Electroless Ni-Sn-P Coatings: Preparation and Tribological Characterization

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BY

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*We hereby recommend that the thesis presented under our supervision by **Mr. Naveen Kumar** entitled "**Electroless Ni-Sn-P Coatings: Preparation and Tribological Characterization**" be accepted in partial fulfillment of the requirements for the degree of Master of Mechanical Engineering.*

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CHAPTER 3: EXPERIMENTAL DETAILS

CHAPTER 1

INTRODUCTION

This chapter provides the introduction to Electroless coating.

It also gives the overview of present scope of work for the thesis

1.1 ELECTROLESS NICKLE COATING

The performance and life of engineering components can be increases by applying different coating over the surface as per requirement and uses of the components . Electroplating and electroless deposition are most economical processes for applying metallic coating of thickness between 10 to 500 μm of many_engineering components. Electroless nickel plating is a chemical reduction process which depends upon the catalytic reduction process of nickel ions in an aqueous solution (containing a chemical reducing agent) and the subsequent deposition of nickel metal without the use of electrical energy. Electroless coatings have found extensive use in different industrial applications including valves for fluid handling, medical equipment and hydraulic cylinders owing to their excellent mechanical, physical, electrical, corrosion and wear resistance properties. By the name itself, electroless means without the use of electricity. It's an autocatalytic method in which the Metallic Ions (Mn+) are reduced in solution by a reducing agent and gets deposited on the surface of the substrate materials.

Once the first layer of Mn+ is deposited, it acts as a catalyst for the process. Electroless deposits are therefore very uniform in thickness all over the part’s shape and size. In fact, one of the major characteristics making its use more prevalent is the ability of the process to provide uniform deposits in valves, deep recesses, bores, internal surfaces, blind holes and threaded parts and also very smooth surface finish is obtained.

Electroless Nickle plating differs from the conventional electroplating process that depends on an external source of dc to reduce nickel ions in the electrolyte to nickel metal on the substrate. EN coating is an autocatalytic deposition of a Ni-Sn-P alloy from an aqueous solution onto a substrate without the application of electric current. Thus the electroless deposition process is unlike the conventional electroplating processes, which depend on an external source of direct current in order to reduce nickel ions in the electrolyte to nickel metal on the substrate. The electroless bath typically comprises an aqueous solution of metal ions, complexing agents, reducing agents and stabilizers, operating in a specific metal ion concentration, temperature, and pH ranges. The deposition rate, properties of coated components and the structural behaviour of the deposits mainly depend upon the plating bath constituents/conditions such as the type and concentrations of the reducing agent, stabilizer, pH and the temperature of the bath, etc.

The chemical reaction for electro-deposition of metal can be expressed as

$$M_{sol}^{n+} + ne^{-} \xrightarrow{cathode} M_{Lattice}$$

and that for electroless deposition is given by

$$M_{sol}^{n+} + Reducing_{sol} \xrightarrow{cataylitic\ surface} M_{lattice} + Oxidation_{sol}$$

and the anodic reaction is just the opposite of it which is given by

$$M_{Lattice} \xrightarrow{Anode} M_{sol}^{n+} + ne^{-}$$

1.2 ADVANTAGES OF ELECTROLESS NICKEL ALLOY COATING

The main advantages of electroless Nickel based composite coating are

1. Resistance against wear and corrosion.

2. Increase in micro hardness.

3. Increase thermal resistance.

4. Smooth & uniform deposit regardless of the geometry of the substrates.

5. Oxidation resistance.

6. Good solderability, bondability and weldability properties.

7. Greater lubricity.

8. Nonmagnetic properties.

9. Good appearance and brightness.

10. Low co-efficient of thermal expansion and high thermal conductivity.

11. Good chemical stability.

12. Uniformity of the deposits , even on complex shapes.

1.3 APLICATION OF ELECTROLESS NICKLE BASED ALLOY COATING

APLICATION	COATING THICKNESS (µm)	COMPONENTS
Automotive	2-40	Heat sinks, carburetor components, fuel injection, differential pinion ball shafts, disk brake pistons, transmission thrust washers, knuckle pins, exhaust manifolds and pipes, mufflers, shock absorbers, lock components, hose couplings, gear and gear assemblies. Fuel pump motors, aluminium

		wheels, water pump components, steering column wheel components, air conditioning compressor etc
Air craft/ Aerospace	10-50	Bearing journals, servo valves, compressor blades, pistons heads, engine main shafts and propellers, hydraulic actuator splines, seal snaps and spacers, landing gear components, pilot tables, oil nozzle components, flanges, engine oil feed tubes, flexible bearing supports, universal joints
Chemical and petroleum	25-125	Pressure vessels, pumps and impellers, heat exchangers, filters components, turbine blades and rotor assembles, compressor blades and impellers, spray nozzles, stainless steel valves, drilling mud pumps, hydraulic systems actuators
Electrical machine	10-30	Motor shafts, rotor blades of stator rings
Electronics	2-30	Head sinks, computer drive mechanisms, chassis memory drums and discs, terminals of lead wires, connectors, diode and transistor cans, interlocks, junction fittings and PCB
Food	10-25	Pneumatic canning machinery, baking pans, moulds, freezers, mixing louts, and feed screw and
Marine	20-50	Marine hardware, pumps and equipment

Material Handling	10-70	Hydraulic cylinders and shafts, extruders, link drive belts, handling gears and clutches
Medical and pharmaceutical	10-30	Disposable surgical instruments and equipment, Sizering screens, pill sorters and feed screws
Military	7-70	Fuse assemblies, tank tarred bearings, radar wave guides, mirrors, motors, detonators and firearms
Mining	25-60	Hydraulic systems, jetting pump heads, mine engine components, piping connections, framing hardware
Wood and paper	10-30	Knife holder corer plates, abrading plates and machine parts

1.4 TYPES OF ELECTROLESS COATINGS

There are a wide varieties of electroless coatings which can be broadly classified into four categories viz, pure nickel, alloy and poly-alloy coatings, composite coatings and electroless nano coatings. The alloy and poly-alloy coatings can be further classified into binary alloy coatings, ternary alloy coatings, and quaternary alloy coatings. In binary alloys there are two elements in the coating microstructure like Ni-P. Similarly in ternary there are three elements present like Ni-Sn-P and in quaternary there are four elements present like Ni-Sn-Cu-P etc.

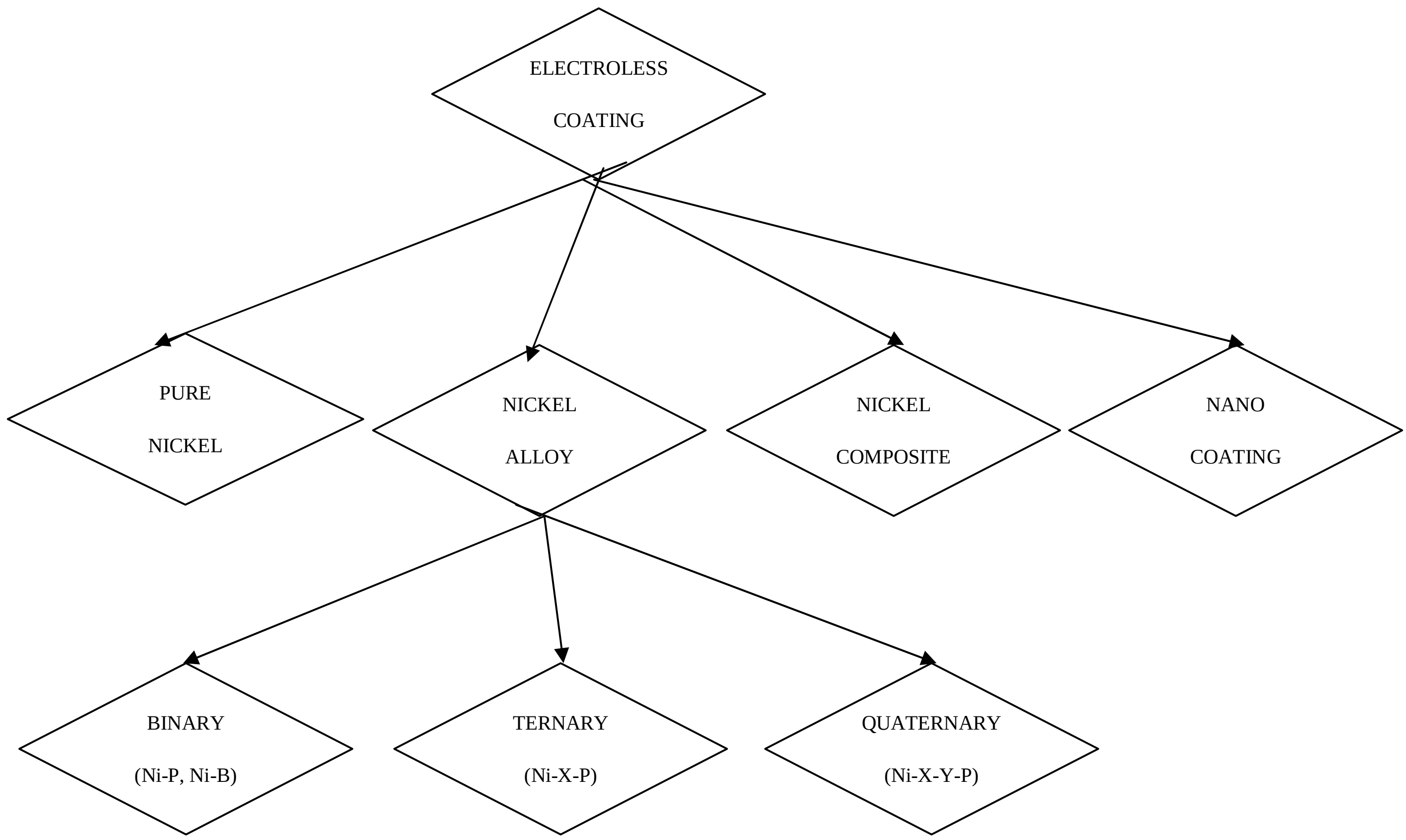


Fig.1: Schematic representation of different Electroless Deposition on Substrate

PURE NICKEL

The 'pure' autocatalytic nickel has great use for certain applications such as semiconductor application. Generally hydrazine is used as reducing agent to deposit pure nickel. This coating is restricted to little industrial interest, due to hydrazine cost and hazards.

NICKEL ALLOYS

When a second element is co-deposited along with nickel to the substrate during electroless plating, then it is a binary nickel alloy coating. The basic binary alloy coatings are nickel-phosphorous (Ni-P) and nickel-boron (Ni-B) coatings. The type of binary coating deposited depends on the reducing agent used for the coating. If hypophosphite is used as reducing agent Ni-P is developed and if borohydrideorborane is used as reducing agent then Ni-B is developed. To improve the coating properties or to have a coating with desired property the third element is co-deposited with the basic Ni-P or Ni-B coatings, which take the form Ni-X -P-or Ni-X-B, where X is the third element. The property of the coating depends on this co-deposited third element. There are several ternary and quaternary coatings being developed to meet the industrial requirements.

COMPOSITE COATINGS

If compound materials are co-deposited with electroless coatings, it is termed as electroless composite coating such as Ni-P-TiO2, Ni-P-Al2O3, Ni-P-B4C, Ni-P-SiC etc. The composite coatings can be divided into two categories, wear resistant composite and lubricating composite coating. Electroless composite coatings often result in sudden decomposition of the bath. This is because the dispersion of fine particles increases the surface area loading of the electroless bath by nearly 700–800 times of that of normal electroless bath and this leads to in stability of the bath. Nevertheless, with the aid of suitable stabilizers, surfactants and method of agitation to keep the composite particles in suspension electroless nickel composite coatings are prepared.

NANO COATINGS

Electroless Nickel Coatings with nano particles dispersed into the Ni-P matrix are called Nano Coatings. Some examples of Nano particles used are Sic, Tio_2,Al_2O_3 etc.

Chapter 2

LITERATURE REVIEW

This chapter provides an outline of electroless Ni-Sn-P coating with its properties along with the relevant literature review required to set a scene for the present study. It also gives the scope of the present work.

2.1 INTRODUCTION

Since the invention of electroless plating technology in 1946 by A. Brenner and G. Riddell, electroless nickel (EN) coatings have been actively and widely studied [1, 2]. Electroless coating is different from the conventional electrolytic coating as the former does not require any electricity for its deposition. It has been found that electroless nickel coating has excellent properties such as good wear and corrosion-resistance and desired electrical and magnetic properties. This makes it feasible for electroless nickel alloy coating to be widely used in various industrial fields such as chemical engineering, mechanical engineering, automobile, electronics, aerospace, etc. Since then it has evolved in to a mature subject of research and development today due to its wide range of applications.

In electroless metal deposition process, no external current supply is required to deposit material on a substrate. Electroless plating is an autocatalytic chemical deposition process where the substrate develops a potential when it is dipped in electroless solution called electroless bath that contains a source of metallic ions, reducing agent, complexing agent, stabilizer and other components. Due to the developed potential both positive and negative ions are attracted towards the substrate surface and release their energy through charge transfer process. Each process parameter has its specific role on the process mechanism and influences the process response variables. Temperature initiates the reaction mechanism that controls the ionization process in the solution and charge transfer process from source to substrate. The overall reaction of electroless metal deposition is [3]:

$$M^{Z+} + Red_{solution} = M_{lattice} + Ox_{solution} \qquad (1)$$

An electrochemical model for the process of electroless metal deposition was suggested by Paunovic and Saito on the basis of the Wagner–Traud mixed-potential theory of corrosion processes. According to the mixed-potential theory of electroless deposition, the overall reaction can be decomposed into one reduction reaction and one oxidation reaction, the anodic partial reaction is

$$Red_{solution} = Ox_{solution} + me \quad (2)$$

And the cathodic partial reaction is

$$M^{Z+} + Ze = M_{lattice} \quad (3)$$

The equilibrium (rest) potential of the reducing agent, $E_{eq,Red}$ must be more negative than that of the metal electrode, $E_{eq,M}$, so that the reducing agent Red can function as an electron donor and M^{z+} as an electron acceptor.

Electroless nickel coatings possess splendid tribological properties like high hardness, good wear resistance and corrosion resistance. Due to these properties the EN coating has found wide applications in aerospace, automobile, electrical and chemical industries. The technological advancement demands the development of newer coating materials with improved properties like resistance against wear and friction. Electroless coatings can be divided into three main categories like (i) alloy coatings, (ii) composite coatings and (iii) metallic coatings. For the improvement of tribological performances many researches are developing and investigating newer variants of electroless nickel coatings like Ni-W-P, Ni-Cu-P, Ni-P-TiO_2, Ni-P-SiC etc [4]. So the enhancement of tribological characteristics by the modification of the coating process parameters has remained a key point of interest in researches.

2.2 ELECTROLESS Ni-P ALLOY COATING

Electroless nickel plating is becoming more popular method of coating due to low tool cost, low temperature process, good quality deposit with uniformity. The basic electroless Ni-P coating has been used as a functional coating due to the advantage of surface roughness [5], friction [6], wear resistance [7] and corrosion properties. The incorporation of additional metal elements into the electroless deposits can be an important means of enlarging the range of chemical, mechanical, physical, magnetic, and other properties attainable. Also, and more importantly, certain metals that cannot themselves be deposited by the autocatalytic mechanism can be induced to co-deposit with an electrolessly depositing metal. Although electroless nickel alloycoatings can serve a lot of purpose, the quest for improved properties such as higher hardness, lubricity, anti-sticking and anti-wear properties has led to the incorporation of many soft and hard particles in the matrix of the electroless nickel. Choice of the particles depends on the specific property that is desired. In the field of tribology, electroless nickel based composite coatings can mainly be divided into two categories, i.e., lubricating composite coatings and wear-resistant composite coatings, according to the types of the doped inorganic and/or organic particulates. The electroless Ni-P based lubricating composite coatings usually contain co-deposited solid lubricants such as WS_2, MoS_2, PTFE (poly tetra fluoro ethylene) and graphite and they usually have a reduced friction coefficient as compared with electroless Ni-P coating. Similarly, the wear-resistant composite coatings usually have co-deposited hard particles such as WC, SiC, Al_2O_3, B_4C and diamond, and they usually have increased hardness and wear resistance as compared with electroless Ni-P coating. The preparation of electroless nickel based composite coatings with excellent comprehensive properties is highly dependent on the stable dispersion of the nanoparticles in plating bath, otherwise the so-called composite coatings would have non-uniformly distributed particulates and numerous defects, owing to the segregation and agglomeration of the nanoparticles with high surface energy and activity in the plating bath

2.3 Ni-Sn-P COATING

Due to the unique properties of electroless Ni−P alloy coating, such as good corrosion resistance[9-11], great wear resistance[12], paramagnetic characteristics[13], and high hardness[14] , it has been widely used in micro-electromechanical systems as well as in the semiconductor industry[15]. Traditionally, the ternary or quaternary Ni alloys were developed by co-deposition technology to improve the properties of electroless Ni−P binary alloy coating, such as Ni –W−P[16,17], Ni – P−B[18,19] , Ni – Cu−P[20-22] , Ni – Co−P[23] , Ni−Sn−P[24-26], Ni – Co – P−Ce[27] , and Ni – Sn – Cu−P[28] etc. For example, researches reported that the Ni−Sn−P alloy with low Tin (Sn) content showed possessing higher corrosion resistance[21,29-31]. However, most of the works conducted on Ni-based alloys were carried out at a higher temperature as 80–95 °C[1,32-35].

