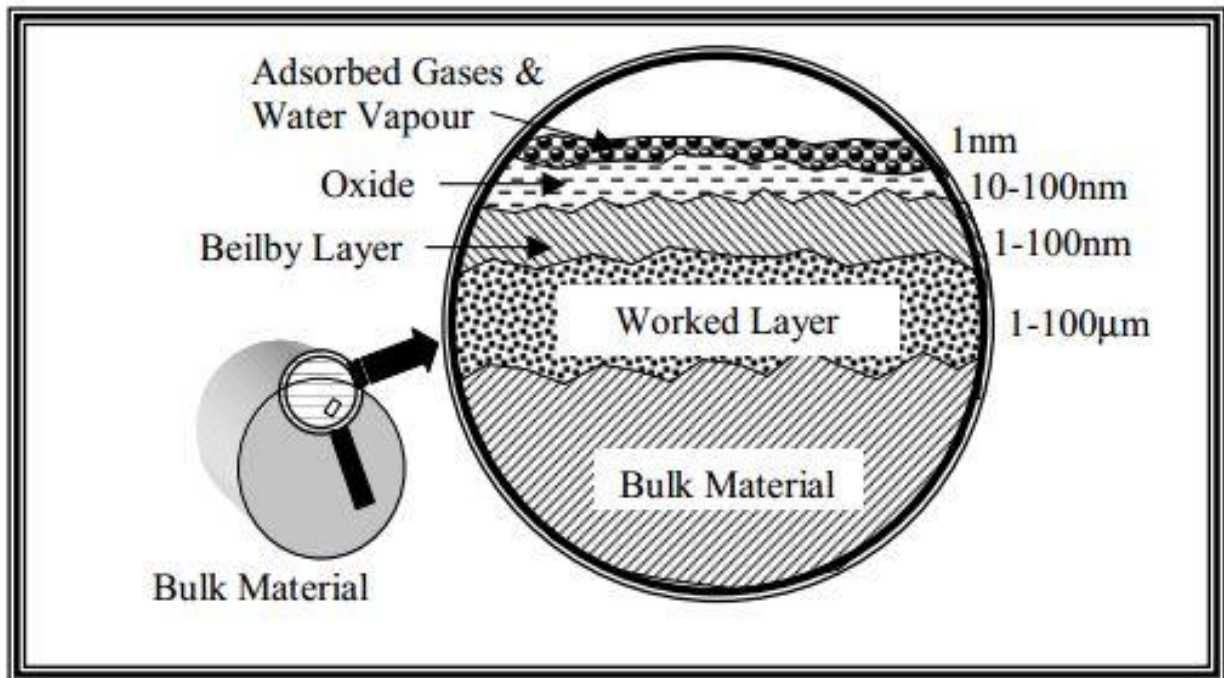
Fig 1. Schematic Diagram of a surface.

2.3 Deposition Techniques

The method by which a coating is provided on substrate. Deposition is a thickness relatively lower like within the range of a few tens of nanometers and some allow single layers of atoms to be deposited at once. This kind of deposition finds application in various fields as *optics (for reflective or anti reflective coating), electronics (insulators, semiconductors), packaging etc.*[3.4]

There are basically two broad categories in which deposition methods are divided:

1. Physical deposition

2. Chemical deposition

3. Other deposition methods

❖ Physical Deposition techniques:

This uses mechanical or thermo mechanical ways to give coating to solids. One of the day to day life examples is formation of frost. Generally physical deposition techniques require a low pressure vapor environment for functioning properly, hence these can be classified as *Physical vapor Deposition (PVD)*

PVD is a type of vacuum deposition method. Here deposition is done by vaporizing the desired coating material on the work piece surface. This involves processes such as evaporation and condensation, involving plasma bombardment at the surface to be coated.

The particles follow a straight path, deposition by physical means are generally directional.

Physical deposition methods include:

- *Evaporation Deposition*

In this method, the material that has to be deposited is heated to a high vapor pressure by resistive heating in a low vacuum.

- *Electron beam physical vapour deposition:*

In this method the material that has to be deposited is heated to a high vapor pressure by electron bombardment where high vacuum is maintained and this is transported by diffusion to be deposited by condensation on the work piece. Deposition rates for this type of deposition ranges from 1 to 10 nanometers.

- *Sputtering:*

Sputtering is also known as sputter deposition. Sputtering involves plasma (usually a noble gas, argon) bombarding the target to knock materials few atoms at a time. Target is generally kept at low temperature. It is not one of the evaporation processes which make this most flexible deposition technique.

- *Pulsed laser deposition:*

In pulsed laser deposition, pulses of focused laser are used to vaporize the surface of a target material and convert that to plasma, this plasma generally reverts to a gas before reaching to a substrate.

- *Cathodic arc deposition:*

In cathodic arc deposition the created electrical arc blasts ion from the cathode. Arc consists of high power density which results in a high level of ionization (30-100%).

❖ Chemical Deposition techniques

In this process, fluid precursor used undergoes a chemical change at the solid surface, forming a solid layer. A day to day life example of chemical deposition is the formation of soot on a cool object when that is placed inside a flame. Since the fluid surrounding the solid object, deposition happens on entire surface, with very little regard to direction; thin films from chemical deposition techniques is not directional in fact it is conformal. [6]

Chemical deposition can be further categorized on the basis of phase of the precursor:

Plating relies on liquid precursors, often a solution of water with a salt of the metal to be deposited. Some plating processes are driven entirely by reagents in the solution (usually for noble metals), but by far the most commercially important process is electroplating. It was not commonly used in semiconductor processing for many years, but has seen resurgence with more widespread use of Chemical-mechanical polishing techniques.

Chemical Solution Deposition (CSD) uses a liquid precursor, usually a solution of organ metallic powders dissolved in an organic solvent. This is a relatively inexpensive, simple thin film process that is able to produce stoichiometrically accurate crystalline phases.

Chemical vapor deposition (CVD) generally uses a gas-phase precursor, often a halide or hydride of the element to be deposited. In the case of MOCVD, an organometallic gas is used. Commercial techniques often use very low pressures of precursor gas.

Plasma enhanced CVD uses an ionized vapor, or plasma, as a precursor. Unlike the soot example above, commercial PECVD relies on electromagnetic means (electric current, microwave excitation), rather than a chemical reaction, to produce a plasma.

❖ Other deposition processes

Some methods fall outside these two categories, relying on a mixture of chemical and physical means:

Molecular beam epitaxy (MBE), slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compounds such as gallium arsenide are usually deposited by repeatedly applying a layer of one element (i.e., Ga), then a layer of the

other (i.e., As), so that the process is chemical, as well as physical. The beam of material can be generated by either physical means (that is, by a furnace) or by a chemical reaction (chemical beam epitaxy) [7].

Spin coating is a procedure used to apply uniform thin films to flat substrates. In short, an excess amount of a solution is placed on the substrate, which is then rotated at high speed in order to spread the fluid by centrifugal force. A machine used for spin coating is called a spin coater, or simply spinner. Rotation is continued while the fluid spins off the edges of the substrate, until the desired thickness of the film is achieved. The applied solvent is usually volatile, and simultaneously evaporates. So, the higher the angular speed of spinning, the thinner the film. The thickness of the film also depends on the concentration of the solution and the solvent. Spin coating is widely used in micro fabrication, where it can be used to create thin films with thicknesses below 10 nm. It is used intensively in photolithography, to deposit layers of photoresist about 1 micrometer thick. Photoresist is typically spun at 20 to 80 Hz for 30 to 60 seconds [8].

2.4 Nickel Plating

2.4.1 Introduction

Nickel plating is used extensively for decorative, engineering and electroforming purposes as the appearance and other properties of electrodeposited nickel can be varied over wide ranges by changing the composition and the operating conditions of the plating solution. Decorative applications contribute for about 80% of the nickel consumption in plating; 20% of consumption is for engineering and electroforming purposes. The annual worldwide consumption of nickel for electroplating purpose is approximately 180 million pounds which accounts for 11 to 12% of total nickel consumption.

2.4.2 Different types of Nickel plating

❖ **Decorative Plating**

Modern decorative nickel coating solutions contain organic additives which modify the electro crystallization process so that bright, highly-leveled nickel coatings can be deposited directly from the solution. Before the introduction of "organic" baths the decorative nickel coatings were produced by polishing nickel-plated parts mechanically, a practice which continued from 1870 to about 1945. Very thin layers of chromium were electrodeposited over polished nickel coatings for the first time in 1927 in order to prevent the tarnishing of nickel in outdoor atmospheres, and this practice continues with the "as-deposited" bright nickel coatings which is now available. An effort was made to develop improved decorative, electroplated nickel coatings began in the late 1940s and that led to the idea of development of multilayer nickel coatings (early 1950s) and micro discontinuous chromium coatings (mid- to late 1960s). Consequently obtained modern multilayer nickel coatings in combination with micro discontinuous chromium have tendency of protecting and enhancing the appearance of most metals and alloys, plastics and other materials for extended periods of time.

❖ **Engineering Plating.**

The engineering applications involving nickel plating include those where a fully bright appearance is not significant. Engineering nickel deposits are mostly sulfur-free and having matte appearance. These deposits are generally done to improve wear and corrosion resistance, to build up worn or undersized parts, to enhance magnetic properties, to make surfaces ready for enameling or for organic coating, to act as diffusion barriers in electronic applications and for various other purposes. Engineering applications exist in various industries like the chemical, nuclear and computer industries.