Considering the demand for energy conservation and requirements for application in electronic fields, developing plating solutions that could be operated at a relatively lower temperature (40–60 °C) is in demand. studied the effect of plating temperature on morphology, crystallographic structure, chemical composition and deposition rate of Ni-P film. However, electroless Ni-based alloys deposition at low temperature is usually at the cost of reducing the deposition rate. According to the literature [21,24-26,27], electroless deposition of Ni−Sn−P alloy coating at low temperature with a relatively high deposition rate has not been reported. In this perspective, the present work focuses on obtaining electroless Ni−Sn−P alloy coating at a low temperature by using sodium stannate (Na2SnO3) as the tin source, investigating the effect of Na2SnO3 on the deposition procedure and the mechanism of Ni−Sn−P electroless deposition procedure at low temperature.

2.4 INFLUENCING PARAMETERS

2.4.1 Bath composition and characteristics

Electroless alloy or poly alloy coatings are produced by the controlled chemical reduction of metallic ions onto a catalytic surface, the deposit itself is catalytic to the reduction reaction and the reaction continues as long as the surface remains in contact with the bath solution or the solution gets depleted of solute metallic ions. The coating is uniform throughout the contours of the substrate because no electric current is used.

Therefore, all parts of the surface area of substrate which are equally immersed in the bath have equal probability of getting ions deposited.

A typical electroless bath consists of nickel source, reducing agent, complexing agent, accelerators, stabilizer, surfactant, buffering agent etc.

Table 2.1 Electroless bath components for nickel-phosphorous-tin coating in table form

Components	Function
Nickel and Tin Ion	Source of metal
Hypophosphite	Reducing agent
Complexing agents	Stabilizes the solution
Accelerators	Activates reducing agent
Buffers	Controlling pH (long term)
Stabilizer	Prevents solution breakdown
pH regulators	Regulates pH of solution (short term)
Surfactants	Increases wettability of the surfaces

2.4.1.1 Source of tin:-

Sodium stannate ($Na_2SnO_3 \cdot 3H_2O$) is used as source of tin metal.

2.4.1.2 Nickel Source:-

Nickel sulphate($NiSO_4 \cdot 6H_2O$) or nickel chloride_hexahydrate($Cl_2H_{12}NiO_6$) is generally used as the source of nickel ion. It provides nickel ions to be deposited on the substrate. It acts as a source for the electroless decomposition.

2.4.1.3 Reducing Agent:-

Apart from nickel salt the most important bath component is the reducing agent It provides the electrons for reduction process of Nickel. Some of the most commonly used reducing agents are Sodium Hypophosphite, Sodium Borohydride, Hydrazine. Among these the predominant one is sodium hypophosphite, which forms as coloursless hygroscopic crystal which are readily soluble in water.

Sodium Hypophosphite bath

Hypophosphite baths are generally used due to high deposition rates, increased stability and greater simplicity of the bath control. The mechanism of the electroless deposition reactions taking place are still not well understood [10] . However there are two mechanisms which are widely accepted, Electro chemical mechanism and Atomic hydrogen mechanism.

In electrochemical mechanism the catalytic oxidation of the hypophosphite yields electrons at the catalytic surface which in turn reduces nickel and hydrogen ions.

In atomic hydrogen mechanism the atomic hydrogen is released as a result of the catalytic dehydrogenation of hypophosphite molecule adsorbed at the surface.

Simultaneously, some of the absorbed hydrogen reduces a small amount of the hypophosphite at the catalytic surface to water, hydroxyl ion and phosphorus. Most of the hypophosphite present is catalytic, which is oxidized to orthophosphite and gaseous hydrogen, causing low efficiency of electroless nickel solutions for alloy coating while the deposition of nickel and phosphorus continues.

2.4.1.4 Complexing agents and stabilizers

There are three principal functions that complexing agents perform in the electroless nickel plating bath :

1 They exert a buffering action that prevents the pH of the solution from falling too fast

2 They prevent the precipitation of nickel salts, e.g., basic salts or phosphites.

3 They reduce the concentration of free nickel ions by forming meta-stable complexes.

Moreover, the complexing agent also influences the reaction mechanism and deposition rate and hence the deposit. The deposition rate gradually increases up to that optimum concentration and then falls. Ethylene diamine is the popularly used complexing agent in case of reduction by borohydride whereas Sodium acetate is used as complexing agent for hypophosphite reduced coating. Ammonium fluoride improves the deposition rate and the buffering capability of Ni–P bath . Generally the complexing agents are made of organic acids or their salts viz. acetate, succinate, propionate, citrate, etc.

In this process, metal deposition is driven by the catalytic oxidation of the reductant on the substrate surface . Major advantages over the electro deposition process include the formation of a uniform deposit on irregular surfaces, direct deposition on surface activated non conductors, and the formation of less porous, more corrosion resistant deposits. However, sudden bath decomposition can result in an increase in costs and the production of environmentally hazardous pollutants due to the large waste generation. To overcome the problems related to the bath decomposition, EN deposition solutions normally contain trace amounts of stabilizers to prevent the homogeneous reactions that trigger the random decomposition of the entire bath.

Some stabilizers function through the preferential adsorption (poisoning) to the catalytic surface. Thus, stabilizer present even in trace quantities may dramatically slow down the rate of the hypophosphite oxidation . The ability of these compounds to stabilize the electroless plating bath is influenced by several parameters such as their concentration, pH, temperature, solution fluid dynamics, the concentration of reducing agents, and the presence of foreign bodies. Of these, the stabilizer concentration is considered to be the most crucial parameter. Each stabilizer characterizes an optimum concentration depending on the characteristics of the metallic coating desired. In addition, stabilizers can have more than one influence on the bath performance and, depending on their concentration, can act as accelerators or inhibitors of the deposition. In addition, they can lead to the co-deposition of S and Pb, act as brighteners and/or leveling agents,and may also influence the P content in the deposit.

2.4.1.5 Effect of surfactants

Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids or a liquid and solid surface. In an electroless nickel bath, presence of surfactant promotes the coating deposition reaction between the bath solution and the immersed substrate surface. Elansezhian et al. studied the effect of two surfactants viz. sodium dodecylsulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB) on the surface topography of electroless Ni–P coating. It was found that surface finish of the coated layer significantly improved when the concentration of the surfactant exceeded about 0.6 g/l. But at the lower levels of concentration the surface finish was found to be poor . Also hardness of deposits increased with the addition of the surfactants. Also by adding the above two surfactants during deposition of Ni–P, the phosphorus content had gone up resulting in improved quality of the deposits. Particularly it improved the corrosion resistance of the coating. Influences of anionic surfactant (sodium dodecyl benzene sulphonate, sodium lauryl sulphate) and cationic surfactant (triethanolamine) on deposition of Ni–P–nanometer Al_2O_3 composite coatings were investigated. Deposition using cationic surfactant (triethanolamine) showed fast deposition rate, good abrasion resistance and uniform dispersion of Al_2O_3 particles

2.4.1.6 Accelerators:-

They are used to activate hypophosphite ions and accelerate the deposition rate. Anions of some mono and dicarboxylic acids, flourides are commonly used as accelerators.

2.4.1.7 Buffering Agent:-

Buffering agents are used to control the pH of the bath. The pH of the bath is maintained in acid range for bath stability, but the generation of hydrogen lowers the pH; to prevent this, alkaline salts of Na and K or ammonium ions are usually added.

2.4.2 Temperature:

Temperature is the most important of parameters affecting the deposition rate of electroless coating. Since many of the individual reaction stages only take place at a significant rate above 50°C, acid-type electroless nickel baths in particular must be operated at temperature values significantly above this value. Generally all the acidic hypophosphite and alkaline borohydride baths operate between 85°C and 95°C. Apart from the deposition rate, temperature also affects the phosphorous content of the deposit and hence its properties. For this reasons, accurate temperature control of electroless nickel baths is essential. The accuracy of thermostat used to control bath temperature should be checked periodically using a mercury-in glass thermometer.

2.4.3 pH value:

Raising the pH has following effect:

1 Increased deposition rate, in a manner more or less linearly dependent on pH at a given temperature.

2 Lowering the solubility of the nickel phosphate. Deposition of this unwanted component may initiate decomposition and often leads to rough deposits

3 Reduction in the phosphorous content of the deposit.

Lowering of the pH can lead to:

1 Prevention of the deposition of basic salts and hydroxides.

2 More effective buffering action of species in the bath.

3 At pH below 4, a retarded deposition rate and attack of the deposit by the solution.

2.4.4 Time:

The coating rate increases with increase in coating time. The more the time available for coating the more thick the coating will be. However, the extent of increase in thickness is not linear throughout the entire duration of plating and it saturates after some time. This is due to the accumulation of oxidation product in the plating bath.

2.5 PROPERTIES OF ELECTROLESS NI-SN-P COATINGS

2.5.1 MICROSTRUCTURE OF COATINGS

2.5.1.1 As Coated

The properties of EN coatings are fully dependent to their microstructural characteristics. The amount of phosphorous and tin that present in electroless Ni-Sn-P deposits control their microstructure and properties.

During the deposition of electroless nickel films, the growth of the film starts at isolated locations on the substrate. The whole substrate is then covered by lateral growth. XRD patterns showed that electroless Ni-Sn-P coatings are mixture of amorphous and crystalline in as-plated condition.

2.5.1.2 HEAT TREATED

When electroless nickel films of different phosphorous and tin contents are heat treated at various temperatures, the phases present in the as-deposited films undergo definite structural changes. The XRD patterns of the heat treated Ni-Sn-P coatings confirm the crystallization of the coatings upon heat-treatment.

When the coated sample is heat treated at 300˚C for 1 hour, it produces a mixture of amorphous and nanocrystalline Ni phase, which is a supersaturated solid solution with P and Sn, precipitates from the Ni-Sn-P coatings. A new crystalline phase of Ni_3P precipitates from the coatings if the annealing temperature reaches 400˚C in addition to the Ni phase. It was noticed that the grain size of the Ni_3P phase is larger than the Ni phase. With the further increase of the temperature the grain size of both the phases increase and it was seen that the grain size of the Ni phase become larger than the grain size of the Ni_3P phase at higher temperature i.e. at 600˚C.

It was revealed that the crystalline phase in the Ni-Sn-P coatings is a supersaturated Ni solid solution with P and Sn. The incorporation of the larger Sn atom in the f.c.c Ni matrix causes a lattice change and peak shift because the peaks of the Ni phase in the XRD patterns have been observed to be slightly shifted to a lower angle for both Ni (111) and Ni (200).

2.5.2 **HARDNESS**

A major factor contributing to increased resistance to mechanical abrasion of electroless coating is hardness. There are three major parameters affecting the hardness of these coatings, namely, tin content, time, and the temperature of the applied post heat treatment. The hardness of an EN deposit is especially important when superior wear resistance is required.

A study on the effect of heat treatment on the microhardness of electroless Ni-P composite coating showed that the particles incorporated into the Ni-P matrix increase the hardness of the coating and such composite coatings are much harder than the Ni-P coating and after heat treatment at 400^0C the hardness of both Ni-P and composite coatings increases where composite coatings showed higher hardness than comparing to the electroless Ni-P coating. Peak profile analysis of electroless nickel coatings showed that the amorphous and crystalline components of the EN coatings changed with the heat treatment. There is a decrease in the amorphous phase with an increase in heat treatment temperature up to 300^0C but beyond 300^0C, no amorphous component was detected in the EN diffraction patterns obtained from the XRD analysis.

The hardness of the deposits could be increased by adding tin either in an amorphous or crystalline state. The adhesion of both deposits is similar as in an as plated state, yet in a heat treated condition and it was seen that the ternary alloy was stronger than the binary one. It is observed that the hardness of the Ni-Sn-P deposit increases slowly up to 1045 HK at 350˚C during a ultrahardness tester loaded with Knoop indenter at a indentation load of 10g and then increases quite markedly to 1623 HK at 400˚C, while the maximum value of hardness for the Ni-P coating is 1240 HK and could sustain at 1136 HK when heat treated at 550˚C.

2.5.3 WEAR RESISTANCE

One of the unique characteristics of EN deposition is the superior wear resistance of the coatings. The mechanism of wear of electroless Ni-P deposit depends on the attractive force that operates between the atoms of nickel from the coating and iron from the counter disk. Adhesive wear is characterized by the transfer of material from one surface to other as a form of wear debris. There are several factors which influence the adhesive wear, those are hardness, degree of adhesion between the interacting surfaces and the rate of formation of surface oxide film. If the materials are hard or have low mutual solubility then mild adhesive wear take place. Mild adhesive wear can lead to considerable formation of oxide layer at the contacting surface resulting in a low or negative wear depth profile.

Wear and friction measurement was carried out on Ni-P and Ni-Sn-P using pin-on- disc wear testing facility with a load of 40N. It is observed that with the increase of tin content the wear resistance of the coating increases. This is due to the solid solution strengthening by tin of nickel matrix. The coefficient of friction is found to be high and further increased with the increase of applied normal load. The frictional coefficient is found to be higher in as plated condition compared to heat treated condition.

From the above discussion it can be said that the wear rate is correlated with the hardness value. The hardness of these coatings is also seen to increase with increasing tin content. It was observed that the wear rate increases with increasing load and Ni-Sn-P coatings show higher wear resistance. In case of electroless deposition, harder deposits are always found to wear out lesser than the softer deposits. Specific wear rate is seen to be lowest in the case of coating subjected to heating at 400˚C. This is due to the maximum hardness of the coatings achieved by heating at this temperature. When heated beyond this temperature the specific wear rate is found to increase due to the softening of coatings by grain coarsening.

It is easy to calculate the wear resistance from the hardness (H) and young's modulus (E). The ratio H/E has been recently introduced as an important factor for the prediction of wear resistance, along with the use of hardness alone. In the case of materials having similar hardness, the best wear resistance is observed when Young's modulus is lower and thus when the H/E ratio is higher.

2.5.4 CORROSION CHARACTERISTICS

Corrosion resistance is mainly associated with the amorphous structure of the coating. But it is evident that the corrosion resistance of the as-plated Ni-Sn-P coating is not the highest, although it is amorphous state. It was seen that the coatings annealed at 200˚C has the lowest value of J_{corr}, while the J_{corr} of the coating treated at 400˚C reaches the highest value, andthen drops down over 400˚C.

In order to describe the variation of the corrosion resistance with annealing temperature the state of residual stress within the coating should be considered. Corrosion resistance of the coatings is affected by the stress state of the coating. Larger tensile stress tends to greater tendency for corrosion to occur. The electroless plating is accompanied by hydrogen evolution. The hydrogen atoms are occluded in as-plated deposits, generating internal tensile stress within the coatings. When the coating is subjected to heating process, relief of the tensile stress is expected, which may enhance corrosion resistance of the coatings.

2.5.5 ROUGHNESS CHARACTERISTICS

A comparative study was done between electroless Ni-P-Sn and sputtered Ni-P-Sn considering the surface characteristics. The surface roughness of the sputtered Ni-P and Ni- P-Sn was found to be smaller than electroless coating surface. But after heat treatment at 400^0C and 450^0C the nodular surface of the electroless deposits tended to be round-off and reduce the roughness. On the contrary the roughness of the sputtered Ni-P and Ni-P-Sn coatings was increased as compared to that of the as-deposited ones. But still sputtered coatings have smaller roughness comparing to the electroless coatings even after heat treatment.

2.6 SCOPE OF PRESENT WORK

The literature review done above clearly reflects that the characteristics of Ni-P-Sn coating have currently become an active field of research. Especially due to its superior qualities as a coating material than Nickel-Phosphorous, the former has created a huge impact among the enthusiasts in this field. Many scientists and researchers have already had much contribution in this regard as seen in the literature review. Although there have already been many contributions in the study of Ni-P-Sn as a coat material, some areas still need to be enlightened more clearly. One of the areas where there is still much scope of work to be done is the tribological properties of the Ni-P-Sn coatings viz. friction and corrosion characteristics. It is seen through the literature review that a very little work has been done in this regard and almost no work has been done to optimize the process parameters of electroless coating in order to have improved tribological properties of electroless Ni-P-Sn coatings. The present work is a humble attempt in that direction.

Chapter 3

EXPERIMENTAL DETAILS

This chapter provides an overview of design of experiments, design factors, the coating process, materials, and instruments used for the experiment.

3.1 INTRODUCTION

The ability to deposit hard coating on a wide range of substrate surface and still maintain adequate structural and functional properties is a very desirable objective in the quest to optimize product economics. The most economical process is to deposit metallic coatings on many engineering components. This is mainly because their rates of deposition can provide the required product quality in acceptable process times at relatively low capital and operating costs.

The preparation of electroless nickel based composite coatings with excellent comprehensive properties is highly dependent on the stable dispersion of the nano particles in plating bath, otherwise the so-called composite coatings would have non-uniformly distributed particulates and numerous defects, owing to the segregation and agglomeration of the nano particles with high surface energy and activity in the plating bath. Fortunately, this can be conveniently realized by capping the nano particles with specially selected surface- modifying agents.

3.2 DESIGN OF EXPERIMENTS

Design of experiments (DOE) is a technique to obtain and organize the maximum amount of conclusive information from the minimum amount of work, time, energy, money, or other limited resource. The DOE approach can economically satisfy the needs of problem solving and product/process design optimization projects in the manufacturing industry. By learning and applying this technique, it is possible to significantly reduce the time required for experimental investigations. Industrial physicists can no longer afford to experiment in a trial-and-error manner, changing one factor at a time. A far more effective method is to apply a computer-enhanced, systematic approach to experimentation, one that considers all factors simultaneously. That approach is called design of experiments (DOE). Experimental design methods have found wide application in many disciplines. In fact we may view experimentation as part of the scientific process and as one of the ways we learn about how systems or processes work. The concepts of design of experiments have been in use since Fisher's work in agricultural experimentation, approximately half a century ago. Fisher successfully designed experiments to determine optimum treatments for land to achieve maximum yield. Numerous applications of this approach, especially in the chemical and pharmaceutical industries, are cited in the literature.

In general, a system or process can be visualized as a combination of machines, methods, people and other resources that transforms some input (substrate materials, chemicals, machines, equipments, energy, manpower, etc.) into an output (deposited mass, compositions, structures, properties) that has one or more observable responses. Some of the process variables ($x_1, x_2,.., x_p$) are controllable (temperature, reducing agent, metal source, pH, bath load, etc.) i.e. they can be suitably changed to control the process response, whereas other variables (z_1, z_2, …, z_n) are uncontrollable (errors in measuring instrument, impurities in substrates, human errors, etc.) i.e. they can't be controlled in any way

The design of experiment is a test or series of tests where preplanned changes are made to the controllable variables of a process or system so that the reason for changes in the

Response can be observed and identified. So, deign of experiments refers to the systematic and scientific methods which are followed for planning the experiments such that the experiments can be performed in the most efficient and economical way to get the required data that will result in valid and objective conclusions. This type of statistical approach to experimental design is required if we wish to draw a meaningful conclusion from the observed data. So, basically, design of experiment (DOE) refers to the process of planning, designing & analyzing the experiment so that valid & objective conclusion can be drawn affectively and efficiently. In performing DOE, we will intentionally make changes to the input process variables or factors in order to observe corresponding changes in the output process.

DOE can be highly effective when it is necessary to:

- Optimize product and process designs.
- Study the effects of multiple factors on the performance.
- Solve production problems by objectively laying out the experiments.
- Study the influence of the individual factors on the performance.
- To study the significance of each factors on the system response.
- To find out the tolerance level of the factors.
- To allocate quality assurance resources based on the objective data.
- It will indicate whether a supplier's part causes problem or not.
- How to combine different factors to their proper settings to get the best results.

3.3 OVERVIEW OF TAGUCHI PHILOSOPHY

By early 1960's a researcher of Japan Dr. Taguchi introduced a technique to make the experimental technique more user-friendly and applied it to improve the quality of manufactured products which is known as design of experiment (DOE). He performed extensive research utilizing the DOE technique to improve the quality of manufactured products. Dr. Taguchi's standardized version of DOE, popularly known as the Taguchi method or Taguchi approach, was introduced in the USA in the early 1980's. Today it is one of the most effective quality building tools used by engineers in all types of manufacturing activities.

In robust parameter design, the primary goal is to find factor settings that minimize response variation, while adjusting (or keeping) the process on target. After determining which factors affect variation, it is necessary to find settings for controllable factors that will either reduce the variation, make the product insensitive to changes in uncontrollable (noise) factors, or both. A process designed with this goal will produce more consistent output. A product designed with this goal will deliver more consistent performance regardless of the environment in which it is used. Engineering knowledge should guide the selection of factors and responses. It is necessary to scale control factors and responses so that interactions are unlikely. When interactions among control factors are likely or not well understood, it is necessary to choose a design that is capable of estimating those interactions. Noise factors for the outer array should also be carefully selected and may require preliminary experimentation. The noise levels selected should reflect the range of conditions under which the response variable should remain robust. Robust parameter design uses Taguchi designs (orthogonal arrays), which allows to analyze many factors with few runs. Taguchi designs are balanced, that is, no factor is weighted more or less in an experiment, thus allowing factors to be analyzed independently of each other.

The application of DOE requires careful planning, prudent layout of the experiment, and expert analysis of results. Based on years of research and applications Dr. Genechi Taguchi has standardized the methods for each of DOE application steps. Thus, DOE using the Taguchi approach has become a much more attractive tool to practicing engineers and scientists. DOE using Taguchi approach attempts to improve quality which is defined as the consistency of performance. Consistency is achieved when variation is reduced. This can be done by moving the mean performance to the target as well as by reducing variations around the target. The prime motivation behind the Taguchi experiment design technique is to achieve reduced variation (also known as ROBUST DESIGN). This technique, therefore, is focused to attain the desired quality objectives in all steps. The classical DOE does not specifically address quality.

3.3.1 OBJECTIVE OF TAGUCHI METHOD

The Taguchi method is based on statistical design of experiments and is applied at the parameter design stage to establish optimum process settings or design parameters. The following are the objectives of applying the Taguchi method:

- Making products and processes insensitive to environmental variations.
- Making products insensitive to product deterioration.
- Making products and processes insensitive to manufacturing variations.
- Making products insensitive to unit to unit variations

Taguchi's philosophy of quality improvement is to place effort onto reducing variation in products and processes at source. Rather than reduce variation in individual components by specifying tighter tolerances, Taguchi method addresses the issue by careful selection of design parameters called the factors. Reduction in variation in the final product is achievable without the additional cost of specifying tighter tolerance on the components.This approach of parameter design results in a more robust design, which is capable of withstanding variation from unwanted sources such as raw materials, components, manufacturing processes and environment.

In order to apply the Taguchi Method on industry, one may require planning, engineering, communication, statistical and work skills. Moreover, right people and right environment are crucial for the effective application of Taguchi methods for tackling process and product quality problems. The participation and commitment of top management are also vital for the successful implementation. The following key points must be taken into taken when introducing Taguchi methodology into design and production.

- Your process performance must be on a specific target.
- Your process performance getting excessive variability.
- Understanding your product and processes.
- Your product performance robust under various environmental conditions.
- Setting up tolerances on the critical parts to minimize variability.
- Variation of product and process

performance Quality improvement of products

and processes

3.3.2 THE TAGUCHI DESIGN METHOD

Taguchi technique is a powerful tool for design of high quality systems. It introduces an integrated approach to find the best range of designs for quality, performance and computational cost in a simple and efficient manner. This method has been utilized widely in engineering analysis to optimize performance characteristics within the combination of design parameters because of its proven success in greatly improving industrial product quality. The main theme of Taguchi Method is stated as, "quality variation is the main enemy and that every effort should be made to reduce the variations in quality characteristic". Taguchi introduces an approach, using experimental design for:

- Designing products/processes so as to be robust to environmental conditions.
- Designing and developing products/processes so as to be robust to component variation.
- Minimizing variation around a target value.

In this optimization technique, the process or product should be carried out in a three - stage approach such as system design, parameter design and tolerance design. System design reveals the usage of scientific and engineering information required for producing a part. This design includes the product design stage and process design stage. In the product design stage, the selection of materials, components, tentative product parameter values etc. are involved. Similarly in process design stage, the analysis of processing sequences, the selection of production equipment, tentative process parameter values etc are incorporated. The parameter design is used to obtain the optimum levels of process parameters for developing the quality characteristics and to determine the product parameter values depending on optimum process parameter values. In addition, it is expected that the optimal process parameter values obtained from parameter design are insensitive to variation in the environmental conditions and other noise factors. Therefore, the parameter design has the key role in the Taguchi method to achieve high quality without increasing the cost factor. Lastly, the tolerance design is employed to determine and to analyze tolerances about the optimum combinations suggested by parameter design. Tolerance design is required if the reduced variation obtained by the parameter design does not reach the required performance. The experimental design methods developed by Fisher had some complexity in a sense that it was not easy to use and another important thing is that, whenever the numbers of process parameters increases, a large number of experiments have to be carried out. To eliminate such problems, the Taguchi method uses a special design of orthogonal arrays to study the entire parameter space with a small number of experiments only. After obtaining the experimental results, these values are transformed into a signal - to- noise ratio.

The traditional method of calculating average factor effects and thereby determining the desirable factor levels (optimum condition) is to look at the simple averages of the results. Although average calculation is relatively simple and it doesn't capture the variability of results within a trial condition. A better way to compare the population behavior is to use the mean squared deviation (MSD), which combines effects of both average and standard deviation of the results. For convenience of linearity and to accommodate wide ranging data, a logarithmic transformation of MSD, called the signal-to- noise (S/N) ratio is recommended for the analysis of the results. So, when the S/N ratio is used for result analysis, the optimum condition identified from such analysis is more likely to produce consistent performance. Taguchi method uses the S/N ratio to measure the quality characteristics. The three categories of quality characteristics are used: smaller - the- better (minimize), larger - the -better (maximize) and nominal - the - best. In Taguchi method, the term 'signal' represents the desirable value (mean) for the output characteristic and term 'noise' represents the undesirable value (Standard Deviation or S.D.) for the output characteristic. Therefore, S/N ratio is the ratio of the mean and the S.D. The S/N ratio is used to measure the quality characteristic deviating from the desired value. Taguchi uses logarithmic functions to determine the signal-to-noise ratios for the three categories of quality characteristic which are as follows:-

. The mathematical definition of S/N ratio is given by S/N = -10 log10(Li)Where Li is the loss function, or called Mean Squared Deviation (MSD). The three categories of S/N ratios are used:

Lower-the-better (LB)

$$L_i = (y_1^2 + y_2^2 + y_3^2 + ...) / n = \frac{1}{n}\sum_{i=1}^{n} y_i^2$$

Higher-the-better (HB)

$$L_i = (\frac{1}{y_1^2} + \frac{1}{y_2^2} + \frac{1}{y_3^2} + ...) /n = \frac{1}{n}\sum_{i=1}^{n} \frac{1}{y_i^2}$$

Nominal-the best (NB)

$L_i = ((y_1\text{-}m)^2 + (y_2\text{-}m)^2 + (y_3\text{-}m)^2 + ..) / n = \frac{1}{n}\sum_{i=1}^{n}(y_i - m)^2$

where,

y1, y2, y3, . . .= Results of experiments

m = target value of result,

n = Number of repetitions

Thus a larger S/N ratio represents a better quality characteristic because of the minimization of noise and the corresponding process parameters are insensitive to the variation of environmental conditions and other noise factors.

Taguchi method is employed with the following procedure in order to optimize the process parameters for electroless Ni-P coating:

- Identify the performance characteristics and select process parameters to be evaluated.
- Determine the number of levels for the process parameters and possible interactions between the process parameters.
- Select the appropriate orthogonal array and assignment of process parameters to the orthogonal array.
- Conduct the experiments based on the arrangement of the orthogonal array.
- Calculate the total loss function and the S/N ratio.
- Analyze the experimental results using the S/N ratio and ANOVA.
- Select the optimal levels of process parameters.
- Verify the optimal process parameters through the confirmation experiment.

3.4 IMPLEMENTATION OF TAGUCHI DESIGN METHOD

In this study the Taguchi design method has been implemented in order to optimize the process parameters in electroless nickel phosphorous tin coating developed on copper substrates. Here we basically studied the tribological properties of electroless nickel phosphorous tin coating.

Our fundamental objective is to optimize the process parameters in order to obtain optimum surface roughness, friction and wear and to find out the optimum testing conditions. In order to obtain multiple performance characteristics a grey relational method along with the Taguchi Technique is also used. Optimization methodology adopted in this study was divided into four phases such as planning, conducting, analysis and validation. Taguchi method of design of experiment involves establishment of large number of experimental situation described as orthogonal arrays to reduce experimental errors and to enhance their efficiency and reproducibility of the laboratory experiments. Each phase has separate objective, inter connected in sequence wise in order to achieve the overall optimization process. Adopting the Taguchi approach, the number of analytical explorations required to develop a robust design is significantly reduced, with the result that both the overall testing time and the experimental costs are minimized.

3.4.1 Determination of controllable factors and their initial level settings

The control parameters are thought to have significant effects on the quality characteristics of the process. Control (process) parameters are those design factors that can be adjusted and maintained within a specific range. Hence the control factors and their level settings are adjusted in such a manner the experimental design are less sensitive to the effects of noise.

The bath compositions and the operating conditions for electroless Ni-P-Sn coating are selected after a large number of trials and proper ranges of the parameters to be varied are suitably chosen. From the existing literature it was found that the source of nickel ions, reducing agent, source of tin ion and annealing temperature were the most important factors which played a major role in controlling the properties of Ni-P-Sn coating. Hence, these factors were incorporated as the controllable factors in the present study and were configured within an inner orthogonal array in order to explore the influence of main and interaction effects for this model. Taguchi method uses orthogonal arrays for determining the optimized coating parameters. A minimum number of experiments is suggested by the orthogonal arrays in which the direct effect of all the factors at their different levels and the interaction of factors at different levels was considered to the response. Coatings' response varied with the variation in bath temperature, concentration of the source and the concentration of the reducing agent and has been taken as our design factors. The variation in the levels of these three parameters are shown in table

Bath Constituents	Values	Operating Condition	Values
Nickel Sulphate (g/l)	15	pH	7-8
Sodium Hypophosphite (g/l)	12 – 28	Temperature	90±3˚C
Sodium Citrate (g/l)	80		
Ammonium hydrogen difluoride (g/l)	15	Duration of coating	2 hrs
Sodium stannate (g/l)	6-10	Bath volume (ml)	250

Table 1 Composition and operating conditions of Ni-Sn-P plating bath

3.4.2 Choice of Orthogonal Array design

Based on the Taguchi method, an orthogonal array (OA) is employed to reduce the number of experiments for determining the optimal coating process parameters. An OA provides the shortest possible matrix of combinations in which all the parameters are varied to consider their direct effect as well as interactions simultaneously. The choice of a suitable orthogonal array (OA) design is critical for the success of an experiment and depends on the total degrees of freedom required to study the main and interaction effects, the goal of the experiment, resources and budget available and time constraints. Orthogonal arrays allow one to compute the main and interaction effects via a minimum number of experimental trials. ‘‘Degrees of freedom’’ refers to the number of fair and independent comparisons that can be made from a set of observations. In the context of DOE, the number of degrees of freedom is one less than the number of levels associated with the factor. In other words, the number of degrees of freedom associated with a factor at *p*-levels is (*p*-1). The number of degrees of freedom associated with an interaction is the product of the number of degrees of freedom associated with each main effect involved in the interaction. In the present investigation, an L_{27} orthogonal array is chosen. It is important to note that the total degrees of freedom for the orthogonal array must be greater than or equal to the total degrees of freedom required for studying the effects.

The standard OAs for factors with three levels are L_9, L_{27} and so on. Here the notation ‘‘L’’ implies that the information is based on the Latin square arrangement of factors. A Latin square arrangement is a square matrix arrangement of factors with separable factor effects. Here the numbers 9, 27, etc. denote the number of experimental trials. For the present experiment, the total degrees of freedom for roughness test can be calculated as for the three level test, the three main factors take 6 [3 × (3 − 1)] DOFs. The DOF for three second-order interactions (A × B, A × C, B × C) is 12 [3 × (3 − 1) × (3 − 1)] and the total DOFs required is 18 and for the friction and wear test the DOFs in the experimental design, for the three level test, the four main factors take 8 [4 × (3 − 1)] DOFs. The DOF for three second-order interactions (A × B, A × C, B × C) is 12 [3 × (3 − 1) × (3 − 1)] and the total DOFs required is 20. The closest number of experimental trials that can be employed for the experiment is 27 (i.e. L_{27} OA). Having identified the most

Levels: **Design Factors**	1	2	3
Concentration Of Sodium Stannate (A) in g/L	6	8	10
Concentration of Sodium Hypophosphite (B) in g/L	12	20	28
Time in minute (C)	60	90	120

Table 2. Factors and their respective levels

Orthogonal arrays were employed to reduce the experiments and to determine the optimal coating. It consists of the 13 columns and 27 rows. The factors A, B and C are represented in column 1, 2 and 5 respectively, while the rest of the columns represent the interactions between the three factors. This is shown in table.