❖ **Electroforming.**

It is electrodeposition carried out for the manufacture of nickel products of different kinds, and it differs from electroplating in one major respect. In case of electroplating, the coating is metallurgically bonded to the substrate and becomes an integral part of the surface. On the other hand, In electroforming, nickel is deposited onto a mandrel or mold nonadherently so that the nickel layer can be separated from the mandrel when it is taken out from the plating solution. Electroforming finds applications which include the fabrication of molds and dies, mesh, and many other products that are indispensable to operations as in textile, aerospace, communication, automotive and photocopying industries.

2.4.3 Basic Process Considerations

Before we describe decorative, engineering, and electroforming plating processes, some basic facts are reviewed that helps in enabling control the nickel plating process, prediction of the amount of nickel deposited, and estimating nickel coating thickness.

❖ **The Basic Process.**

Nickel plating is similar to other electroplating processes in which soluble metal anodes is employed. It requires the flow of direct current between two electrodes which are immersed in a conductive and aqueous solution of nickel salts. As the current flows it causes anode to dissolve and cathode to become covered with nickel. The nickel in solution exists as divalent positively charged ions (Ni^{++}). As current flows Ni^{++} react with two electrons ($2e^{-}$) and is converted to metallic (Ni^{0}) at the cathode surface. The reverse of this occurs at the anode, where Ni^{0} is dissolved in order to form divalent Ni^{++} which then enters the solution. The nickel ions that are discharged at cathode are replenished by those that are formed at the anode.

❖ **Hydrogen Evolution and Cathode Efficiency.**

The discharge of nickel ions is not the only reaction that can take place at the cathode; infact a small percentage of the current is also consumed in the discharge of hydrogen ions from water. This results in the reduction of the cathode efficiency for nickel deposition i.e. 100% to 92 to 97%, which depends on the nature of the electrolyte. The hydrogen atoms that are discharged form bubbles of hydrogen gas at the surface of cathode.

❖ **Anode Efficiency.**

Under normal operating conditions the efficiency of dissolution at the anode is 100% and as such no hydroxyl ions are discharged from the water. If the pH of the solution happens to be very high, however, hydroxyl ions may be discharged in preference to the dissolution of nickel, and oxygen will be evolved. In such conditions, the nickel anode becomes passive and ceases to dissolve nickel.

❖ **Nickel Ion and pH Changes.**

Under normal conditions, concentration of nickel ion and the pH value of the solution will slowly increase as plating proceeds. The rate of increase in concentration of nickel ion depends on the difference between efficiencies of anode and cathode. As cathode efficiencies may vary from 92 to 97%, whereas anode efficiency always remains 100%, the rate of increase in nickel ion concentration depends on the type of the plating solution used and not on the type of soluble nickel anode material.

2.4.4 The Watts Solution and Deposit Properties
The nickel plating solution described by Watts in 1916 proved to be a major milestone in the development of nickel plating technology. This solution eventually replaced all other solution

that people were using till that time. It remains the basis for most decorative nickel plating processes, and it is also used for engineering applications and for electroforming. Watts's solution is operated at elevated temperatures and is capable of being used with high current densities.

The constituents of the Watts bath have several functions:

❖ **Nickel sulfate** is found in commercially pure forms. This is relatively inexpensive than other salts of nickel and acts as the major source of the nickel ions in solution. Generally a high nickel sulfate concentration is used in case of high current density requirement.

❖ ·**Nickel chloride** serves basically to improve anode corrosion, but it also helps in increasing conductivity and uniformity of coating thickness. Excessive presence of chloride in the solution increases the corrosivity of the solution as well as the internal stress of the deposits. (Internal stress refers to forces created within the deposit as a consequence of the electrocrystallization process and/or the simultaneous deposition of impurities such as hydrogen, sulfur, and other elements. Internal stress can be either tensile [contractile] or compressive [expansive] and it may cause plating problems if excessively high.)

❖ **Boric acid** is used in nickel plating solutions for buffering purposes; concentration of Boric acid may affect the appearance of the deposits. The deposit may become frosty in high current density areas at 30 g/ of boric acid, and then as the concentration of boric acid approaches 15 to 23 g/L, the deposit obtained may be burnt and cracked. No such effect on appearance is observed at high boric acid concentrations up to saturation (45 g/L).

❖ **Wetting agents or surfactants** formulated specially for nickel plating solutions are almost always added n order to control pitting. Its function is to lower the surface tension of the plating solution so that air and hydrogen bubbles do not cling to the parts being plated. [9]

2.5 Electrodeposition

2.5.1 Introduction

Electrochemical deposition of metals and alloys involves the reduction of metal ions from aqueous, organic, and fused-salt electrolytes. In this book we treat deposition from aqueous solutions only. The reduction of metal ions Mz^+ in aqueous solution is represented by

$$\mathbf{Mz^+ + e^- = M^0} \qquad (1.1)$$
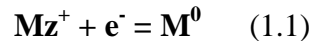
This can be accomplished by means of two different processes:

(1) **an electrodeposition**

Process in which z electrons (e) are provided by an external power supply, and

(2) **an electroless (autocatalytic) deposition** process in which a reducing agent in the solution is the electron source (no external power supply is involved). These two processes, electrodeposition and electroless deposition, constitute the electrochemical deposition.[10]

Electrodeposition is also known as electroplating which is a short form of "electrolytic deposition".

2.5.2 Brief Mechanism

In case of Nickel deposition using Watts's solution electrolytic solution contains positively charged Ni^{++} and anions from the components of the Watts solution. When electric current is passed through the solution, cations Ni^{++} migrate towards cathode where they get discharged and deposit as metallic nickel.

$$\mathbf{Ni^{++} + 2e^- = Ni^0 \ (metal)}$$
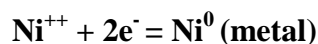
Nickel from anode dissolves into solution for the maintenance of electrical neutrality,

$$Ni = Ni^{++} + 2e^-$$

The overall process is referred to as *Electrolysis.* If in spite of the Nickel anode some noble metal anode is used the overall reaction at the anode is the oxidation of water.

$$2H_2O = 4H^+ + O_2 + 4e^-$$

Practically electrodeposition processes occur in a complicated way. With the application of potential, ions rearrange near the surface of electrode which results in the formation of an electrical double layer known as *Helmholtz double layer*, followed by the formation of another layer known as diffusion layer. These two layers collectively together is known as *Gouy-Chapman layer.*[11]

The process occurs as follows:

❖ *Migration*

The hydrated metal ions from the solution moves towards the cathode under the influence of applied current by the process of diffusion and convection.

❖ *Electron transfer*

As the hydrated metal ions enter the diffused double layer near the cathode surface, water molecules of the hydrated ion get aligned. Then the metal ions enter the Helmholtz double layer where it gets stripped of its hydrated envelope.

❖ Thus obtained dehydrated ion is neutralized now and gets adsorbed at the surface of cathode.

❖ The atoms then start migrating over the surface of the substrate until they find an active site for adsorption. After getting adsorbed at the active site they form a strong chemical bond with the surface. Kinks or steps if present on the surface act ad the active site for adsorption of atoms.

Thickness of the coating is decided by the time duration for which process was carried out. Typically, layer thickness ranges from 1 to 30 micrometer. Electro deposition of single elements as well as codeposition of two or more elements is possible such as Cu-Zn alloy or Au-Sn alloys.
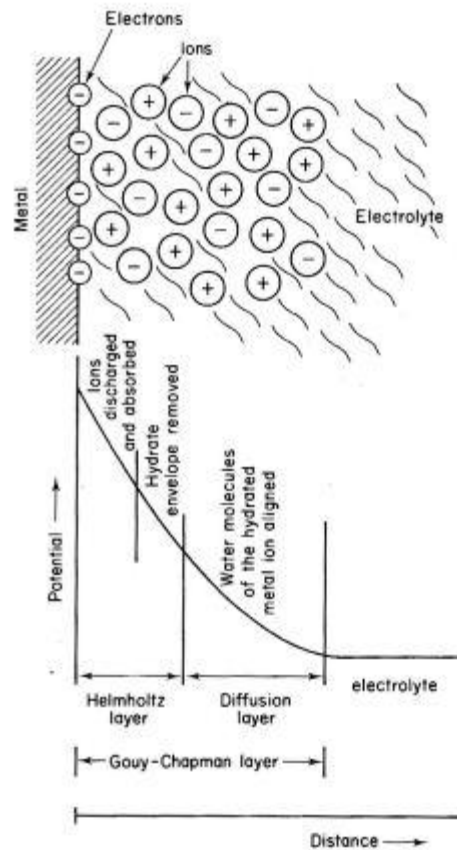

Fig 2. Electrical Double layer [12]

2.5.3 Factors influencing electrodeposition

Factors that affect the electrodeposition process can be summed up; these affect the morphology

and composition of the process. Factors are: [13,14,15,16,17,18]

- ❖ Density of current

- ❖ Nature of ions in the solution: anion and cation

- ❖ Temperature and Bath composition

- ❖ Concentration of ions in solution

- ❖ Power supply current waveform

- ❖ Presence of impurities

- ❖ Chemical and physical nature of the substrate surface

2.5.4 Advantages of electrodeposition

Advantages of electrodeposition over other processes are:

- ❖ Specifity and selectivity of the process is high.

- ❖ Electrodeposition process has Low detection limit and high sensitivity

- ❖ Electrodeposition process is a simple process involving

- ❖ High speed and enhanced accuracy.

- ❖ Cost effective process.