No.	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]	[10]	[11]	[12	[13]
1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	2	2	2	2	2	2	2	2	2
3	1	1	1	1	3	3	3	3	3	3	3	3	3
4	1	2	2	2	1	1	1	2	2	2	3	3	3
5	1	2	2	2	2	2	2	3	3	3	1	1	1
6	1	2	2	2	3	3	3	1	1	1	2	2	2
7	1	3	3	3	1	1	1	3	3	3	2	2	2
8	1	3	3	3	2	2	2	1	1	1	3	3	3
9	1	3	3	3	3	3	3	2	2	2	1	1	1
10	2	1	2	3	1	2	3	1	2	2	1	2	3
11	2	1	2	3	2	3	1	2	3	3	2	3	1
12	2	1	2	3	3	1	2	3	1	1	3	1	2
13	2	2	3	1	1	2	3	2	3	3	3	1	2
14	2	2	3	1	2	3	1	3	1	1	1	2	3
15	2	2	3	1	3	1	2	1	2	2	2	3	1
16	2	3	1	2	1	2	3	3	1	1	2	3	1
17	2	3	1	2	2	3	1	1	2	2	3	1	2
18	2	3	1	2	3	1	2	2	3	3	1	2	3
19	3	1	3	2	1	3	2	1	3	3	1	3	2
20	3	1	3	2	2	1	3	2	1	1	2	1	1
21	3	1	3	2	3	2	1	3	2	2	3	2	3
22	3	2	1	3	1	3	2	2	1	1	3	2	1
23	3	2	1	3	2	1	3	3	2	2	1	3	2
24	3	2	1	3	3	2	1	1	3	3	2	1	3
25	3	3	2	1	1	3	2	3	2	2	2	1	3
26	3	3	2	1	2	1	3	1	3	3	3	2	1
27	3	3	2	1	3	2	1	2	1	1	1	3	2

Table 3. L_{27} Orthogonal arrays with design factor.

3.5 Instruments used

- Electronic Balance (Resolution → 0.01 g) used for weighting the chemicals used.

Citizen Scale (i) Pvt. Ltd. Model No. CTZ302, S.No. 133 , Temp. 5-40 degree CelsiusSupply 230V, 50Hz

Fig.2: Electronic Balance

- ❖ Magnetic Stirrer Model-5MLH PLUS

EUTECH INSTRUMENTS, Model No.- S/N 2351165

REMI Elektrotechnik Ltd, RPM-1500, Temp.- 350°C

Fig.3: Magnetic Stirrer Model-5MLH PLUS

Fig.4: Magnetic Stirrer CE Model- 2MLH

- ❖ Dimmerstat

Automatic Electric Ltd., Max Load- 8AMPS, Max KVA- 2.16, Input- 240V , 50-60 Hz, Output :0-270V

- ❖ Heater, used for heating the chemical bath.

Fig.5: Dimmerstat& Heater

- ❖ Glass Beakers of denominations 50ml, 250ml and 500 ml, used for preparing and containing the chemicals, BOROSIL

Fig.6: Glass Beakers of denominations 50ml, 250ml and 500 ml

- Tweezers

Fig.7: Tweezers

Mercury thermometers

3.6 Chemical used

- Nickel (II) Sulphate Hexahydrate , Merck Life Sciences Private Limited(NiSO4. 6H2O)

- Sodium stannate(Na2SnO3·4H2O)) , LOBACHEMIE
- Ammonium hydrogen difluoride(NH4HF2), LOBACHEMIE
- Tri-sodium Citrate Dihydrate (Na3C6H5O7. 2H2O), Merck Life Sciences pvt. Ltd.
- Sodium hypophosphite (NaH2PO2·H2O), Merck Life Sciences Pvt. Ltd.

Fig.8 chemical used in bath preparation

- Palladium (II) Chloride Anhydrous (PdCl2) ,Merck Life Sciences Pvt. Ltd.
- Water Distilled (H2O) , Merck Life Sciences Pvt. Ltd.

Fig .9: distrill water

- Hydrochloric Acid(HCl) about 37%, Merck Life Sciences Pvt. Ltd

3.7 EXPERIMENTAL SETUP

3.7.1 Preparation Of Sustrate Material

For Electroless coating, Copper Strips (20 x 15 mm2) having a thickness of 0.1 mm and 99.0% purity bought from Lobachemi were cut from copper foil to be used as a substrate. After the selection of sample substrates for metal deposition, samples are subjected to rigorous cleaning processes to get rid of any foreign particles and corrosion products, at first prepared sample is rinsed with distilled water for 2 minutes to clean off any dirt particles, then cleaned sample is again acid cleaned with HCl (25% dilute) for 10 minutes to ensure the removal of any surface layer formed like rust and other oxides, finally the acid cleaned sample is rinsed again with distilled water for 2 minutes to remove acid on the surface of the samples. Then Sample is activated in Palladium chloride solution for 8-10 seconds at 55 ºC to overcome the initial energy barrier and kick start the deposition process. Then rinsed with distilled water for few seconds**.**

3.7.2 Preparation Of Electroless Ni-Sn-P Bath

Nickel sulphate is used as the source of nickel with sodium hypophosphite, which is the reducing agent and sodium citrate was added as complexing agent. The bath is prepared by adding the constituents in appropriate sequence. The pH of the solution is maintained around 9.5 by continuous monitoring with pH meter and temperature of bath is maintained by 90±2 C.The required chemicals are measured in a balance with 0.01gm resolution and then dissolved in distilled water to prepare the electroless bath. The composition of the bath is given in Table 1. Once the electroless bath is ready and the surface activation is done, the substrates were dipped in the electroless coating bath. The substrates were kept immersed in the bath for 2 hour to allow the coating to be deposited. After deposition the samples are rinsed with distilled water and then properly dried.

Bath Composition	Quantity Avg.
Nickel Sulphate ($NiSO_4.6H_2O$)	15 g/L
Sodium stannate($Na_2SnO_3·4H_2O$)	6-10 g/l
Sodium Hypophosphite (Sodium Phosphinate)($NaH_2PO_2. H_2O$)	12-28 g/l
Tri-sodium Citrate Dihydrate ($Na_3C_6H_5O_7. 2H_2O$)	80 g/l
Ammonium hydrogen difluoride(NH_4HF_2)	15 g/l
Time	1-2 hr
Bath volume	250 cm^3
temperature	85°C-95°C

Table 4: Bath Composition for Ni-Sn-P coating over copper substrates

Electroless Ni-P-Sn bath preparation step

A large number of trial experiments have been performed before deciding upon the sequence of the steps involved and the ranges of the process parameters. The following procedure has been adopted for deposition of electroless Ni-Sn-P coating on mild steel samples :

- A couple of 250 ml beakers were cleaned properly and 100ml distilled water was taken in one of the beakers (A) and 150ml distilled water was taken in the other beaker (B).
- In beaker A the following chemicals are added sequentially with stirring and heating done by a magnetic stirrer cum heater :
    1. Nickel sulphate $\rightarrow$ (3.75 g)
- In beaker B the following chemicals are added sequentially with stirring and

heating done by a magnetic stirrer cum heater :

1. Ammonium Hydrogen Difluoride $\rightarrow$ (200 g)
2. Sodium Hypophosphite $\rightarrow$ (3 – 7 g)
3. Tri- Sodium Citrate Dihydrate$\rightarrow$ (35 g)
4. Sodium Stannate$\rightarrow$ (1.5–2.5 g)

- The warm solutions in beakers A and B are then mixed to make a total bath volume of about 250 ml.
- In the total bath the sodium Stannate (6-10g) is added.
- The pH is measured by pH strips (range : pH1 - pH14) and is found to be in the range of 7 – 8 which is kept constant.

The steps for electroless Ni-P-Sn deposition

- The Copper specimens, after thorough cleaning are given a pickling treatment with dilute hydrochloric acid for one minute. Subsequently, they are rinsed in distilled water prior to coating.
- The prepared 250ml of the electroless bath solution was taken in a 400 ml beaker and placed on a temperature controllable heater. The temperature was slowly raised to the deposition temperature (90°C).
- Activation solution (Palladium chloride) was taken in a separate beaker and heated to a temperature of about 50°C - 55°C.
- The cleaned mild steel samples were first rinsed in distilled water and then dipped in the activation solutions for about a few seconds and again rinsed in distilled water.
- The activated samples were then placed in the sample holder and submerged in the electroless bath.
- While performing the deposition the temperature was kept constant by manual monitoring with a thermometer.
- After two hour of deposition the samples were taken out and rinsed with distilled water.

The above procedure is repeated one more time more for each specimen. After effectively two hours of deposition, the samples are taken out of the bath and dipped into distilled water. After that the samples are heat treated.

3.8 Scanning Electron Microscopy (SEM)

Scanning electron microscope is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons which scans the specimen surface in vacuum, imaging one point at a time. The interaction of the electron beam with every point of the specimen surface is registered, forming the entire image. The signals used by a scanning electron microscope to produce an image result from interactions of the electron beam with atoms at various depths within the sample. In secondary electron imaging, or SEI, the secondary electrons are emitted from very close to the specimen surface. Consequently, SEM can produce very high-resolution images of a sample surface.

Since the wavelength of the electron beam is much lower than the wavelength of the visible light, the magnification of SEM is much higher, nearly thousands of times, than that of the optical microscopes. Resolution of SEM is about 1nm to 20nm.The SEM analysis was performed on the SOF software, employing aJEOL-Jsm 7610F machine

Fig.10 (a) Scanning Electron Microscope

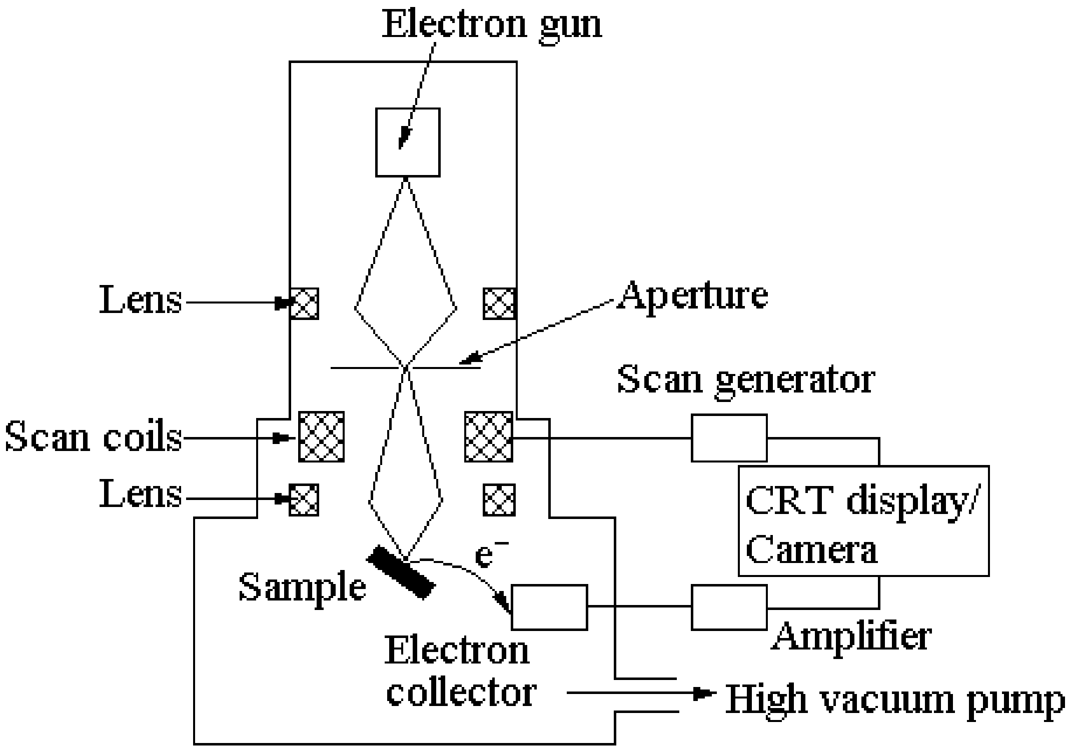


fig: 10 (b)Schematic diagram of the Scanning Electron Microscopy

3.9 Energy Dispersive X-Ray Analysis (EDX)

Energy dispersive X-ray analysis (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample Its characteriz a unique atomic structure allowing a unique set of peaks on its electromagnetic emission spectrum(which is the main principle of spectroscopy).

To stimulate the emission of characteristic X-rays from a specimen, a high-energy beam of charged particles such as electrons or protons, or a be ation capabilities are due in large part to the fundamental principle that each element has am of X-rays, is focused into the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer.

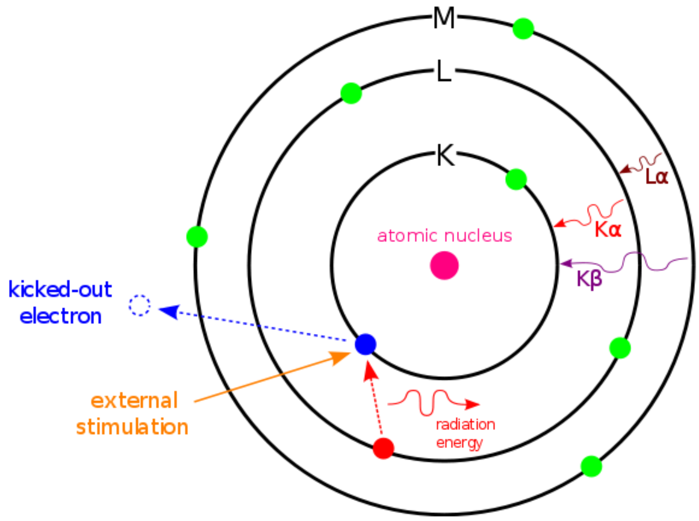


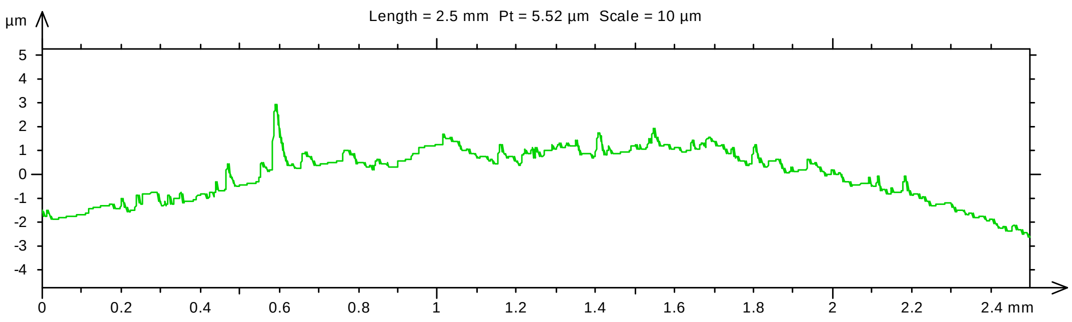
Fig.11: Schematic of the principle of EDX

As the energies of the X-rays are characteristic of the difference in energy between the two shells and of the atomic structure of the emitting element, EDX allows the elemental composition of the specimen to be measured.

3.10 Measurement Of Surface Roughness

Surface roughness is the deviation or undulation of a surface from a mean level for a particular sample length. Taylor-Hobson Talysurf is a stylus and skid type of instrument working on carrier modulating principle. Its response is more rapid and accurate as comparred to Temlinson Surface Meter. The measuring head of this instrument consists of a sharply pointed diamond stylus of about 0.002 mm tip radius and skid or shoe which is drawn across the surface by means of a motorised driving unit. In this instrument the stylus is made to trace the profile of the surface irregularities, and the oscillatory movement of the stylus is converted into changes in electric current by the arrangement as shown in Fig. The arm carrying the stylus forms an armature which pivots about the centre piece of E-shaped stamping. On two legs of (outer pole pieces)'the E-shaped stamping there are coils carrying an a.c. current. These two coils with other two resistances form an oscillator. As the armature is pivoted about the central leg, any movement of the stylus causes the air gap to vary and thus the amplitude of the original a.c. current flowing in the coils is modulated. The output of the bridge thus consists of modulation only as shown in graph.Example

Fig 12 surface roughness diagram

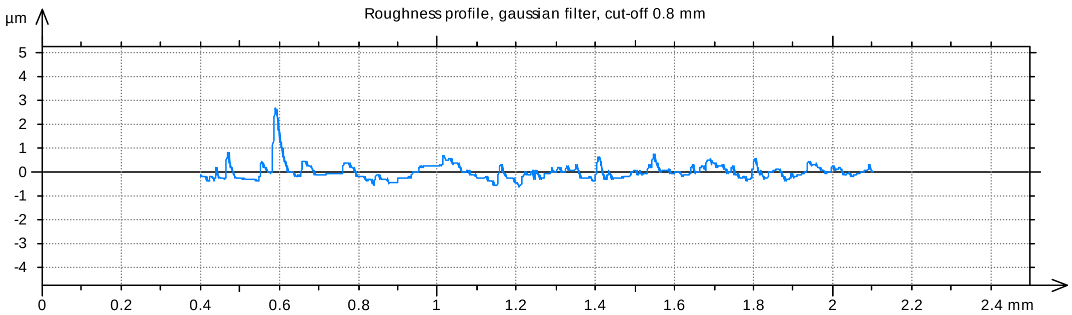


Parameters calculated on the profile Profile

```
* Parameters calculated by mean of all the sampling
lengthes.
* A microroughness filtering is used, with a ratio
of 2.5 µm.

Roughness Parameters, Gaussian filter, 0.8 mm

   Ra    = 0.234 µm
   Rq    = 0.334 µm
   Rp    = 1.71 µm
   Rv    = 0.575 µm
   Rt    = 3.24 µm
   Rsk   = 3.54
   Rku   = 24.7
   Rz    = 2.28 µm
   Rmr   = 0.9 %    (1 µm under the highest peak)
   Rdc   = 0.458 µm (20%-80%)
   RSm   = 0.0824 mm
   RDq   = 3.1 °
   RLq   = 0.0388 mm
   RLo   = 0.171 %
   RzJIS = 1.14 µm
   R3z   = 1.08 µm
   RPc   = 1.18 pks/mm      (+/- 0.5 µm)
   Rc    = 0.803 µm
   Rfd   = 1.36
   RHSC  = 2 peaks  (1 µm under the highest peak)
   RDa   = 1.45 °
   RLa   = 0.0581 mm
   Rmax  = 3.19 µm
   Rtm   = 2.28 µm
   Ry    = 3.19 µm
   RH    = 0.858 µm
   RD    = 12.1 1/mm
   RS    = 0.0971 mm
   RVo   = 0.00228 mm3/mm2  (80%)
   RTp   = 0.9 %    (1 µm under the highest peak)
   RHTp  = 0.458 µm (20%-80%)
   Rrms  = 0.334 µm
```



3.11 Measurement Of Micro-Hardness

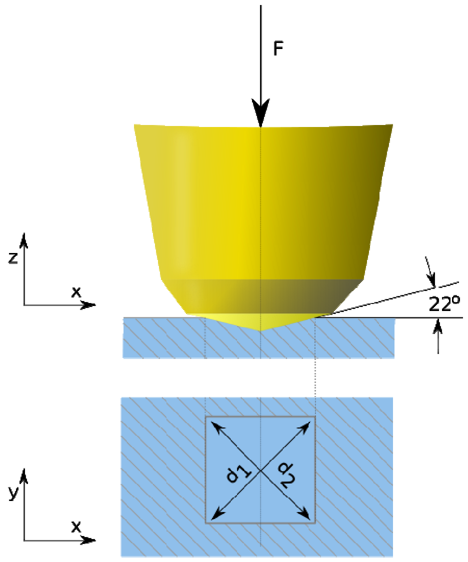
Hardness of electroless nickel is a very important factor in many successful applications

The Vickers microhardness Ni-Co-P coated mounted sample is taken as per ASTM standard E384-16 using a hardness tester fitted with a diamond indenter that is four-sided pyramid with a square base and an apex angle between opposite sides of 136° (±5’). A load of 10 gf is applied while the dwell time and indentation speed are kept at 10 s and 25µm/s respectively. An average of 6 hardness values is acquired from the microhardness tester.The indentation depth should be 10-20% of the coating thickness in order to avoid the substrate’s effect on hardness The Vickers’s hardness was calculated.By using the following equation.

$$HV = \frac{1.8544F}{d^2}$$

Where, F is load in gram and d is the mean of two diagonals created by pyramidal indent in millimetre.