- ❖ Electrodeposition process has ability to produce fully dense nanostructure free of porosity

- ❖ It has capability of being single step process

2.5.5 Applications of electrodeposition

Electrodeposition is used in many industrial based applications. These applications can be

categorized in basically four groups:

- ❖ **Decoration** A more expensive metal can be coated onto a base metal in order to improve the appearance of a base metal. This can be used for jewelry, furniture fittings etc.

- ❖ **Protection** The coating is given to a base material in order to prevent the base material from corrosion, oxidation or wear. Corrosion resistance coating includes chromium coating, cadmium coating and zinc coating.

- ❖ **Electroforming** This is used in manufacturing of moulds, dies, screens and record stampers.

- ❖ **Enhancement** Coatings with improved electrical and thermal conductivity, reflectivity and solderability etc.

2.6 Pulsed DC

In pulse electrodeposition current or potential is varied swiftly between two different values. This gives a series of pulses which have same amplitude, duration and polarity separated by zero current. Pulses consist of an ON time (T_{ON}) and OFF time (T_{OFF}).During ON time current and/potential is applied and during OFF time current supply is cut off. In case of DC plating current is constant and the movement of metal ions depends on their diffusion coefficient. Whereas in the case of PC/PRC modulated current waveforms are used which helps in enabling to control the composition of deposited film and thickness of the film by varying the pulse amplitude and width. Pulse DC favor the initiation of grain nuclei and hence increase the number of grains per unit area that result in finer grained deposit with better properties than DC plated coatings. Under the pulsed deposition condition the Nernst diffusion layer gets splitted into two individual diffusion layers. Because of this thin Nernst diffusion layer high current density can be applied with pulse DC. This enhances nucleation rate and hence finer depositions can be obtained.
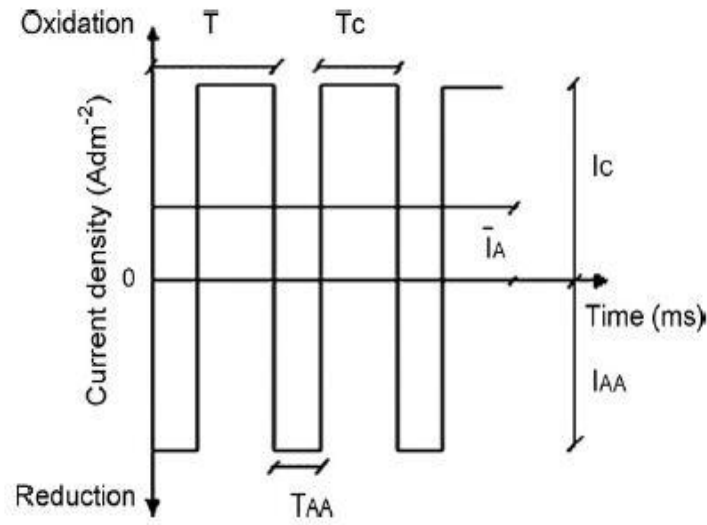
Fig 3. A typical pulse reverse waveform [19]

2.6.1Types of pulse waveforms

Waveforms can be divided into two groups *1) unipolar*-pulses don't have polarity and all the pulses are in one direction. *2) bipolar*- both cathodic and anodic pulses are mixed in bipolar pulses. There can be three major waveforms in pulse deposition:

- ❖ **Rectangular pulses**
- ❖ **Periodic Reverse pulses**
- ❖ **Symmetric Sinusoidal pulses**

Rectangular pulse deposition contains pulses of rectangular shapes of current and potential which are separated by zero current or potential.

Periodic reverse deposition The applied current or potential is swifted periodically from cathodic and anodic polarization.

Superimposed sinusoidal deposition The waveform is the sum of direct cathodic current (dc) and sinusoidal alternating wave current. Waveform may consist of both cathodic and anodic portion if dc offset is less than the amplitude of the sine wave.
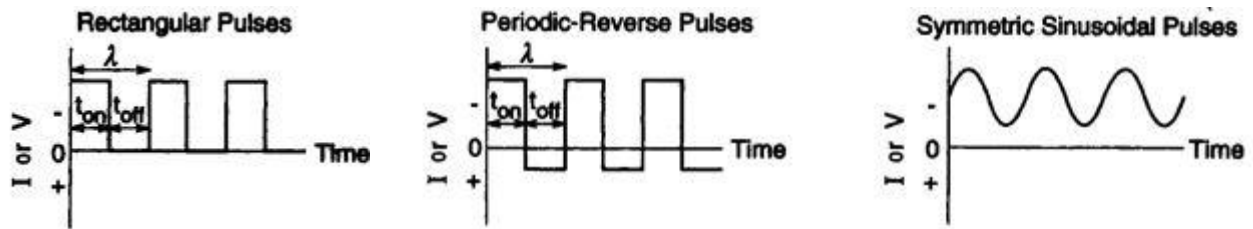

Fig 4. Major pulse waveforms for deposition

2.6.2 Advantages of pulse DC over DC

❖ In electroplating, as the process continues a negative diffusion layer is formed around the cathode. When we use DC, this layer grows to definite thickness and obstructs the motion of ions from reaching the part. While with the pulse DC, during T_{OFF} when current/potential is switched off, this layer gets discharged to some extent. Hence in PED this thin layer provides easier passage to the ions through the layer onto the part.

❖ In DC, high current density regions get more depleted of the ions than low current density regions as in DC ions move to the cathode from higher concentration region which results in depletion of ions. In PED, during T_{OFF} ions migrate towards the depleted region of current density. During the T_{ON} more uniform distribution of ions is present for deposition. [20]

2.6.3 Pulse and pulse reverse current parameter

In conventional DC there is only one parameter that can be varied and that is *current density (I)*

but in the case of PED three different independent variables can be varied viz.

1) ON time i.e. T_{ON}

2) OFF time i.e. T_{OFF}

3) Peak current density(I_P)

In PED, duty cycle (γ) corresponds to the percentage of total time of a cycle and is given by

$$\gamma = T_{ON} / (T_{ON} + T_{OFF})$$

Also, $$\gamma = f * T_{ON}$$

Where f (frequency) is reciprocal of cycle time (T), can be given as

$$f = 1/ (T_{ON} + T_{OFF}) = 1/T$$

In general pulse deposition involves Duty cycle of 5% or more and T_{ON} from μs to ms.

PC will deposit metal at the same rate as DC provided with the fact that the average pulse current

density equals the latter. The average current density (IA), in pulse plating is defined as

$$I_A = \text{peak current } (I_P) * \text{duty cycle } (\gamma)$$

2.6.4 Advantages of pulse deposition technique

❖ PED significantly raises the limiting current density (I_L) by replenishing metal ions in the

   diffusion layer during $T_{OFF.}$

❖ In PED, by modification of pulse parameters, deposits with desired composition, structure, porosity and hydrogen content can be obtained.

❖ Pulse plating enables the reduction of the additive requirement by 50–60%.

❖ Pulse DC eliminates thickness build up at high current density areas during current reversal and improves step coverage without pores reaching down to the substrate.

❖ In PED, homogeneity in deposition is increased due to high throwing power even at complex shaped parts.

❖ In PED layer density increases and elimination of pores occur.

❖ Resulting layer properties are improved example hardness.

❖ In enhances the acceleration of galvanic processes.

❖ Enhances functionalizing by combination with dispersion coating.

2.6.5 Significant outcomes of PED

❖ Reduction in the deposited crystallite size which ranges in microns with DC down to Nano range using pulse plating.

❖ Significant increase in density is observed as well as homogeneity of the deposited metal layers is enhanced.

❖ Dramatically improvement of the layer properties is obtained e.g. the corrosion stability.

❖ Alloy composition can be controlled by just altering the pulse sequence.

❖ Microstructure of the deposition can be tailored by modifying the pulse sequence.

❖ Systems like nickel, copper, gold, silver, rhodium, chromium, zinc and tin can be easily deposited using pulse plating.

❖ Some processes like Rack plating, barrel plating and continuous strip plating processes can be realized in practical.

2.6.6 Disadvantages of PED

There are very few and minor disadvantages associated with electrodeposition carried out using pulse DC, major disadvantages are:

- ❖ Generally the cost of a pulse rectifier is much higher than a DC unit. It involves a highly regulated and sophisticated design that costs more to manufacture.
- ❖ This technology requires concerned person to think and plan ahead because a series of procedures needs to be followed in order to get the best results.
- ❖ It possesses threat to some of the chemical manufacturer as the requirement for additives is reduced.

2.6.7 Technological Applications

Pulse plating is used on a larger scale for plating on electronic connectors and switch contacts. Development of less stressed pulse plated deposits made it easy to stamp and form contacts after plating. The economic gains achieved by using pulse DC surpass the relatively high cost of pulse power supplies. Manufacturers of semiconductor lead (Pb) frames prefer use of PC in order to increase the reliability of wire bonds and to enhance deposition rate. High-speed gold and silver-plating solutions are specially formulated for pulse deposition and are now available commercially. In Printed Circuit Boards (PCB) industry, there is a need for miniaturization of high-density interconnections which is possible by PED. Circuit traces can be brought closer together without shorting one another with the use of pulse technology, for high-density circuitry applications in microelectronics industry. Pulse current can produce invariably fine-grained structures so that physical, chemical and mechanical properties of many metals and alloys can be enhanced. Pulse and the related techniques enable the production of newer types of deposits, which were considered impossible till now. Pulse technique might give birth to some become

some other electrochemical processes also in future (e.g., electro-discharge machining, electro-etching and electro-cleaning).

CHAPTER 3

EXPERIMENTAL SECTION

3.1 Electrodeposition on steel samples

3.1.1 Sample Details

Ten rectangular pieces of mild steel approximately 2.4 cm x 1.3 cm x .3cm were taken initially. The samples were polished and then electroplated. Out of 10 mild steel samples, one was to be used as a reference sample; electrodeposited by dc and for other samples the deposition was done by pulse dc by varying frequency (viz. 1kHz, 8kHz, 14kHz) and duty cycle (viz. 10, 20 and 50). These samples were obtained from mild steel plate pieces in workshop.

3.1.2 Sample Preparation

❖ Ten rectangular pieces of mild steel samples were first put to rough polishing and then polished using emery paper 1/0, 2/0, 3/0, 4/0 in order to give a fine surface finish and to remove the dust from the surface and rust, if present.

❖ The dimension of the rectangular pieces was approximately 2.4 cm $\times$ 1.3 cm. Care was taken to avoid any damage to the polished surface as Ni ions are more attracted to protrusions and corners rather than recesses in the object. An area of 3.12 cm^2 was marked on the steel samples and left uncovered while carefully covering the rest with a non conducting paint (nail paint).

❖ The samples were stored in a desiccator to prevent it from corrosion and other surface degradation phenomenon.

3.1.3 Electroplating solution preparation

❖ 1 Litre of electroplating solution was prepared for deposition purpose. The beaker containing solution was covered with aluminium foil so that concentration of solution does not get affected and also to prevent the impurities from getting into the solution.

❖ Magnetic stirrer was used to ensure the availability of uniform solution for electrodeposition of steel samples.

❖ The solution used for electroplating purpose was *Watts Bath.* Composition of solution was 350 g/l Nickel Sulfate, 45 g/l Nickel Chloride and 37 g/l Boric Acid.
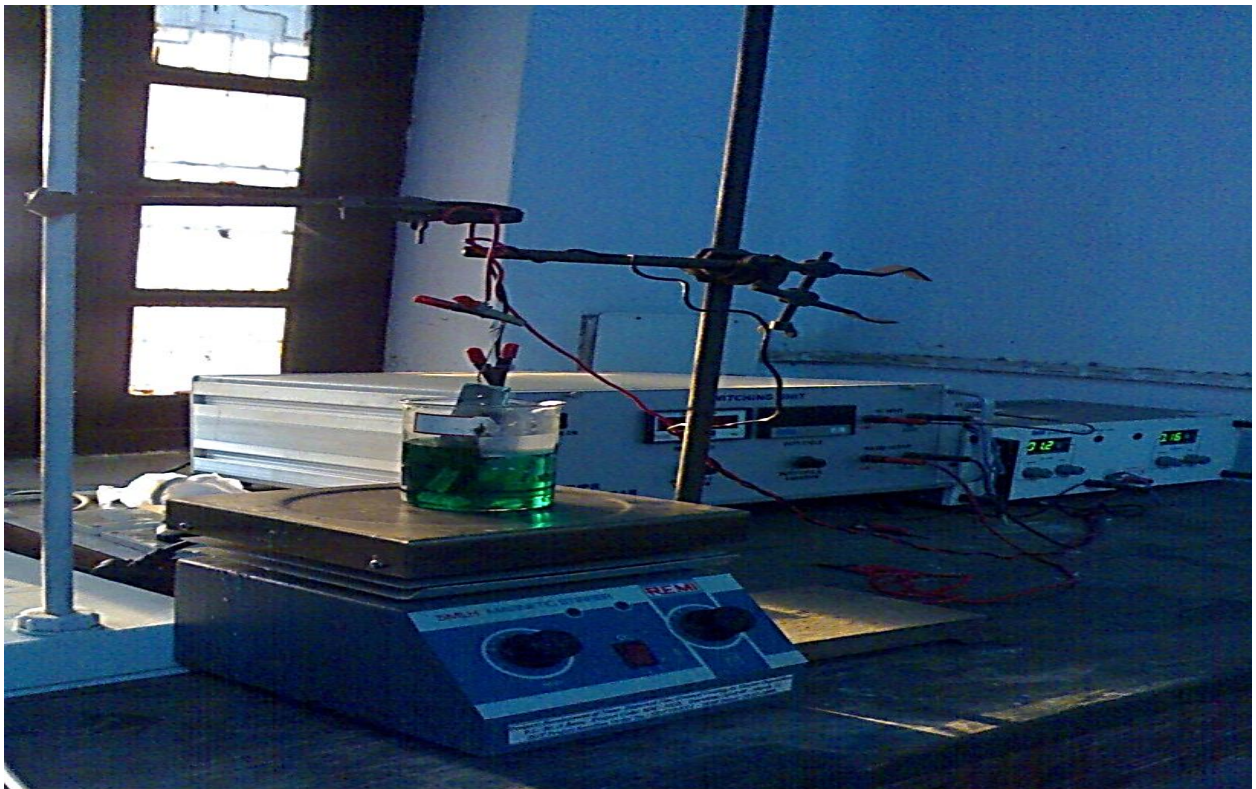

Fig 5. Experimental set up

3.1.4 Deposition Conditions

❖ One of the ten mild steel samples was coated using conventional dc while other samples were coated using pulse DC changing the parameters duty cycle and frequency.

❖ The appropriate current for deposition was determined by multiplying the current density ($5A/dm^2$) with the area of steel sample ($3.12cm^2$) to be coated.

$$\textbf{Current (i) = current density x deposition area}$$

$$= \textbf{5A/dm}^2 \textbf{ x 3.12}cm^2$$

$$=\textbf{0.16 A (approx.)}$$

Since other than the amplitude of dc current no other parameter can be varied, this was to be a reference sample.

❖ Nine other similar samples were coated with electro-pulsed deposition by varying frequency (viz. 1, 8 and 14 kHz respectively) and also duty cycle (viz. 10, 20 and 50).

❖ Each sample was deposited for 20 minutes each provided the temperature was precisely maintained in the range of 50-60°C.

❖ Deposition was carried out in constant current mode where current was maintained to be 0.16 A for each deposition.

❖ Nickel electrode served as anode and mild steel sample served as cathode for the deposition purpose.

❖ Magnetic stirrer was used throughout the process to enable uniform deposition of Nickel over the steel sample.

❖ Microprocessor based pH system was used to regulate the temperature within the desired range i.e. 50-60°C.

S. no.	Sample name	Current(A)	Voltage(V)	Temperature(°C)	Frequency (kHz)	Duty Cycle(%)
	S1	0.16	1.4	50	-no-	-no-
2	S2	0.16	10.4	55	1	10
3	S3	0.16	13.1	52	8	10
4	S4	0.16	5.7	60	1	20
5	S5	0.16	9.6	50	14	10
6	S6	0.16	6.8	50	8	20
7	S7	0.16	7.7	50	14	20
8	S8	0.16	3.2	50	1	50
9	S9	0.16	3.2	50	8	50
10	S10	0.16	3.7	55	14	50

Table 1. Details of sample deposited with parameter

3.2 Characterization

3.2.1 X-Ray Diffraction (XRD)

❖ X-ray diffraction was carried out in the range of scanning angle 20° to 80° at a scanning rate 3° per minute, with CuKα radiation (λ=1.5406 Å) using Philips X' PERT System X-Ray Diffractometer for all the ten samples

❖ From the accumulated data obtained using Philips X'PERT high score software for Nickel coated steel samples intensities for planes (111), (200) and (220) were obtained comparing the data with the standard JCPDS data.
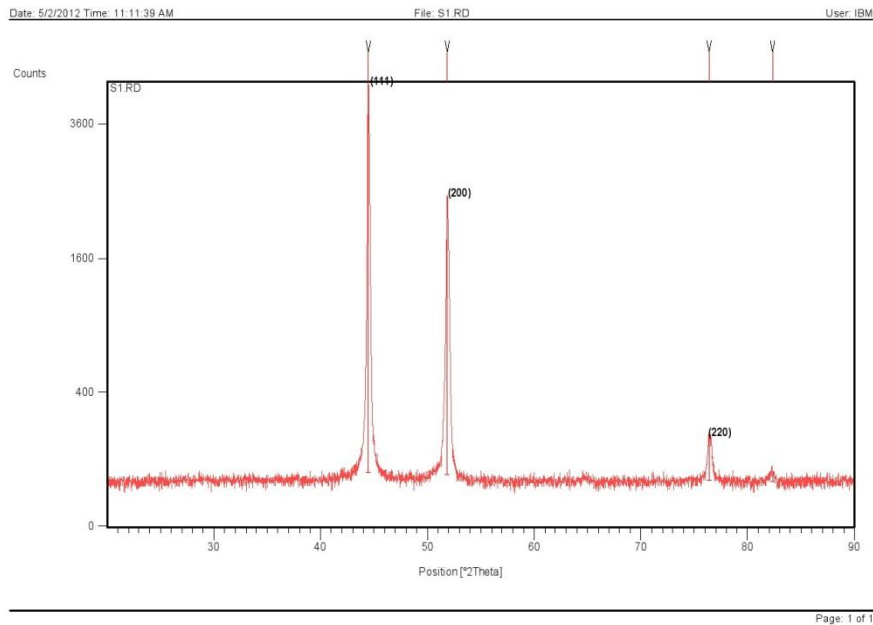

Fig 6. An example of XRD data obtained using PHILIPS X'PERT system X-Ray

Diffractometer

A diffraction pattern is obtained due to the interaction of X-rays with any crystalline substance. X-ray diffraction is a tool used for the investigation of the finer of material. For pure substances X-ray diffraction is like a fingerprint of a substance. Diffraction pattern obtained in a mixture of substances is independent for different substances contributing to the mixture. [21] Initially, x-ray diffraction was used only for crystal structure determination. But now however, other informations can also be revealed just not only for structure

determination, but also investigations like chemical analysis and stress measurement, the study of phase equilibrium and the measurement of particle size, the determination of the orientation of one crystal or the ensemble of orientations in a polycrystalline aggregate can also be done. It imparts information regarding the presence of various compounds and phases.