Fig.13: Schematic of Vickers Hardness Indentation



3.12 Optical Microscopy

The microscope that is used for the specimen illustration or obtaining the microstructure of the given samples is a Metallurgical microscope. A metallurgical microscope refers to a high power microscope used for the purposes of viewing opaque objects (objects in which light cannot pass through) these types of microscopes are different from the typical biological microscopes in that they use the principle of reflected light microscopy.The metallurgical microscope differ from the other microscopes in the method by which the specimen illustration is done. Frontal lighting is used in the metallurgical microscopes for illuminating the opaque metal surface. This is achieved by using a plain glass reflector that is installed in the tube. A schematic diagram of the optical microscope is shown below in Fig.

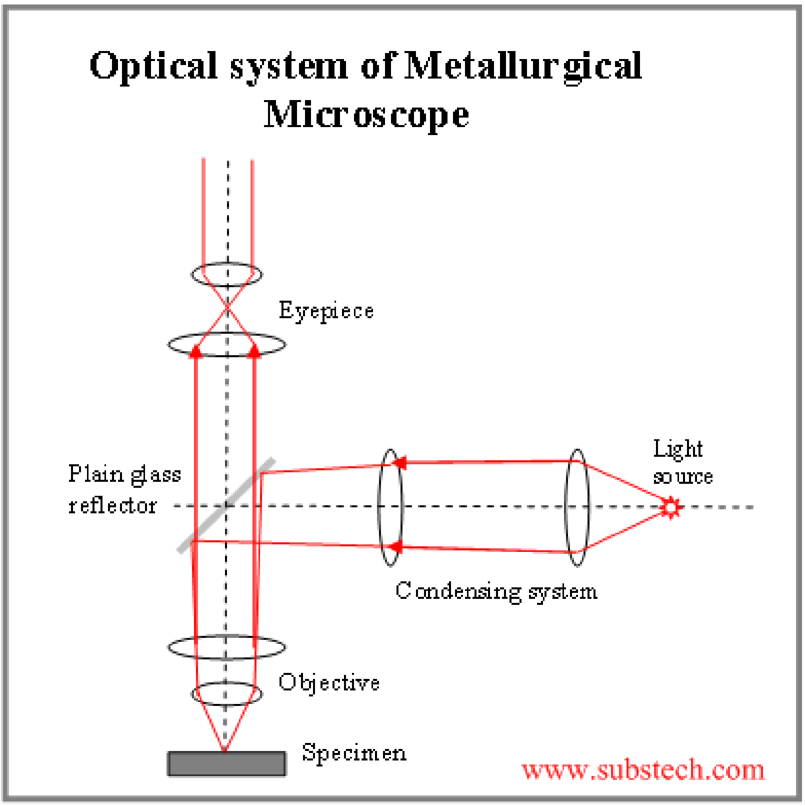


Fig.14: Schematic diagram of the optical microscope

Fig.15:The Optical microscope used while performing the tests.

3.13 X-Ray Diffraction Analysis

X-ray crystallography is a technique used for determining the atomic and molecular structure of a crystal, in which the crystalline atomscause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three dimensional picture of the density of electrons within the crystal. The basic law involved in the diffraction method of structural analysis is the Bragg's law. Atoms scatter X-ray waves, primarily through the atoms' electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an X-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron (or lighthouse) is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg's law:

Here d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the beam. These specific directions appear as spots on the diffraction pattern called reflections. Thus, X-ray diffraction results from an electromagnetic wave (the X-ray) impinging on a regular array of scatterers (the repeating arrangement of atoms within the crystal).

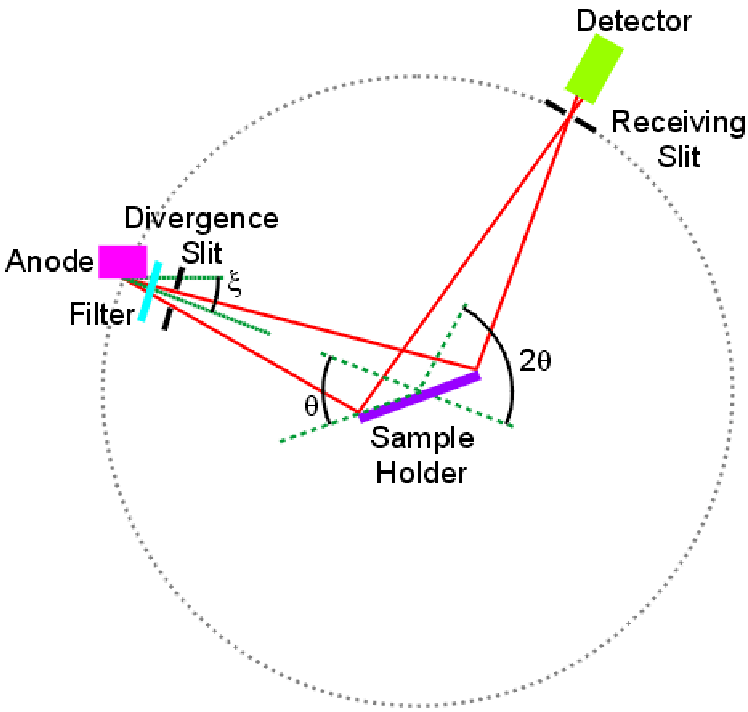


Fig. 16: Schematic of the principle of X-Ray Diffraction

Fig.17: Rigaku Ultima III X ray diffractometer

3.14 Central Composite Design

RSM is a statistical and mathematical technique that was used for the modelling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response. Using a rotatable central composite design (CCD) of experiments the response surfaces were developed. The CCD contains 6 central points, 8 factorial points, and 6 axial points.

The software was used to analyse the collected data by following the steps : Appropriate model was selected. The Fit Summary button shows the sequential *F*-tests, lack-of-fit tests and other suitability measures that was used to assist in selecting the appropriate model.

CCD is extensively used statistical method based on the multi-variant nonlinear model for the optimization of process variables. It is also used to measure the reversion of model equations and operating parameters from the appropriate experiments. Three important process parameters viz Sodium Stannate (Na_2SnO_3. $3H_2O$), sodium Hypophosphite ($NaH_2PO_2H_2O$) and temperature were considered for optimization. The relation between the response and the process parameters equation was formed called regression equation six central points were considered for the formation of a full factorial regression equation.

3.15 Characterization Of Substrate

Characterisation of Copper Substrate

From a roll of Copper foil (10mm thick, Pure copper>99.0% purity, make '*lovachemie'*) that was used as substrate for making electroless deposit experiment, a sample of 15mm x15mm section was cut out for micro-structural observation. The Optical Microscopy Image of copper substrate with Ferric Chloride($FeCl_2$) etching and un-etched microstructure of that copper foil used has been submitted in Fig.1(a)(b) From SEM observation the clear deformation lines in textured form can be visible without revealing much details.. The optical microscopy and SEM analysis was performed on the Lica and aJEOL-Jsm 7610F machine. It has been observed that the deformation lines in textural form can in the visible without any further detail of copper substrate.

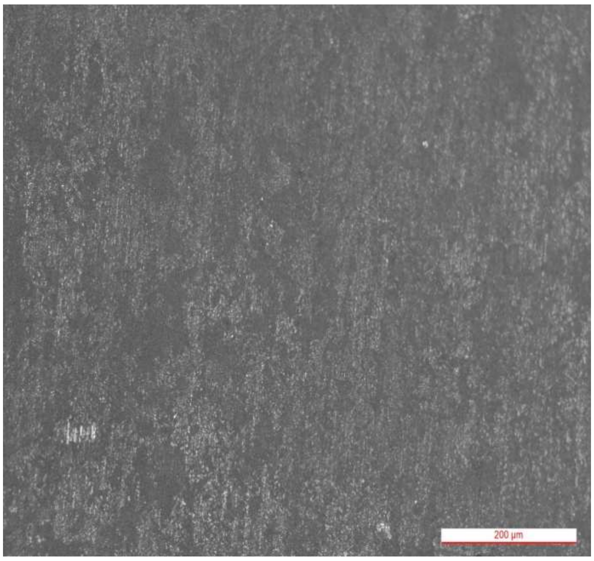


Fig.16 :Optical Microscopy Image of copper substrate with Ferric Chloride($FeCl_2$) etching

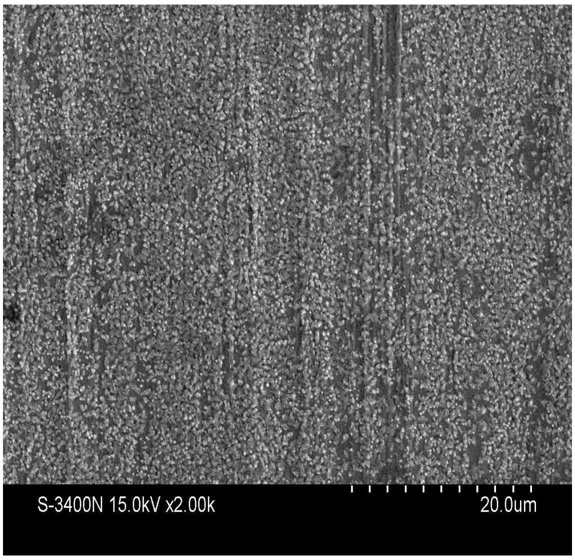


Fig.17 :The microstructure of Copper foil used in the experiment under SEM in un-etched condition reveals only flow lines for deformation without any substantial details.

3.2 phase analysis of copper substrate

samples were characterised by XRD using X-ray diffraction in RigakuUltima-III machine which range of 2θ was from 20° to 80° with a scan speed of 2° min−1) in Cu Kα radiation. X-ray diffraction studies of copper substrate confirmed the routine diffractogram of (FCC) Copper and it has showed only copper phase prominently.

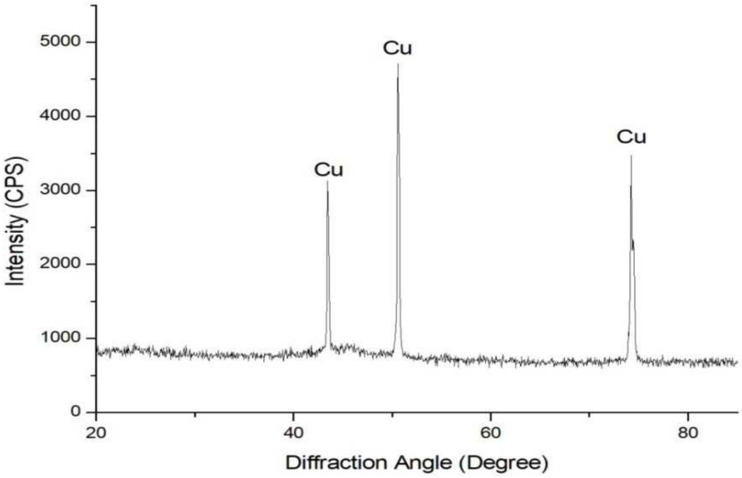


Fig.18 Energy Dispersive X-ray (EDX) pattern of Copper substrate

Fig.19

Compositional analysis of copper substrate

EDX analysis

Chapter 4

RESULTS AND DISCUSSIONS

In this chapter the significant factors and their interactions affecting the surface roughness and micro hardness of electroless Ni-Sn-P coating has been reported. An attempt has also been made for optimization of multiple performance characteristics. Results of SEM and EDX analysis are also reported.

4.1 Introduction

This chapter presents the results and discussions for the optimization of coating process parameters of electroless Ni-Sn-P coating. The analyses are done for optimizing the coating process parameters for optimum surface roughness, micro hardness. All the two analysis are done separately in order to find out the suitable coating process parameters combination for each of the above two responses. Then with the grey relational analysis optimization of multiple performance characteristics for micro hardness and also for multiple roughness parameters are done and suitable process parameters combinations are reported accordingly.

After obtaining the suitable process parameters combination, confirmation tests for all the optimum combinations are done in comparison with the initial process parameters combination in order to validate the optimum parametric combinations. Finally the results of Energy dispersive x-ray analysis (EDX),and Scanning electron microscopy (SEM) analysis are discussed. The EDX analysis is carried out to find the actual composition of elements which present at the coating.

4.2 Effect Of Parameters Of Surface roughness on Taguchi Method

Surface Roughness (Ra) Of Ni-Sn-P On Taguchi Method

4.2.1 Response Variable

The performance characteristics of these experiments/coatings is the surface roughness of the coatings. The bath parameters of the electroless deposition is optimised in order to get optimal (minimum) surface roughness

4.2.2 Determination Of Surface Roughness

The surface roughness of the coated samples was measured by Taly-Surf machine, Taylor Hobson Precision Instrument Surtronic 3+. After calibrating the Taly Surf with the standard specimen, the electroless Ni-Sn-P coated samples were tested under the same. 27 runs were considered to synthesise the coating following the Taguchi Method Design of experiments. Each runs contains 3 specimens of the size stated before. After evaluating the roughness values for each run, the instrument was checked with the standard specimen. The surface roughness corresponding to the each experiment is shown in table .

Sodium Stannate(B) in g/L	Sodium Hypophosphite(A) in g/L	Time (C) (min.)	Surface Roughness (R_a) in µm
6	12	60	0.238
6	12	90	0.391
6	12	120	0.343
6	20	60	0.487
6	20	90	0.481
6	20	120	0.471
6	28	60	0.386
6	28	90	0.234
6	28	120	0.471
8	12	60	0.181
8	12	90	0.195
8	12	120	0.334
8	20	60	0.261

8	20	90	0.115
8	20	120	0.049
8	28	60	0.224
8	28	90	0.419
8	28	120	0.372
10	12	60	0.663
10	12	90	0.375
10	12	120	0.269
10	20	60	0.325
10	20	90	0.444
10	20	120	0.264
10	28	60	0.316
10	28	90	0.265
10	28	120	0.417

Table.5 Surface Roughness of each experiment

4.2.3 Signal to Noise Ratio(SN) ratio analysis

The Signal to Noise ratio is used to optimise the bath parameters and obtain a particular combination of the levels of three different factors. Signal to Noise (SN) ratio is calculated by Smaller is better.

The S/N ratio corresponding to each experiment is shown in table 5.

Experiment Number	Surface Roughness (R_a) in µm	S/N ratio
1	0.238	12.4685
2	0.391	8.1565
3	0.343	8.1565
4	0.487	9.2941
5	0.481	6.2494
6	0.471	6.3571

7	0.386	6.5396
8	0.234	3.9719
9	0.471	6.4479
10	0.181	4.5977
11	0.195	7.8509
12	0.334	5.9342
13	0.261	11.6672
14	0.115	18.7860
15	0.049	5.2721
16	0.224	12.9950
17	0.419	7.5557
18	0.372	8.6125
19	0.663	3.5697
20	0.375	8.5194
21	0.269	11.4050
22	0.325	9.7623
23	0.444	7.0133
24	0.264	5.1612
25	0.316	2.9017
26	0.265	11.5351
27	0.417	7.5973

Table.6 S/N ratio table for smaller is better

The Signal to Noise ratio response table for each level of factors has been shown in table.