For systematic study of texturing, texture coefficient (TC) was calculated using the below mentioned equation of each plane for all the samples,

$$\mathbf{TC_{hkl} =((I_{hkl} / I_{0hkl}) / \Sigma (I_{hkl} / I_{0hkl})) \times 100\%}$$

Where TC= texture coefficient

I=intensity obtained from the textured sample

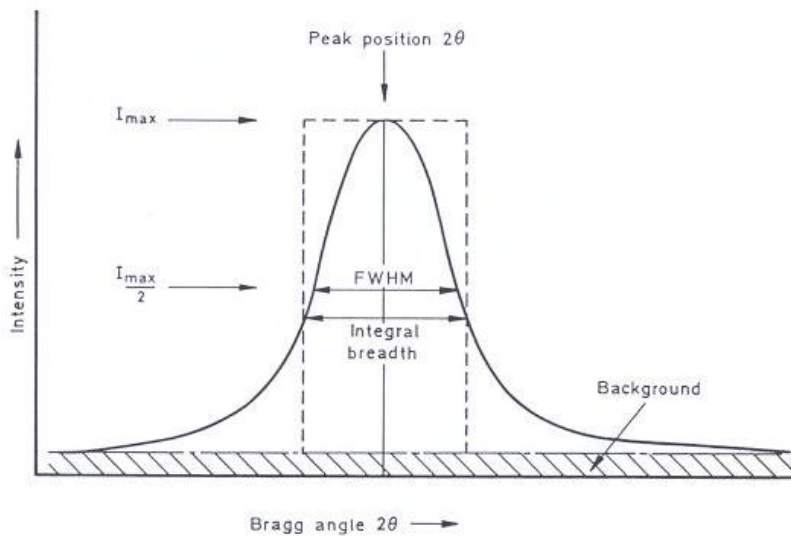I_0=Intensity of standard oriented sample from JCPDS data.

Fig 7. Schematic representation of XRD peak for the determination of grain size

The crystallite size is calculated by measuring the Bragg peak width at half the maximum intensity and putting its value in Scherrer's formula. The constant of proportionality, K (the Scherrer constant) depends on the method how the width is determined, crystal shape, and the size distribution. K=0.94 for FWHM of spherical crystals with cubic symmetry. (K ranges from 0.62 to 2.08). FWHM is useful in determining: grain size and residual stress. Here it has been used to calculate the grain size.[21]

Scherrer's formulae is given as,

$$B_c = k \, \lambda \, / \, L \, Cos \, (\theta)$$

Where λ= wavelength, L= average crystallite size and k= .9

3.2.2 Scanning Electron Microscope (SEM)

Scanning electron microscope is a kind of electron microscope that images a sample by scanning it with the help of electron beam. Electrons interact with the atoms of the sample to reveal different information like composition, topography and electrical properties etc. Electron beam is produced from a source which can be Filament, anode and vacuum etc. Different electrons emitted by the electron gun interact differently with the sample atoms and gives various information. Secondary electrons reveal information about the topography of sample. Back scattered electrons gives us information regarding the composition of the sample. Similarly X–rays produced give us information regarding the chemistry of the sample like elements present etc. Depth of field for SEM is very large which enables a larger area to be focused at one time. It has a good combination of good resolution, larger depth of field and higher magnification making it a very useful instrument in academic and research field.

3.2.3 Microhardness Measurement

❖ Hardness was measured using Vickers's hardness tester.

❖ Load used form hardness measurement was 25gf and the dwell time was 10 seconds.

❖ For each steel samples 4 different hardness values were taken changing the position of indentation. In microhardness determination less load is used. A diamond indenter gives an impression on the surface with a specific load. Hardness value varies with the indentation formed via indenter. In our case we used Vicker's Hardness tester where hardness is expressed in terms of Vickers Pyramid Number (HV) or Diamond Pyramid Hardness (DPH).

S.no.	Sample name	H1(HV)	H2(HV)	H3(HV)	H4(HV)
1	S1	302.7	248.8	206.9	210.2
2	S2	270.6	193.0	254.0	223.3
3	S3	281.6	282.7	273.7	281.9
4	S4	296.5	275.6	306.7	255.9
5	S5	250.6	256.1	214.2	223.3
6	S6	279.0	210.2	216.9	200.9
7	S7	230.6	319.0	254.9	244.0
8	S8	243.3	234.7	201.6	228.8
9	S9	236.9	233.7	231.4	216.4
10	S10	275.0	249.7	230.4	260.7

Table 2. Hardness values obtained for each sample.

3.3 Overview of Experimental Procedure

10 rectangular specimens of mild steel specimens of dimension 2.4 cm x 1.3 cm were cut from mild steel plate. One of the surfaces was marked for coating and rest were given an insulated coating.

These 10 samples were named from S1-S10 and coated with Nickel by electroplating. The solution used was Watts bath containing Nickel Sulfate, Nickel Chloride and Boric Acid. Current density was $5A/dm^{2.}$

These samples were subjected to XRD, SEM and hardness measurement for the characterization purpose.

4.1 X-Ray Diffraction

❖ **Texture Measurement and Grain Size Determination**

Figure 8-10 shows the XRD pattern obtained for all the coated samples. Each figure represents the XRD pattern for different frequencies. XRD profile obtained for the samples is stacked frequency wise viz.1kHz,8kHz and 14kHz.For all the figures, base XRD profile is for DC coating which is taken as reference and the other three are of different duty cycles viz. 10, 20 and 50.
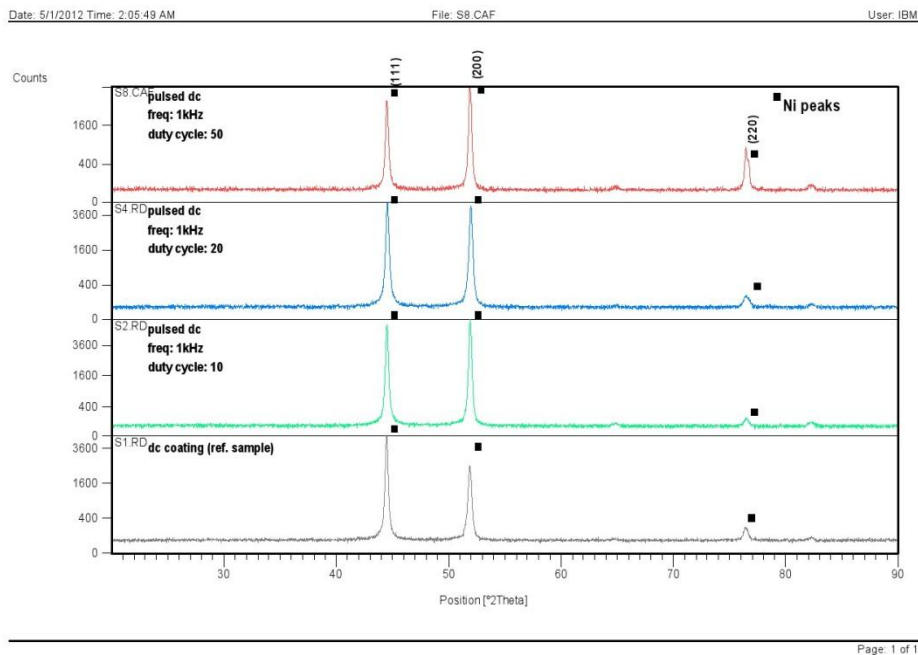