Level	A	B	C
1.	7.516	7.851	8.200
2.	9.252	8.840	8.849
3.	7.496	7.573	7.216
Delta	1.756	1.267	1.633
Rank	1	3	2

Table.7 Response Table S/N ratio

Level	A	B	C
1	0.4346	0.4251	0.4256
2	0.3816	0.3950	0.3929
3	0.4476	0.4436	0.4452
Delta	0.0660	0.0486	0.0523
Rank	1	3	2

Table 8 Response Table for Means

The response table incorporates the ranks based on delta statics. Delta statistic for each factor is the resultant of the highest average minus the lowest average. Rank 1 is given to the highest delta value and rank 2 to the next highest and likewise. Table 6 represents the mean of S/N ratio of each levels in a factor. The higher value of S/N ratio corresponds to the optimized level in that factor.

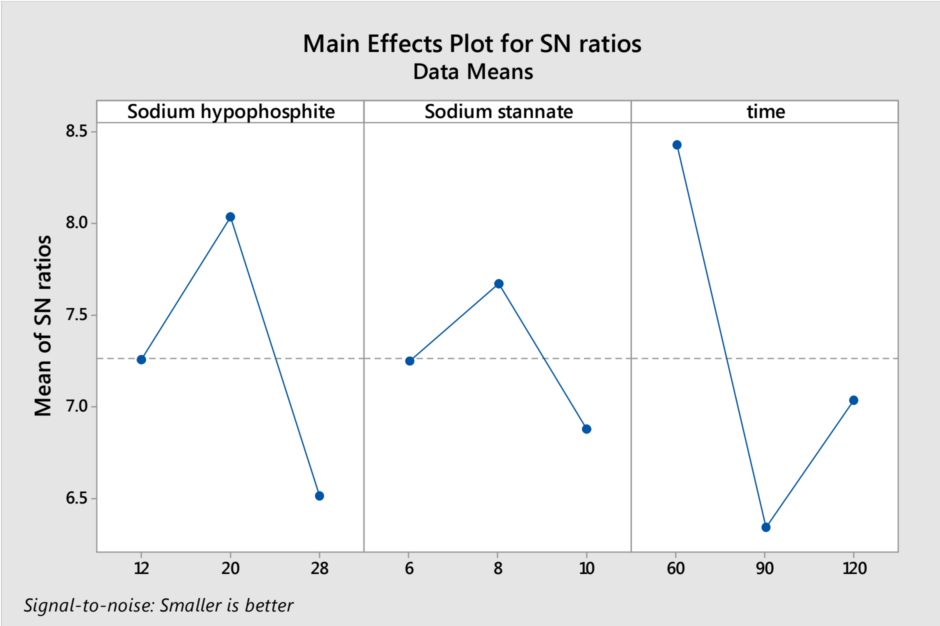


Fig.20 Main Effect Plot for S/N ratio

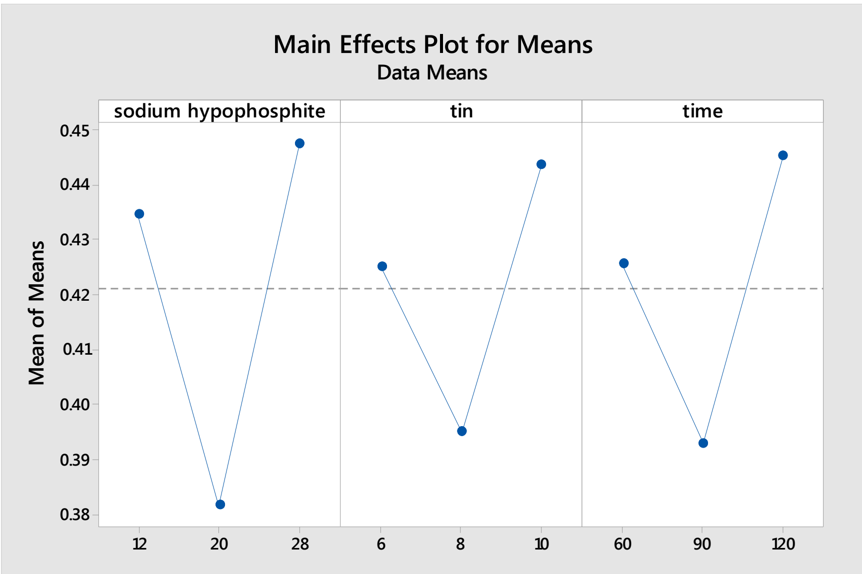


Fig.21 Main effects plot for means

Prediction	
S/N Ratio	Mean
6.10891	**0.493889**

Fig 22: The interaction plot of A and B is shown in Fig.

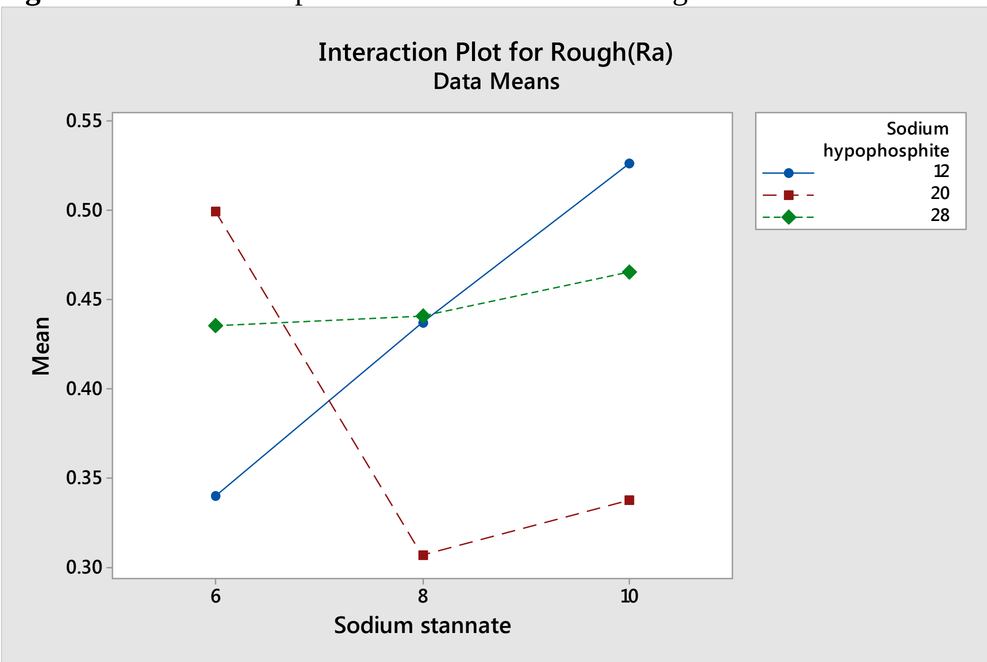


Fig.23 The interaction plot of A and C is shown in fig.

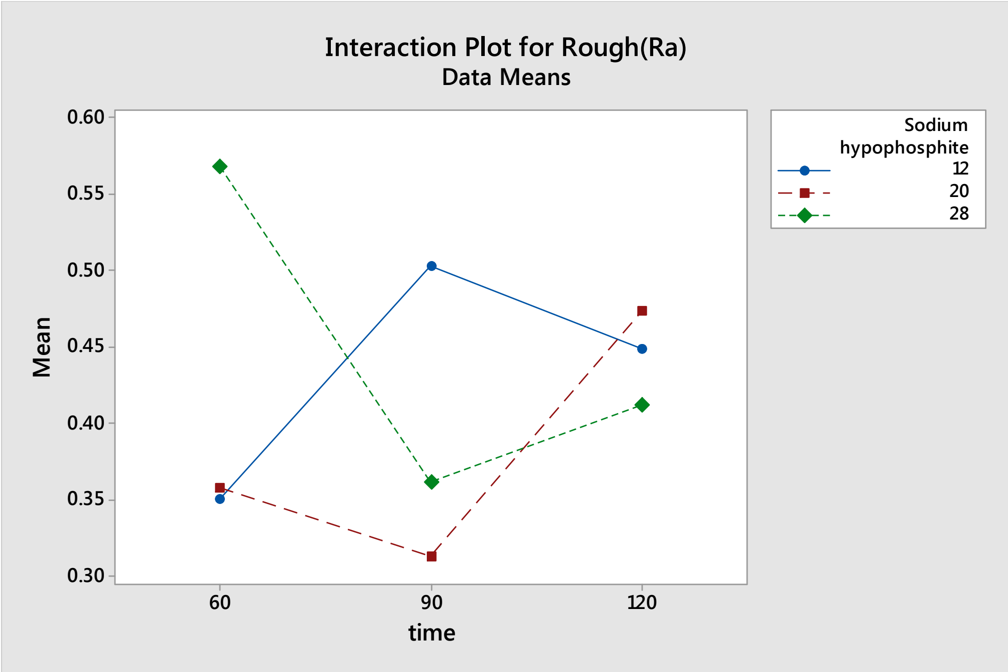


Fig.24 The interaction plot of B and C is shown in fig 5.

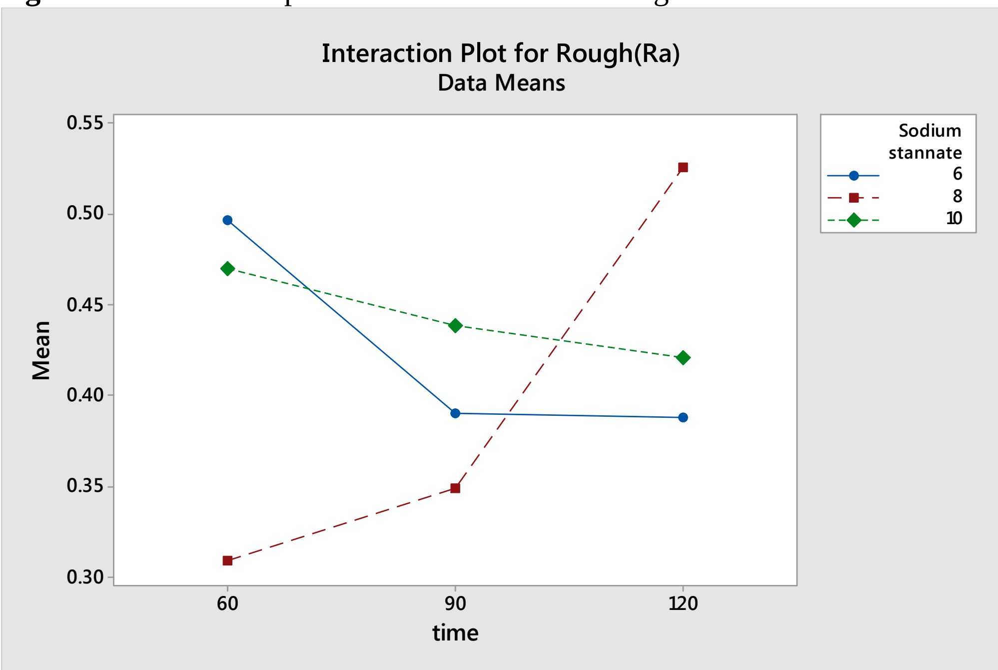


Fig.25

The mean of S/N ratios, the main effects plot for surface roughness and the interaction of each factors with one another at different levels is shown in the Fig. 1, Fig. 2 and Fig. 3-5 respectively.

The interaction plots signifies the extent to which the factors have interacted with each other. If the plots remain parallel to each other then it can be interpreted that no significant interactions has taken place between the two factors. If the plots intersect with each other or intercept each other a number of times then it signifies that strong interaction has taken place between the two factors. Fig shows strong interaction between Sodium Stannate and Sodium Hypophosphite whereas Fig. 5 and 6 show moderate interactions between Sodium Stannate time of bath and Sodium Hypophosphite and Time of electroless bath respectively.
The optimal minimum surface roughness obtained from this experiment is A1B3C3. The surface roughness for this optimal parameters is 0.493889 µm.

4.2.4 Analysis Of Variance (ANOVA)

Source	Degree Of freedom	Sum of Squares	Mean Square	F ratio	p-Value
A	2	0.02200	0.011001	0.57	0.585
B	2	0.01258	0.006289	0.33	0.729
C	2	0.01081	0.005407	0.28	0.761
A*B	4	0.13387	0.033467	1.75	0.232
A*C	4	0.10727	0.026818	1.40	0.317
B*C	4	0.09375	0.023437	1.22	0.373
ERROR	8	0.15314	0.019143		
TOTAL	26	0.53342			

Table. 9.ANOVA Results.

From table 7, based on p-value and F-ratio, it is inferred that the factors A and B will have good effect on the surface roughness of the coating. The interaction between the factors A and B will have significant impact on the surface roughness of the coatings.

4.3 EFFECT OF COATING ON MICRO-HARDNESS

4.3.1 MICRO-HARDNESS OF Ni-Sn-P ON TAGUCHI METHOD

4.3.1.1 Response Variable

The response variable in this present study is the hardness of the Ni-Sn-P coating. It is a single response optimisation process where the three factors are concentration of sodium hypophosphite (A), Sodium Stannate (A) and the coating Time (min) of the bath (C).

4.3.1.2 Hardness Measurement

The present study investigates the hardness of Ni-Sn-P coating which was deposited over soft Copper strips electrolessly.The hardness for each experiment has been shown in table 6.

Cobalt Sulphate(B) in g/L	Sodium Hypophosphite(A) in g/L	Time (C) (min.)	Harndess ($VHN_{10\,g}$)
6	12	60	1096
6	12	90	1050
6	12	120	1120
6	20	60	1060
6	20	90	1090
6	20	120	1103
6	28	60	1009
6	28	90	1150
6	28	120	1193
8	12	60	1004
8	12	90	1196
8	12	120	1250
8	20	60	1050
8	20	90	1107
8	20	120	1103
8	28	60	1156
8	28	90	1183
8	28	120	1296
10	12	60	1004
10	12	90	1157
10	12	120	1320

10	20	60	1075
10	20	90	970
10	20	120	996
10	28	60	1007
10	28	90	983
10	28	120	1056

Table.10.hardness of taguchi designe

3.2.3 Results and Discussions

Analysis of Signal to Noise Ratio:

Signal to Noise ratio (S/N) is the ratio of the valuable information to irrelevant data. The more positive the value of S/N the better the quality. Taguchi method uses S/N ratio to investigate the performance of the coating. The S/N ratio can be applied in three different ways for checking the performance. There are:

- Lower the better
- Nominal the best
- Larger the better

The higher the hardness of the coating the better is the performance of the coating. So we apply 'larger the better' S/N ratio to find the optimal coating parameters.

S/N ratio for larger the better is given by:

$$S/N = -10 \, Log_{10} \, (1/n * (\Sigma 1/y^2))$$

Where y is the measured hardness and n is the number of the experiment.

4.2.5 Signal to Noise Ratio

The Signal to Noise ratio is used to optimise the bath parameters and obtain a particular combination of the levels of three different factors. Signal to Noise (SN) ratio is calculated by Larger is better.

The S/N ratio corresponding to each experiment is shown in table 11.

Experiment Number	Micro hardness (VHN_{10g})	S/N ratio
1	1096	61.2592
2	1050	61.4597
3	1120	62.2521
4	1060	60.0347

5	1090	61.2667
6	1103	62.4115
7	1009	60.6282
8	1150	59.7354
9	1193	59.9652
10	1004	60.0606
11	1196	59.8511
12	1250	60.4733
13	1050	61.2592
14	1107	61.4597
15	1103	62.2521
16	1156	60.0347
17	1183	61.2667
18	1296	62.4115
19	1004	60.6282
20	1157	59.7354
21	1320	59.9652
22	1075	60.0606
23	970	59.8511
24	996	60.4733
25	1007	61.2592
26	983	61.4597
27	1056	62.2521

S/N ratio for each level has been shown in table 11.

Level	A	B	C
1.	60.96	61.14	60.42
2.	61.18	60.59	60.88
3.	60.49	60.91	61.33
Delta	0.69	0.54	0.91
Rank	2	3	1

Table12: Response table for S/N ratio (larger is better)

Level	sodium hypophosphite	sodium stannate	time
1	1119	1144	1051
2	1149	1073	1110
3	1063	1115	1171
Delta	86	71	120
Rank	2	3	1

Table. 13 **Response Table for Means**

The delta corresponds to the difference in maximum and minimum S/N value of levels in each factor. The rank is then designated based on the delta value. The highest S/N value of the level in the each factor corresponds to the optimal level of that factor. Thus we can clearly determine from table 6 that the optimal bath paramters are A1B2C2, which is the 5^{th} experiment and the corresponding hardness number of the experiment is 1110 $VHN_{10\ g}$.

The main effects plot for S/N ratio also explains the same thing in Fig. 23:

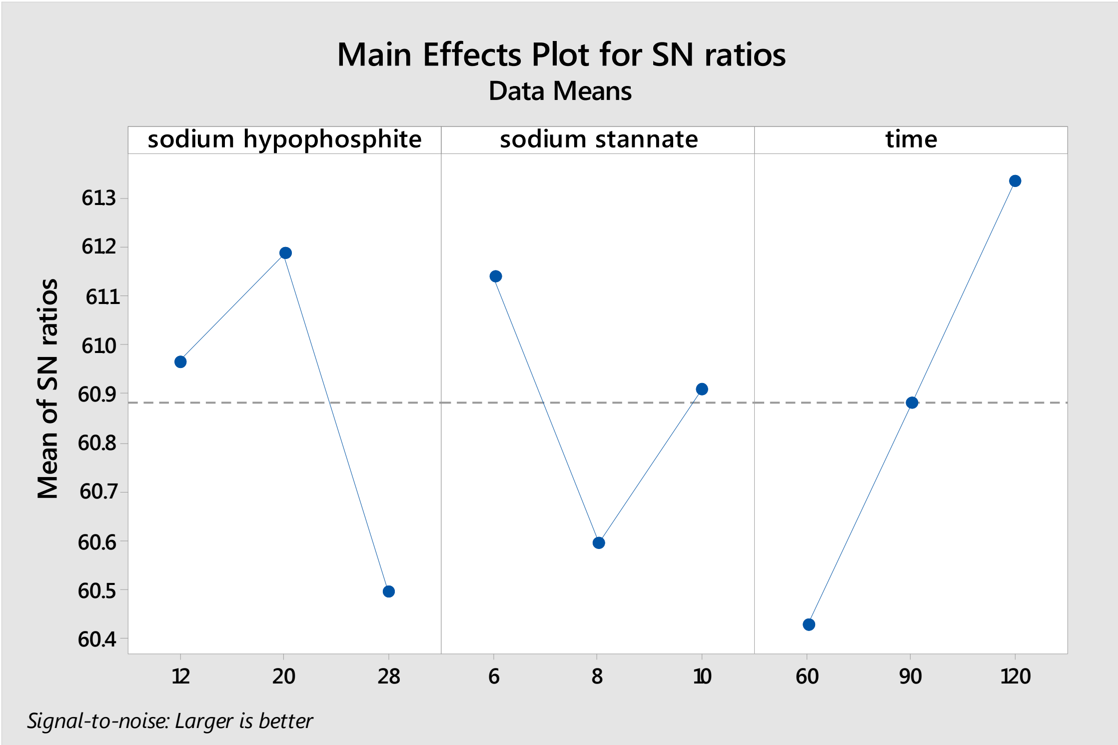


Fig.26: Main effects plot for S/N ratio

The main effects of hardness plot (Fig. 24) can be interpreted to find which factors play a more significant term in determining the hardness of the coating. The factors having the plot close to the mean line or the horizontal line will have the no significant effect on the hardness. Thus, from Fig. 2 we can conclude that factor C (time of coating the bath) will have no significant effect on hardness while the factors A (concentration of sodium stannate) and B (concentration of Sodium Hypophosphite) plays a significant role in determining the hardness of the electross coatings.

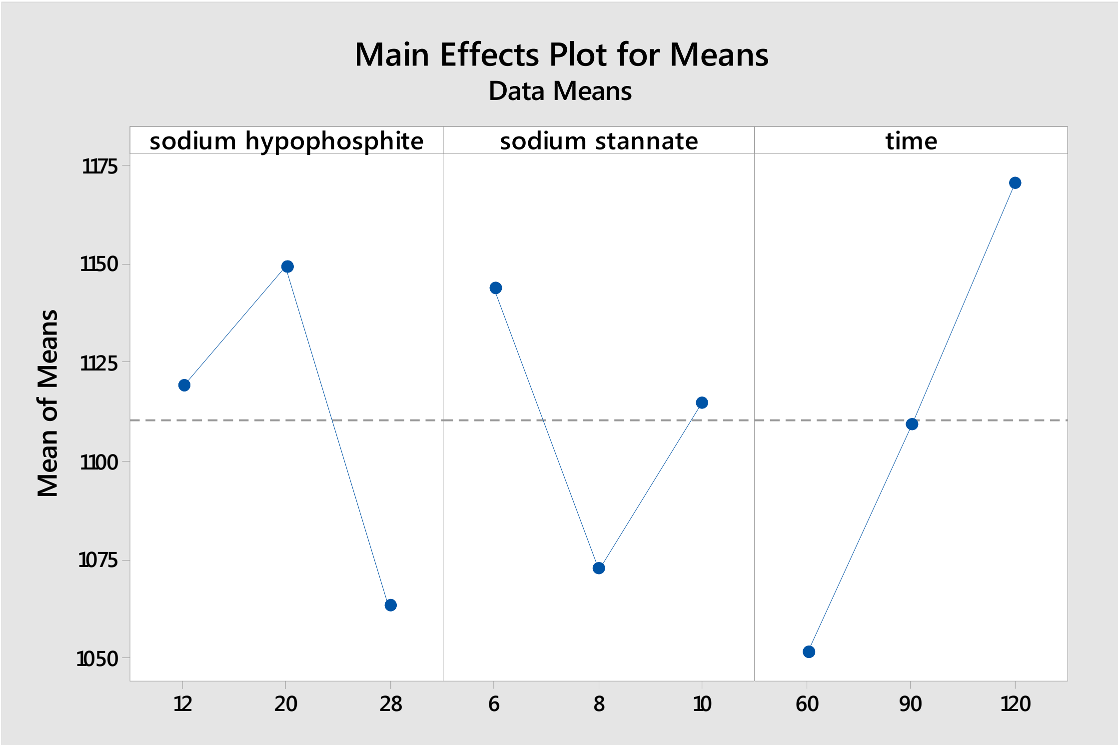


Fig.27: Main effects plot for hardness

The interaction between the factors has been shown in Fig. 22-24. From the interaction plot we can interpret whether interaction has taken place between the two factors or not. If the lines are parallel to each other then it indicates no interaction has taken place between the factors while if the lines are inclined to each other then it suggests that some interaction has taken place. If intersection takes place between the lines then it suggests strong interaction has taken place between the two factors.

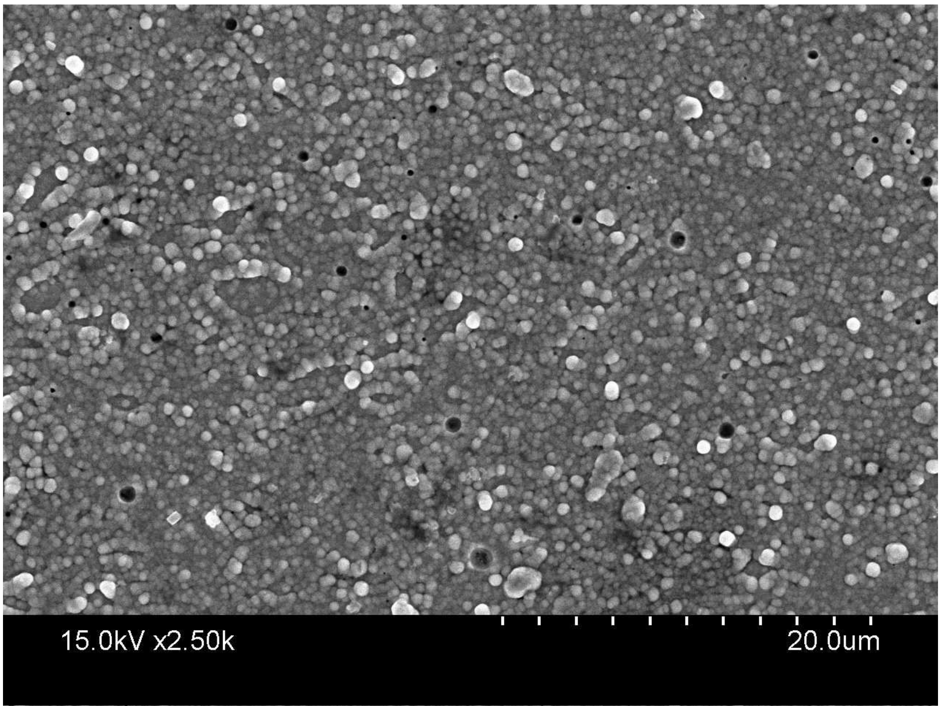
.

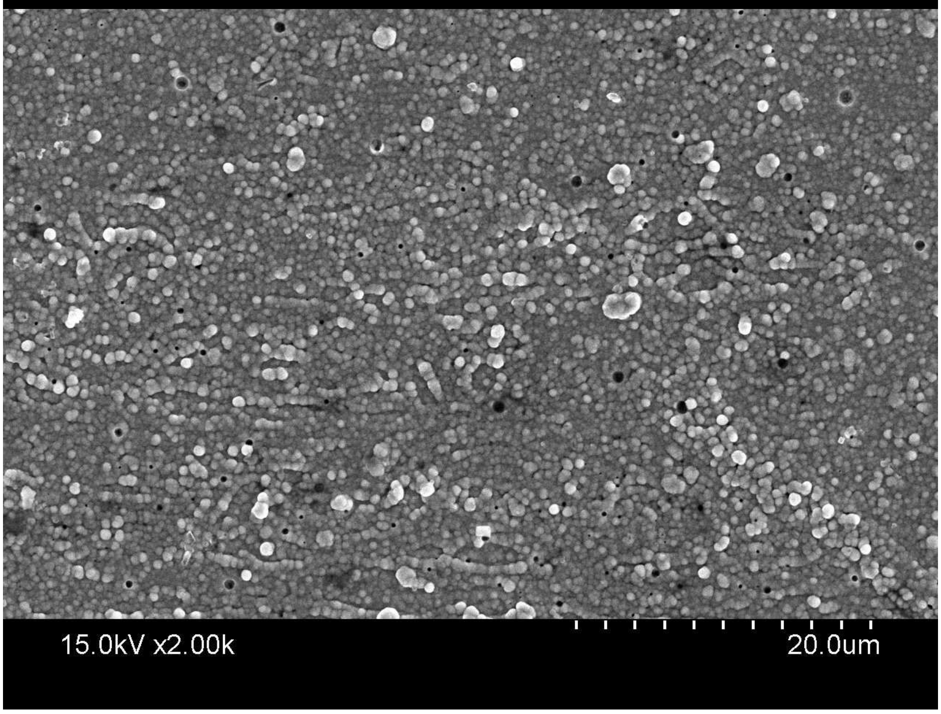
3.2.4 Coating’s Characterisation

Microstructural and Composition Study

Fig.s 6 and 7 show the SEM micrographs of the as-deposited Ni-Sn-P coating with optimal paramters.

Fig. 28 shows the surface of the coating. The Surface of the coating is not very porous and depositions of Tin can be seen in the image.





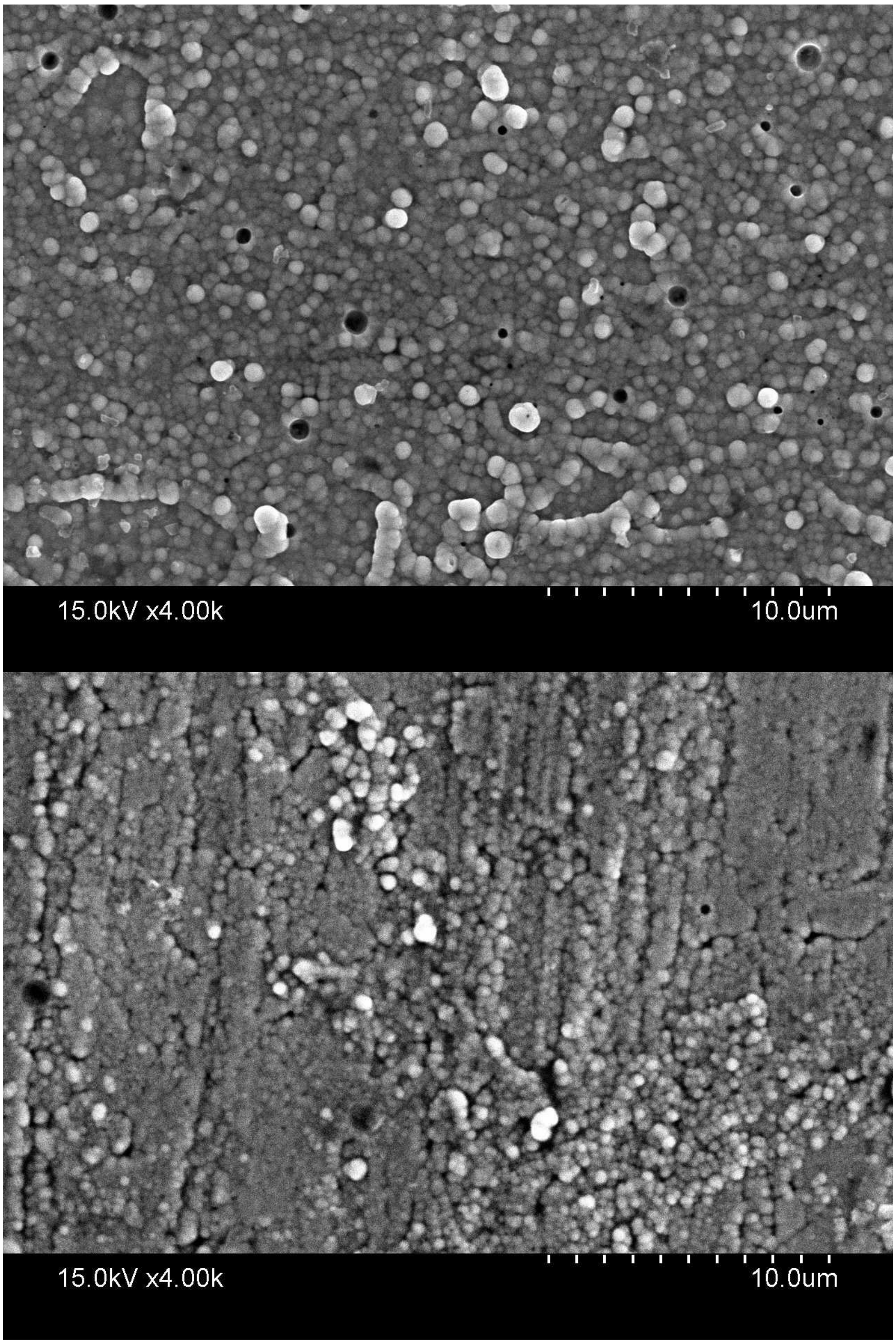


Fig 28 : SEM of coated copper substrate

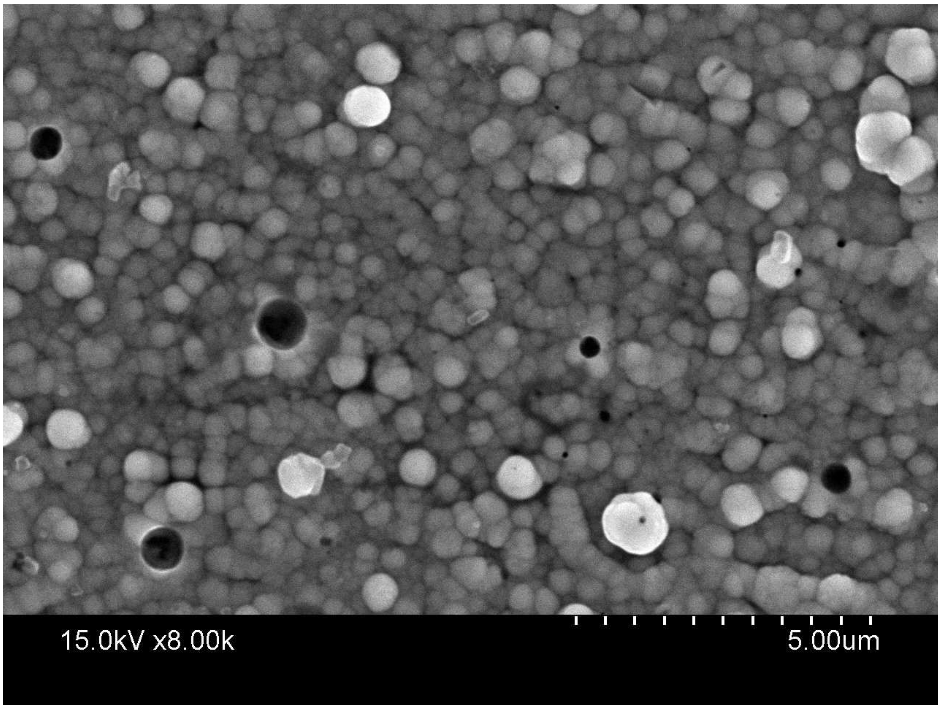


Fig.29: FESEM image of the as-deposited coating as viewed from the top

EDX analysis calculates the percentage of elements in the coating. The EDX analysis is shown in and the percentage of the elements are shown in the .