Fig 8. XRD patterns for 1 kHz with duty cycles (10, 20 and 50) and DC coating stacked together.
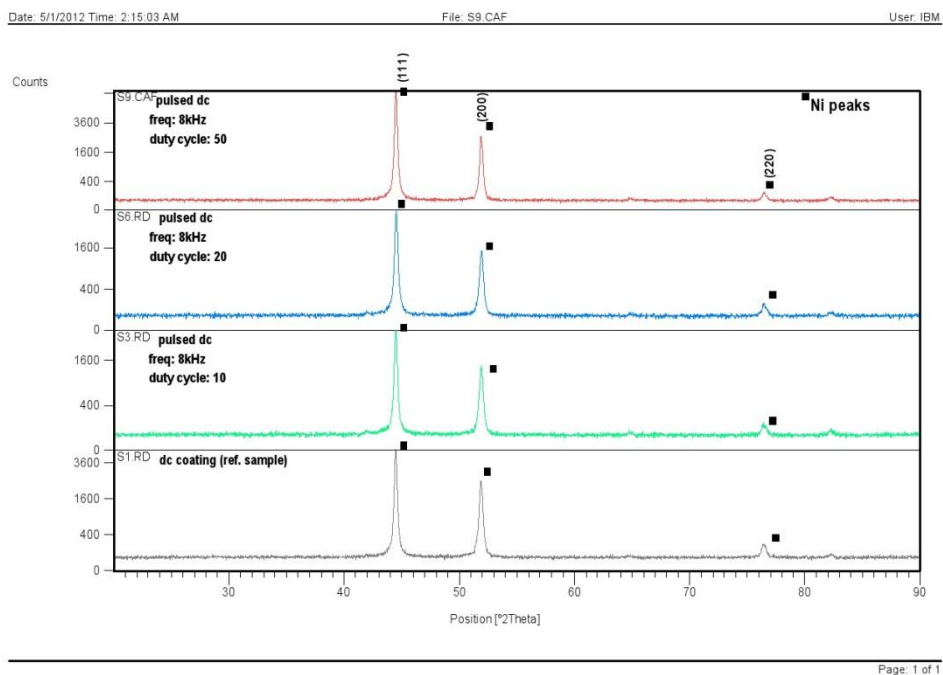
Fig 9. XRD patterns for 8 kHz with duty cycles (10, 20 and 50) and DC coating stacked together.
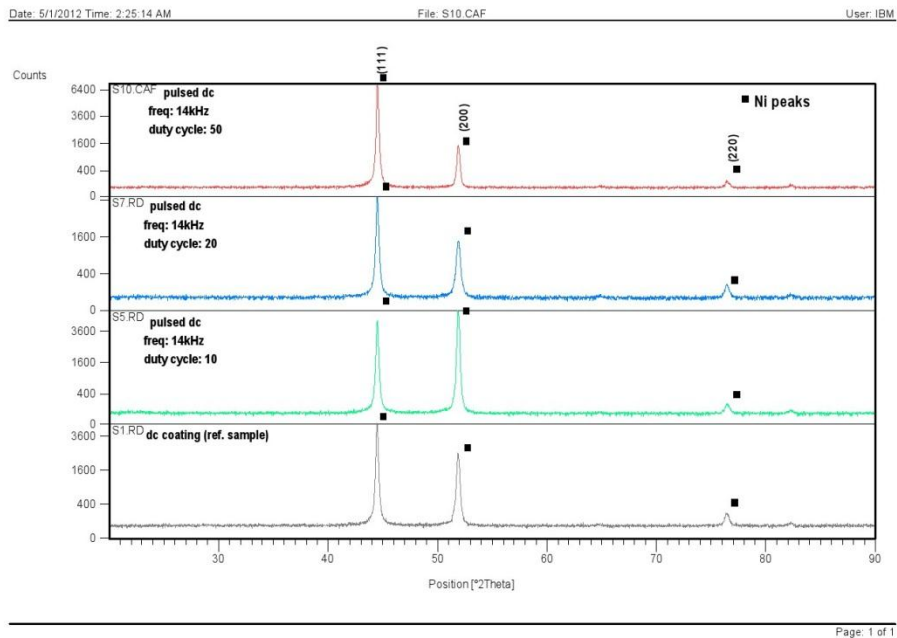

Fig 10. XRD pattern for 14 kHz with duty cycles (10, 20 and 50) and DC coating stacked together.

Careful observation of Fig.8-10 reveals different relative peak intensities corresponding to different planes of Nickel with change in deposition parameters viz. frequency and duty cycle.

In each pattern some peaks are more prominent than others. In the 2θ range used here, three peaks were obtained corresponding to Nickel of planes viz. (111), (200) and (220).

Frequency (kHz)	Sample name	Duty Cycle (%)	Grain size(nm)	Texture Coefficient			Hardness (HV)
				(111)	(200)	(220)	
-no-	S1	-no-	36.3	40.4824	**53.2663**	6.2513	208.55
1	S2	10	39.6	26.8814	**70.8921**	2.2266	249.3
	S3	20	48.4	30.3551	**65.4864**	4.1585	279.975
	S4	50	62.2	18.2699	**57.5688**	24.1613	301.6
8	S5	10	39.6	44.6409	**49.2974**	6.0617	253.35
	S6	20	48.4	45.7415	**47.3244**	6.9341	209.33
	S7	50	54.5	**50.6347**	45.9828	3.3825	243.17
14	S8	10	36.3	24.3398	**71.8994**	3.7608	227.1
	S9	20	43.6	**49.3718**	42.1722	8.456	229.6
	S10	50	48.4	**65.3077**	31.1198	3.5725	261.8

Table 3

The XRD data was used in determining the preferred orientation and grain size of the deposits along (111) as mentioned in 3.2.1. Table 3 shows the Texture Coefficient (TC) data calculated for three different planes, i.e. (111), (200)and (220) resulting in a TC value of each of the three planes corresponding to any particular sample. This analysis was done for all the ten steel

samples, each representative of a different coating parameter combination. The TC values obtained for each planes of a sample are listed in Table 3 against the sample name and coating parameters. The highest TC values of a plane for any particular sample have been highlighted to give an idea about the preferred orientation for that particular coating parameter provided to the sample.

XRD data obtained from using Philips X' PERT System X-Ray Diffractometer was also used to determine the grain size of the deposit for each of the ten coating parameters. The grain size was calculated as mentioned in 3.2.1 using Scherrer's equation. The grain sizes obtained for each of the samples (viz. S1-S10) are listed against their sample no. as shown in table 3.

With reference to Table 3, it is evident that for a fixed frequency with increasing duty cycle, Texture coefficient for (200) decreases while Texture Coefficient for (111) and Texture Coefficient for (220) increases. Also for any particular duty cycle with increase in frequency, Texture Coefficient (200) is decreasing.

4.2 Microhardness Measurement

The hardness was determined by Vickers hardness tester with 25g load. Four sets of values were taken for each sample at different points, and the average of best three was determined. The average best value is listed in table 3 against the sample name. Also hardness values are plotted with increasing grain size to see if there is any variation.
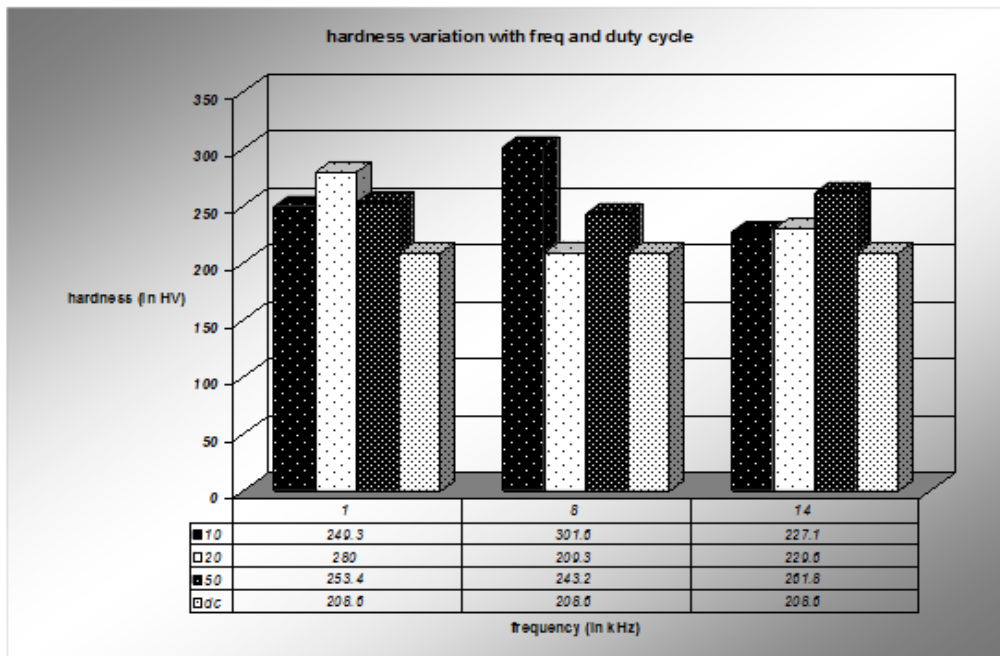
hardness variation with freq and duty cycle

	1	8	14
■10	249.3	301.6	227.1
□20	280	209.3	229.6
■50	253.4	243.2	261.6
□dc	208.6	208.6	208.6

frequency (in kHz)

Fig 11.The above graph illustrates the variation of hardness with frequency for each of the three duty cycles viz. 10, 20 and 50.
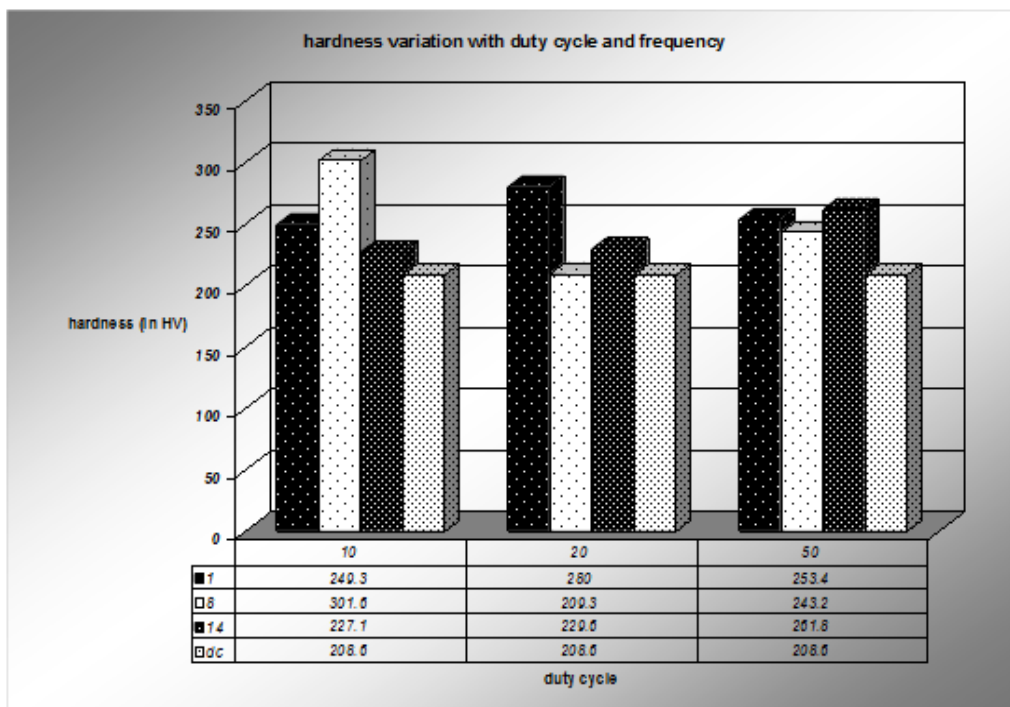

hardness variation with duty cycle and frequency

	10	20	50
■1	249.3	280	253.4
□8	301.6	209.3	243.2
■14	227.1	229.6	261.6
□dc	208.6	208.6	208.6

duty cycle

Fig 12. The above graph illustrates the variation of hardness with duty cycle for each of the three frequencies viz. 1, 8 and 14 kHz.