Fig 30 :

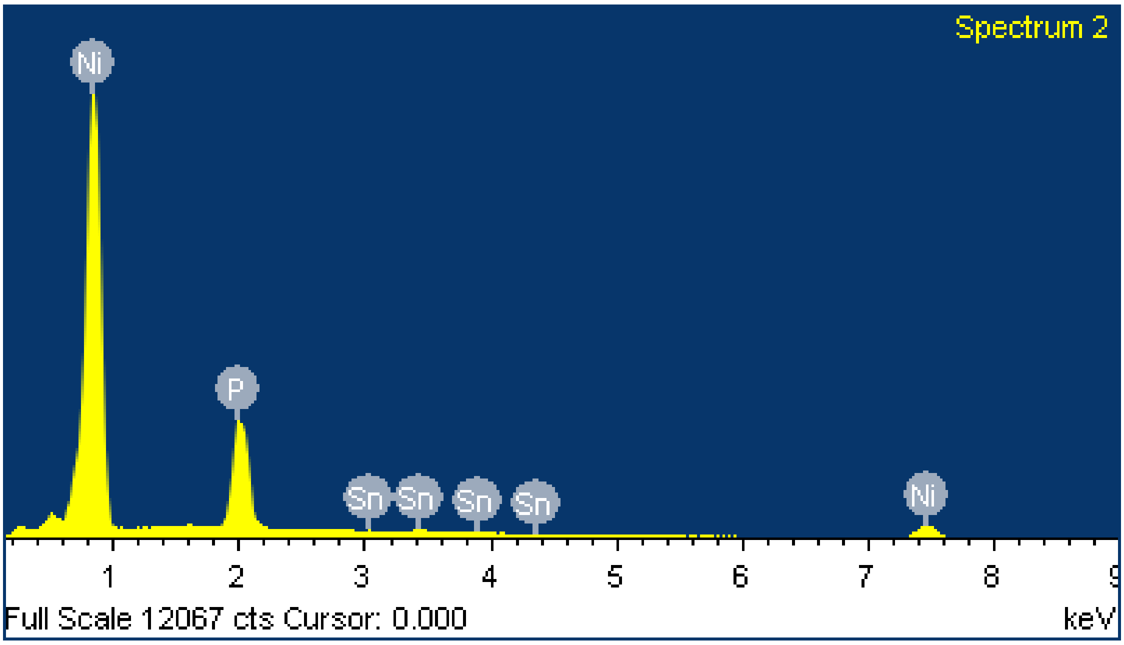


Table .Weight Percentage of the elements in the coating

Spectrum processing :

No peaks omitted

Processing option : All elements analyzed (Normalised)

Number of iterations = 2

Standard :

P GaP 1-Jun-1999 12:00 AM

Ni Ni 1-Jun-1999 12:00 AM

Sn Sn 1-Jun-1999 12:00 AM

Element	Weight%	Atomic%
P K	48.07	64.92
Ni K	46.60	33.20
Sn L	5.33	1.88
Totals	100.00	

4.3   Microstructural aspect and composition study

The SEM micrographs of the substrate and coating with optimal parameters is shown in Fig. 6 and 7 respectively. The image 6 shows the presence of long grains which then gets deposited by globular particles on the surface of the coating as shown in

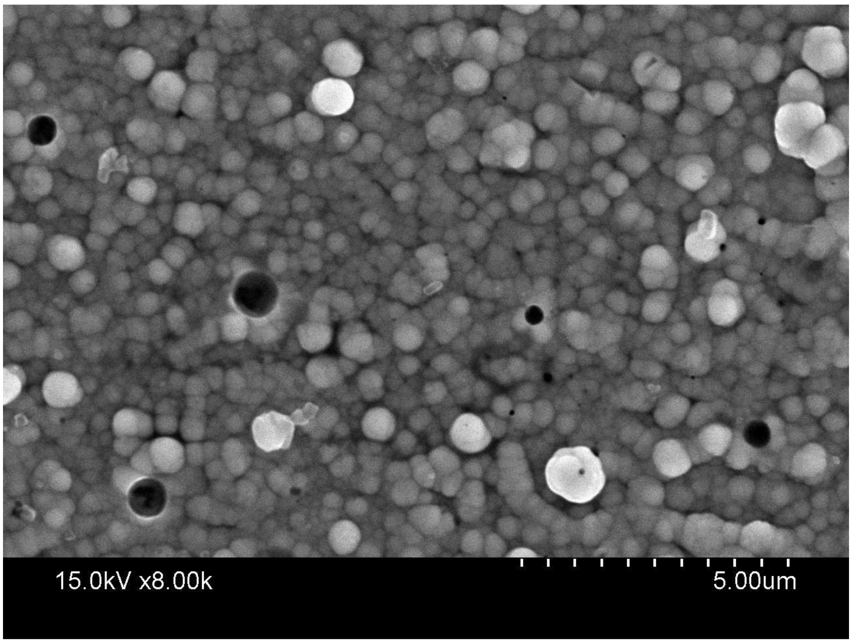


Fig. 31

The XRD is used to identify the various phases in the coatings in the as-deposited form. The XRD analysis showed that the coating in the as-deposited form is amorphous in nature. The highest peak was observed at 50.6□ which was of Co_3P.

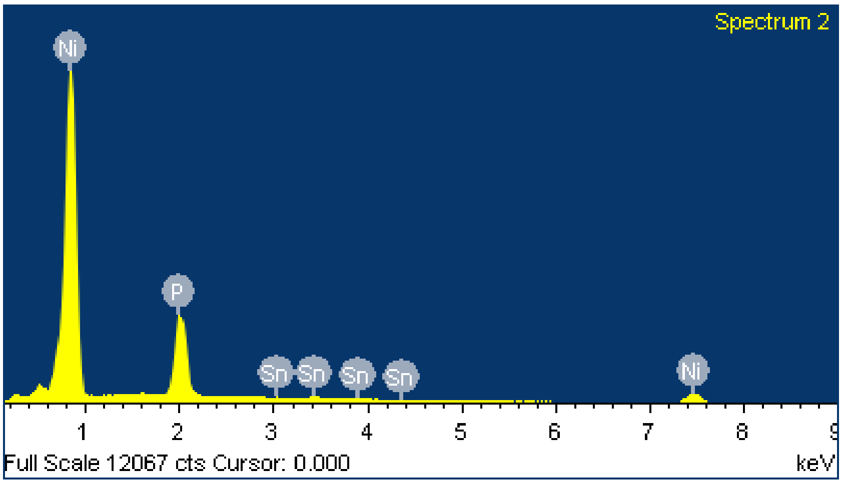


Fig 48. EDAX spectra of the coating surfaces

EDAX analysis is done to calculate the percentage of the elements present in the coating. Fig 9 shows the EDAX analysis of the coating where Nickel has more weight percentage with respect to others. Table 8 shows the percentage distribution of each element in the coating.

Element	Weight Percentage
Nickel	46.60
Tin	5.33
Phosphorus	48.07

Table 14.Composition of the coating as investigate by EDAX.

Chapter5

CONCLUSIONS AND FUTURE SCOPE OF WORK

In this chapter conclusions from the present study and the possible directions of future work are described.

5.1 CONCLUSIONS

In the present thesis the roughness and micro hardness behaviour of electroless Ni-Sn-P coating is studied. Taguchi's L_{27} orthogonal array design has been employed to optimize the coating process parameter combination for minimum roughness and miceo hardness. Both the main effects as well as interaction effect of the parameters are studied. Also the significance of the design parameters and their interactions considered in a particular study is obtained through ANOVA. From the present study the following conclusions are drawn:

- The optimal coating process parameter combination for minimum surface roughness (R_a) is found to be A1B3C3. The concentration of the concentration of Sodium Hypophosphite (A) and the tin source (B) are the significant parameters affecting the resulting surface roughness. The interaction between A*B is found to be most significant.
- The optimal coating process parameter combination for micro hardness is found to be A2B3C3 and the most significant parameter is the concentration of the Sodium Hypophosphite (A) for the resulting surface roughness giving a contribution of 14%. None of the interactions is found to be significant.
- The compositional study of Ni-Sn-P electroless coating is done by energy dispersive x-ray analysis (EDX) method and found to be 5.14% of tin on the surface of coated surface and for this is bath composition is sodium hypophosphite (20g/l) , sodium stannate(source of tin) is (8g/l) and coating time 90 minute.
- In case of multiple roughness optimization, the improvement of grey relational grade from initial to optimal condition is 0.5423.,
- The microstructure study of the coating reveals that the Ni-Sn-P surface consists of a large number of Ni-Sn-P nodules. With heat treatment, a relatively coarse grained structure is evolved indicating the occurrence of crystallization. The SEM

micrograph of the worn out surface show that the wear mechanism is generally adhesive in nature with no plowing effect or abrasive particle.

FUTURE SCOPE OF WORK

Suited for industrial applications The present study is a preliminary work so far as the optimization of coating process parameters for minimization of roughness, micro hardness of the Ni-Sn-P coated surfaces. Future study on the topic may evaluate one or more of the following aspects:

- More numbers of process parameters may be considered at a time for better control over the design space so that improved tribological performance of electroless Ni-Sn-P coating is obtained.
- Similar studies considering the effect of tin content on the tribological behaviour of the coating could be conducted.
- Similar studies with different bath constituents (i.e. different complexing agent, stabilizer, etc.) may be conducted and the results compared.
- Different combination of chemicals for electroless Ni-Sn-P alloy coatings can be considered in the future for tribological performance study.
- Optimization of various tribological parameters and corrosion properties may be carried out.

There is always a quest for obtaining corrosion and wear resistant as well as smooth surface for industrial applications which is simultaneously cheaper to produce. The studies concerning the electroless Ni-Sn-P coating, if properly conducted could well reveal its potential to be a coating, tribologically.

References

[1] A Brenner, GE Riddell, Journal of Research of the National Bureau of Standards, 37(1), 1946, 31-34 and Proc. American Electroplaters Soc., 33 (1946) 16.

[2] A Brenner, GE Riddell, Journal of Research of the National Bureau of Standards, 39, 1946, 385-395 and Proc. American Electroplaters Soc., 34 (1947) 156-170.

[3] M Pounovic, M Schlesinger, Fundamentals of electrochemical deposition, Second edition, John Wiley & Sons, Inc., Hoboken, New Jersey, 2006.

[4] P Sahoo, SK Das, Tribology of electroless nickel coatings – A review, Materials and Design 32 (2011) 1760-1775.

[5] P Sahoo, Optimization of electroless Ni – P coatings based of surface roughness, Tribology Online, 3 1 (2008) 6-11.

[6] P Sahoo, Friction performance optimazition of electroless Ni – P coatings using the Taguchi method, Journal of Physics D: Appl. Phys, 41 (2008) 095305.

[7] P Sahoo, Wear behaviour of electroless Ni – P coatings and optimization of process parameters using Taguchi method, Materials and Design, 30 (2009) 1341-1349.

[8] F Pearlstein, RF Weightman, R Wick, Metal Finishing, 61 (1963) 77-81.

[9] A Brenner, Electrodeposition of alloys, vol. 2, Academic press, New York, 1963.

[10] G.L. Zhao, Y. Zou, H. Zhang, Z.D. Zou, Correlation between corrosion resistance and the local atomic structure of electroless, annealed Ni-P amorphous alloys, Mater. Lett. 132 (2014) 221–223.

[11] Q. Zhao, Y. Liu, Comparisons of corrosion rates of Ni−P based composite coatings in HCl and NaCl solutions, Corros. Sci. 47 (2005) 2807–2815.

[12] B. Jiang, S.L. Jiang, A.L. Ma, Y.G. Zheng, Erosion-corrosion behavior of electroless Ni-P coating on copper-nickel alloy in 3.5 wt.% sodium chloride solution, J. Mater. Eng. Perform. 23 (2014) 230–237.

[13] P. Makkar, R.C. Agarwala, Wear and corrosion characteristics of alumina dispersed Ni−P nanocomposite coating developed by electroless technique, J. Mater. Sci. 50 (2015) 2813–2823.

[14] A. Abdel Aal, A. Shaaban, Z. Abdel Hamid, Nanocrystalline soft ferromagnetic Ni – Co − P thin film on Al alloy by low temperature electroless deposition, Appl. Surf. Sci. 254 (2008) 1966–1976.

[15] H. Ashassi-Sorkhabi, H. Dolati, N. Parvini- Ahnadi, J. Manzoori, Electroless de- position of Ni − Cu − P alloy and study of the influences of some parameters on the properties of deposits, Appl. Surf. Sci. 185 (2002) 155–160.

[16] Z. Sukackienė, L. Tamašauskaitė-Tamašiūnaitė, V. Jasulaitienė, A. Balčiūnaitė,

[17] A. Naujokaitis, E. Norkus, Electroless deposition of CoBW coatings using morpho- line borane as a reducing agent, Thin Solid Films 636 (2017) 425–430.
[18] J.N. Balaraju, N.T. Kalavati, V.K. Manikandanath, William Grips, Phase transfor- mation behavior of nanocrystalline Ni – W − P alloys containing various W and P contents, Surf. Coat. Technol. 206 (2012) 2682–2689.
[19] J.N. Yang, S.C. Balaraju, H. Chong, C.Q. Xu, V.V. Liu, Z. Chen Silberschmidt, Significantly retarded interfacial reaction between an electroless Ni – W − P me- tallization and lead-free Sn-3.5 Ag solder, J. Alloys Compd. 565 (2013) 11–16.
[20] Y. Wang, J. He, W. Wang, J. Shi, N. Mitsuzaki, Z. Chen, Preparation and char- acterization of Ni-P/$Ni_{3.1}B$ composite alloy coatings, Appl. Surf. Sci. 292 (2014) 462–468.
[21] G. Stremsdoerfer, H. Omidvar, P. Roux, Y. Meas, R. Ortega-Borges, Deposition of thin films of Ni − P and Ni – B − P by dynamic chemical plating, J. Alloys Compd. 466 (2008) 391–397.
[22] H.S. Yu, S.F. Luo, Y.R. Wang, A comparative study on the crystallization behavior of electroless Ni − P and Ni – Cu − P deposits, Surf. Coat. Technol. 148 (2001) 143–148.
[23] J. Georgieva, S. Armyanov, Electroless deposition and some properties of Ni – Cu – P and Ni – Sn – P coatings, J. Solid State Electrochem. 11 (2007) 869–876.
[24] Z. Rajabalizadeh, D. Seifzadeh, The effect of copper ion on microstructure, plating rate and anticorrosive performance of electroless Ni – P coating on AZ61 magne- sium alloy, Prot. Met. Phys. Chem. Surf. 50 (2014) 516–523.
[25] D. Seifzadeh, A. Rahimzadeh Hollagh, Corrosion resistance enhancement of AZ91D magnesium alloy by electroless Ni – Co − P coating and Ni – Co – P − SiO_2 nano- composite, J. Mater. Eng. Perform. 23 (2014) 4109–4121.
[26] J. Georgieva, S. Kawashima, S. Armyanov, E. Valova, A. Hubin, Y. Koyama, O. Steenhaut, J. Haydu, J.L. Delplancke, Ts. Tsacheva, Electroless deposition of Ni-Sn- P and Ni – Sn – Cu – P coatings, J. Electrochem. Soc. 152 (11) (2005) C783–C788.

[27] B.W. Zhang, H.W. Xie, E□ect of alloying elements on the amorphous formation and corrosion resistance of electroless Ni — P based alloys, Mater. Sci. Eng. A 281 (2000) 286–291.

[28] J. Yuan, J. Wang, Y. Gao, J. Mao, W. Hu, Preparation and magnetic properties of Ni – Co – P – Ce coating by electroless plating on silicon substrate, Thin Solid Films 632 (2017) 1–9.
[29] M. Heshmati, D. Seifzadeh, P. Shoghi, M. Gholizadeh-Gheshlaghi, Duplex Ni – Zn – Cu – P/Ni – P electroless coating on magnesium alloy via maleic acid pre- treatment, Surf. Coat. Technol. 328 (2017) 20–29.
[30] W.X. Zhang, Z.H. Jiang, G.Y. Li, Q. Jiang, J.S. Lian, Electroless Ni – Sn — P coating on AZ91D magnesium alloy and its corrosion resistance, Surf. Coat. Technol. 202 (2008) 2570–2576.
[31] H. Shimauchi, S. Ozawa, K. Tamura, T. Osaka, Preparation of Ni − Sn Alloys by an electroless-deposition method, J. Electrochem. Soc. 141 (1994) 1471–1476.
[32] Y. Zou, Y.H. Cheng, L. Cheng, W. Liu, E□ect of tin addition on the properties of electroless Ni – P — Sn ternary deposits, Mater. Trans. 51 (2010) 277–281.
[33] J.T. Winowlin Jappes, B. Ramamoorthy, P. Kesavan Nair, Novel approaches on the study of wear performance of electroless Ni − P/diamond composite deposits, J. Mater. Process. Technol. 209 (2009) 1004–1010.

[34] H. Beygi, H. Vafaeenezhad, S.A. Sajjadi, Modeling the electroless nickel deposition on aluminum nanoparticles, Appl. Surf. Sci. 258 (2012) 7744–7750.

[35] L.S. Yuan, Y.X. Zheng, M.L. Jia, S.J. Zhang, X.L. Wang, Nanoporous nickel-copper-phosphorus amorphous alloy film for methanol electro-oxidation in alkaline medium, Electrochim. Acta 154 (2015) 54–62.

[36] J. Yu, T. Jing, J. Yang, Q. Li, Determination of activation energy for crystallizations in Ni – Sn — P amorphous alloys, J. Mater. Process. Technol. 209 (2009) 14–17.