Basically the hardness values were used to observe the trend in its variation with the change in parameters of coating; besides this these were also checked for variation with increasing grain size. A different coating conditions resulted in a different preferred orientation of coating and grain size of the and thus in turn resulted in a different hardness value. Our aim was to see under what conditions here the maximum hardness values were obtained. It is expected that as the plane of preferred orientation makes an increasing angle with the (100) plane the strain energy of deposit increases so hardness values in such cases should be high.

❖ **Variation of Hardness with the coating parameters**

With reference to the Fig 11 and Fig 12, the highest hardness value was obtained corresponding to intermediate value of frequency (8 kHz) and lowest duty cycle (10%). This was followed by hardness value corresponding to lowest frequency (1 kHz) and intermediate value of duty cycle

(20%). The third in line was the value corresponding to highest frequency and highest duty cycle (14 kHz) and highest duty cycle (50%).

Although the first two highest hardness values were obtained for preferred orientation corresponding to plane with minimum strain energy, the grain size of the hardest coating was the finest. This can be said based on the grain size value listed in Table 3, calculated from XRD data and also confirmed from SEM images. The third hardest deposit however corresponded to the preferred orientation for plane with highest strain energy, this was the case of deposition done at highest frequency and highest duty cycle, here the highest TC was observed on plane on highest strain energy that making an angle of 54.57° with (100) plane) i.e. on (111) plane.

❖ Variation of hardness with the grain size

With reference to Fig 13, the hardness values were plotted with increasing grain size and it was found that no significant variation was observed. This is expected as the grain size is in nm and the variation in grain size is itself not much (in the nm range) so the hardness remains the same. This observation was supported by the Ex-situ SEM images obtained.

Besides this it was observed that grain sizes were smaller for coating at low frequency and higher duty cycle and for higher frequency and lower duty cycle. Both of these cases here has resulted in highest hardness values.
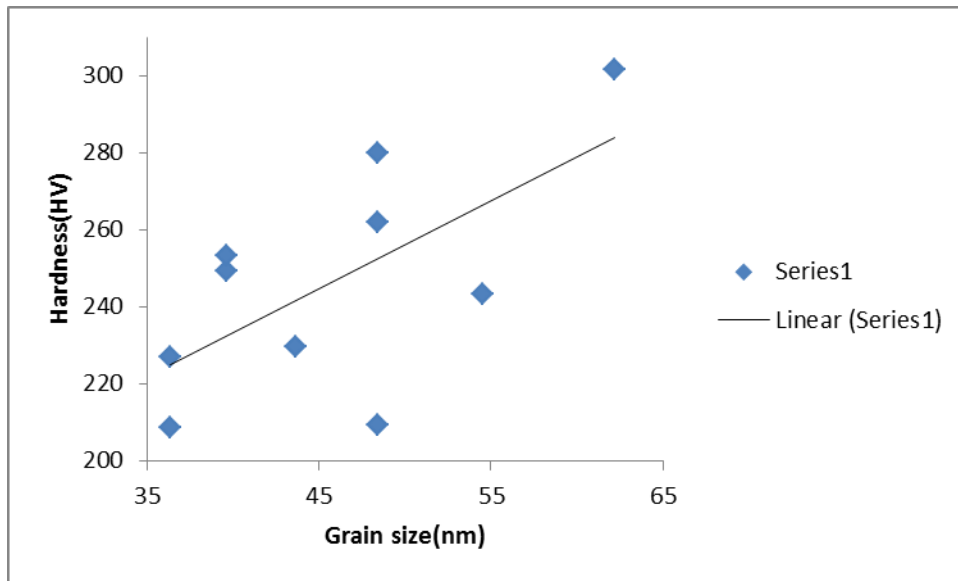
Fig 13. Variation of Hardness with Grain size

4.3 Scanning Electron Microscope Analysis

Scanning electron vacuum used was maintained to be 10^{-4} Pa. SEM used was JEOL JSM-6480 SEM. Images as a result of SEM are given in the next pages,
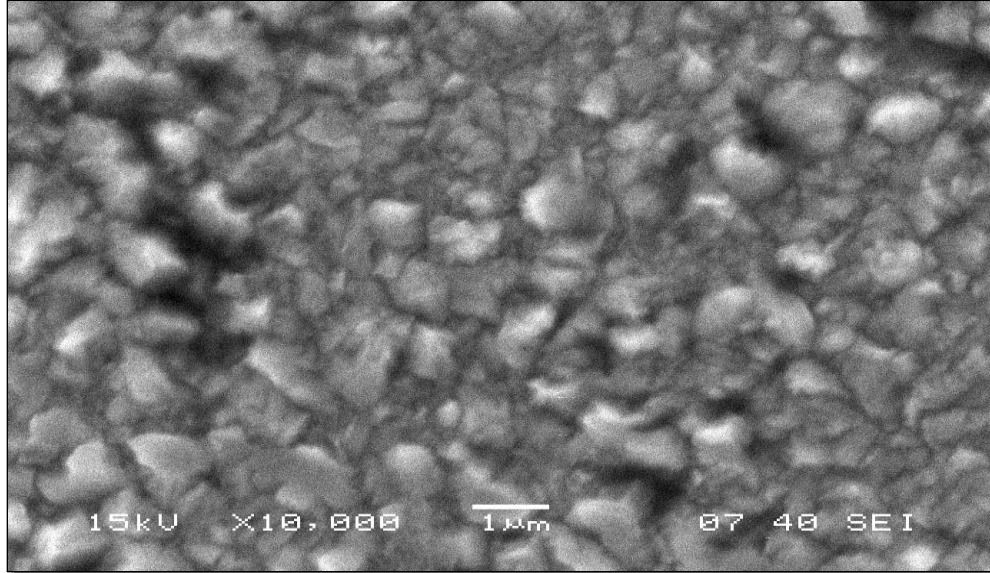
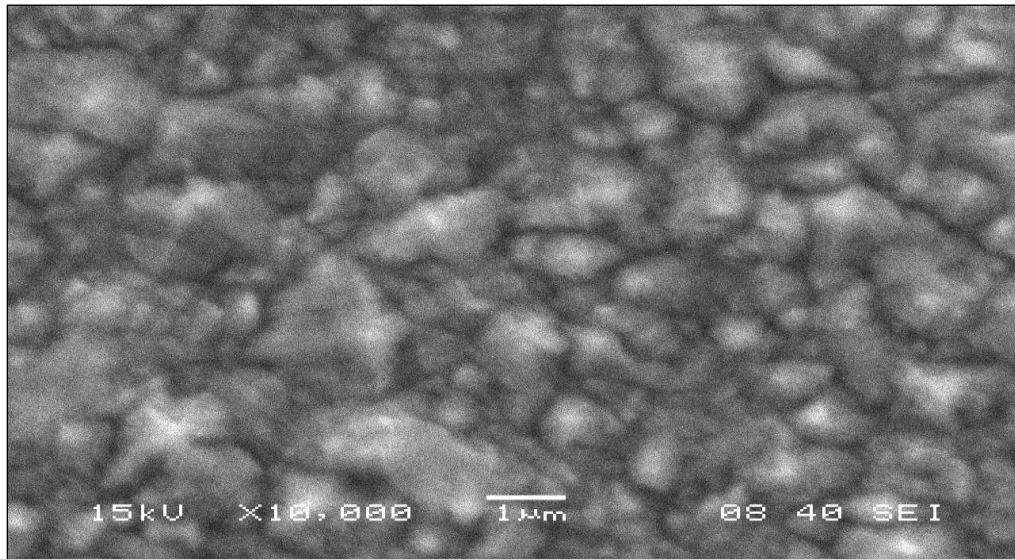Fig 14.1 SEM image for DC coated sample

Fig 14.2 SEM image for sample coated with pulsed DC, frequency 15 kHz, duty cycle 10
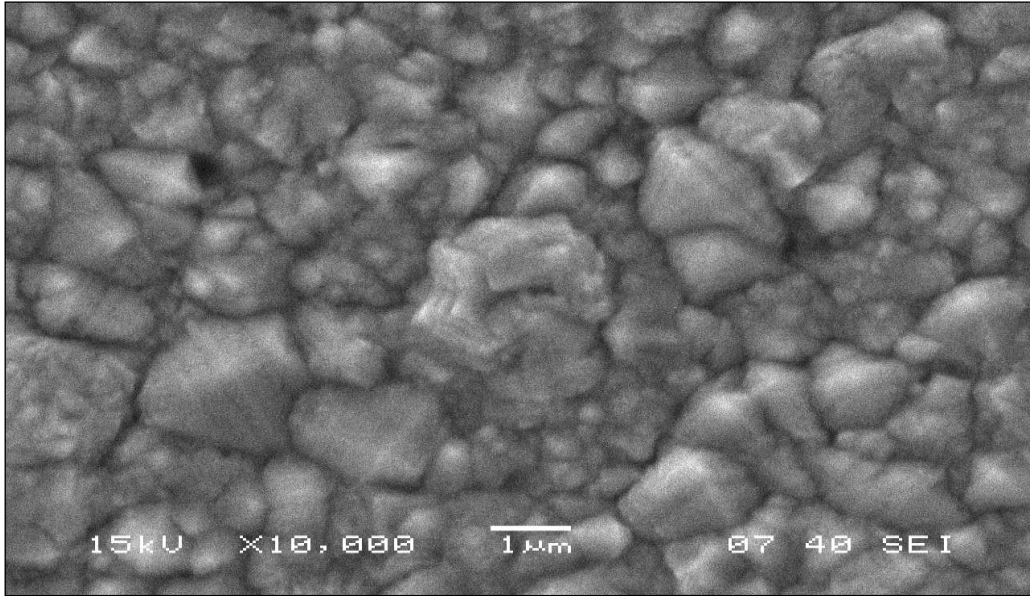
Fig 14.3 SEM image for sample coated with pulse DC, frequency 1 kHz, duty cycle 10
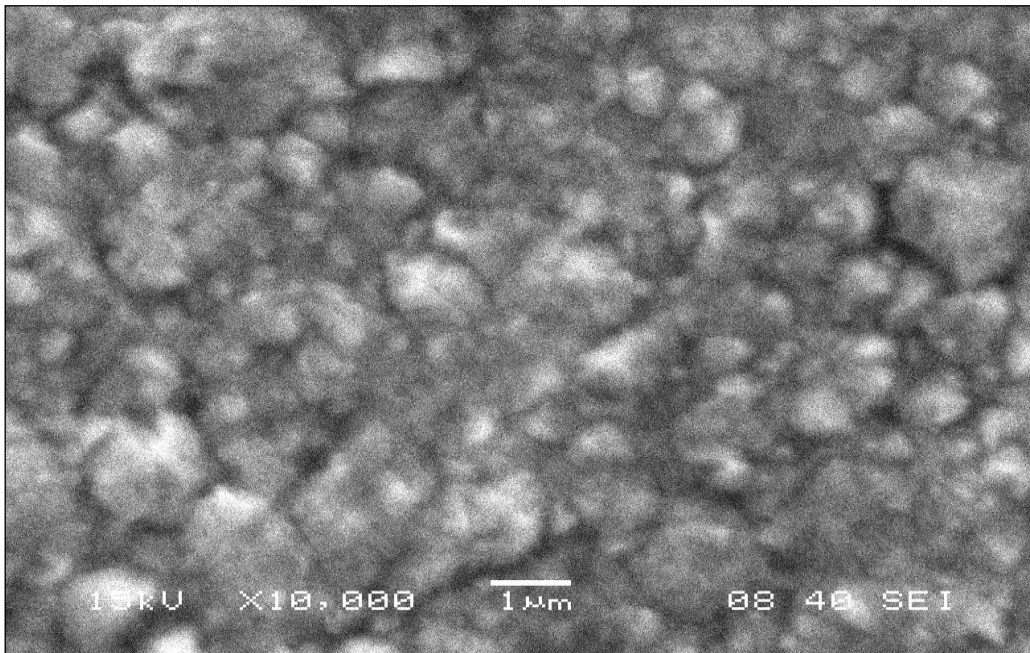

Fig 14.4 SEM image for sample coated with pulse DC, frequency 1 kHz, duty cycle 20
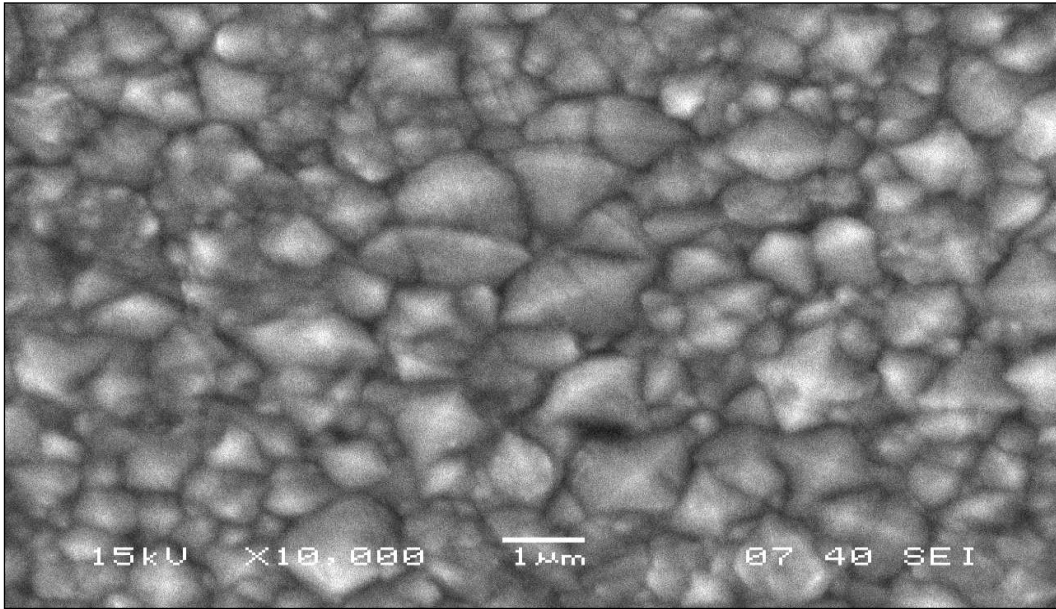
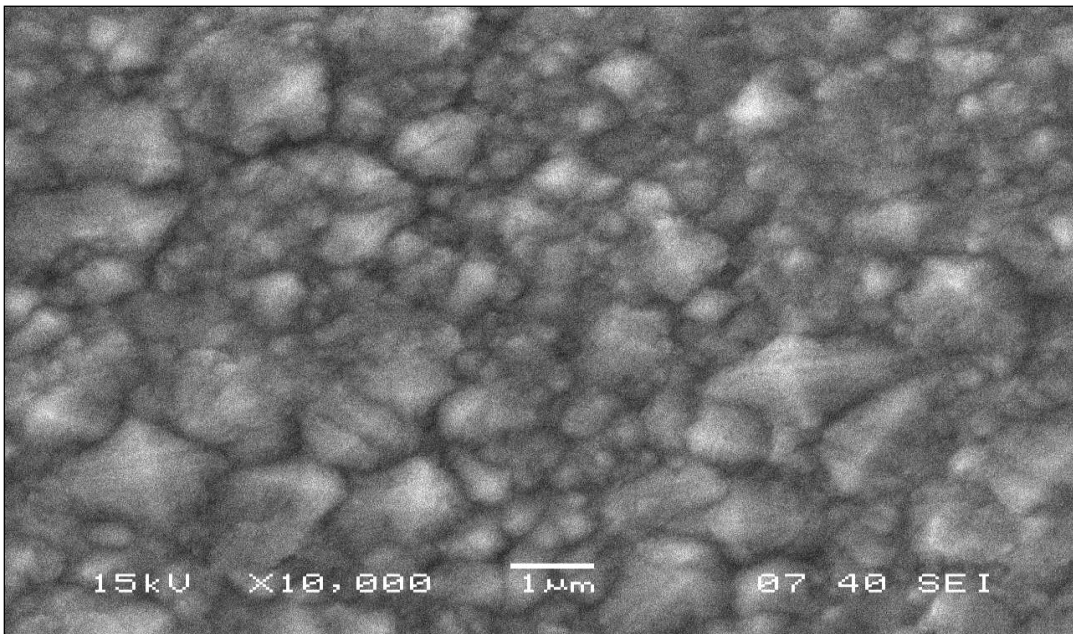Fig 14.5 SEM image for sample coated with pulse DC, frequency 8 kHz, duty cycle 10

Fig 14.6 SEM image for sample coated with pulse DC, frequency 8 kHz, duty cycle 20

Comparing the above figures 14.1-14.6, it was found that 8 kHz and 10% duty cycle coating had smallest grain size among these. This goes well with other observations viz. the highest hardness obtained for this coating, and also smallest grain size as calculated from XRD data. Otherwise on a whole no significant difference is observed in surface morphology of these six samples.

CHAPTER 5

CONCLUSION

From the present study the following conclusions can be obtained:

1. Nickel coating on mild substrate were successfully deposited by electro deposition from watt's bath with varying pulsed DC parameters.

2. For any particular frequency, with increase in duty cycle TC (200) decreases with increase in TC (111) and TC (220). Thus as duty cycle increases the preferred orientation tends to be corresponding to the plane of higher strain energy.

3. For any particular duty cycle, with increase in frequency, TC (200) is again decreasing, thus it can be concluded that with increasing frequency for a particular duty cycle, the preferred orientation again tends to be corresponding to the plane of higher strain energy.

4. The hardness was higher for deposit corresponding to finer grain sizes and also in case of preferred orientation being on the plane of higher strain energy (here in case of Ni this plane being (111)). Also the hardness values do not differ significantly with grain size, because variation in grain size itself is not any significant.

5. Ex-situ SEM images confirm the observation that fine grain size and harder deposition were obtained in case of higher frequency and lower duty cycle (8 kHz and 10% duty cycle).

CHAPTER 6

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