CHAPTER-I

INTRODUCTION

1.1 Nanocrystalline Metals

Nanotechnology is the design, fabrication, properties and applications of materials or structures in nanometer scales, typically ranging from sub nanometers to several hundred nanometers. One nanometer is $10^{-3}$ micrometer or $10^{-9}$ meter. Nanomaterials or structures may possess new physical properties or exhibit new physical phenomena. Nanotechnology also promises the possibility of creating nanostructures of metastable phases with non-conventional properties including superconductivity and magnetism [1-4]. Nanocrystalline metals are defined as metallic systems whose structures and components exhibit novel and significantly improved physical, chemical and biological properties, phenomena and processes due to their nanoscale size.

Nanocrystalline metals were synthesized by number of methods such as mechanical alloying, spray conversion processing, electrodeposition, electroless deposition, rapid solidification from the melt, physical vapour deposition, chemical vapour deposition, co-precipitation, sol-gel processing, plasma processing, auto-ignition, laser ablation, hydrothermal pyrolysis, sonochemical synthesis etc.[5-16].

There are two approaches to the synthesis of nanocrystalline metals: top-down and bottom-up. The top-down approach starts with materials with conventional crystalline microstructures, typically metals and alloys, and the bottom up approach involves manipulation of atomic and subatomic particles [17-19].
Nanocrystalline metals have also been fabricated by utilizing the porous alumina membrane as the templates by sol-gel process [20-25], chemical vapour deposition [26, 27], electro-[28, 29] and electroless deposition [30, 31].

Various structural characterization methods that are most widely used in characterizing nanomaterials and nanostructures include: X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission microscopy (TEM) and scanning probe microscopy (SPM). Characterization of nanomaterials and nanostructures has been largely based on the surface analysis techniques and conventional characterization methods developed for bulk materials. For example, XRD has been widely used for the determination of crystallinity, crystal structures and lattice constants of nanoparticles, nanowires and thin films; SEM and TEM together with electron diffraction have been commonly used in morphological characterization of nanoparticles. Optical spectroscopy is used to determine the size of semiconductor quantum dots.

In nanocrystalline metals, large fractions of atoms upto 40 % are boundary atoms. Thus the interface structure plays an important role in determining the physical and mechanical properties of nanocrystalline metals. Nanocrystalline metals have improved chemical, mechanical and electrical properties, lower melting points, higher energy gaps, non-thermodynamic structures and optical behaviour that go beyond the capability of the original material.

Nanocrystalline metals generally exhibit significantly higher yield strength, high hardness, enhanced diffusivity and reduced tensile elongation relative to their microcrystalline counterparts. They have been found to exhibit superplasticity at lower homologous temperatures and higher strain rates than their microcrystalline counterparts.
Despite the fact that nanocrystalline metals exhibit high strength and hardness, they are very brittle with little tensile ductility compared to their coarser-grained counterparts [32, 33].

The ionization potential is generally higher for small atomic clusters than for the corresponding bulk material. Nanocrystalline metals have very high surface area to volume ratios and potentially different crystallographic structures. They exhibit a high reactivity and strong tendency towards agglomeration. Catalysis using finely divided nanocrystalline metals can increase the rate, selectivity and efficiency of chemical reactions such as combustion or synthesis whilst simultaneously and significantly reducing waste and pollution.

The increase in surface area and surface free energy with decreasing particle size leads to changes in interatomic spacings. The large surface area to volume ratio results in a substantial proportion of atoms having a different magnetic coupling with neighbouring atoms, leading to different magnetic properties. Giant magnetoresistance (GMR) is a phenomenon observed in nanoscale multilayers consisting of a strong ferromagnet (e.g., Fe, Co) and a weaker magnetic or non-magnetic buffer. (e.g., Cr, Cu); it is usually employed in data storage and sensing.

Nanocrystalline metals, show large changes in optical properties, such as colour, as a function of particle size. They show similar size-dependent behaviour in the frequency and intensity of light emission as well as modified non-linear optical properties and enhanced gain for certain emission energies or wavelengths. Other properties, which may be affected by reduced dimensionality, include photocatalysis, photoconductivity, photoemission and electroluminescence [34].
Nanocrystalline metals and coatings may find many applications in thermal barriers, engineering, catalysis, sensors, media storage, energy devices and in electronics.

1.2 Nanocrystalline Nickel

Since its first introduction in the early 1980s, nanocrystalline nickel (NC-Ni) has been made by the underlying fundamental physical and chemical principles which can be classified into five groups. The first three techniques on the basis of groups are, vapour phase processing (e.g. PVD, CVD, inert gas condensation), liquid phase processing (e.g. rapid solidification, atomization, sonication of immiscible liquids) and solid state processing (equal channel angular pressing, mechanical attrition and annealing of amorphous precursors. The other two groups are chemical synthesis (e.g. sol-gel processing, inverse micelle technology, sonochemical synthesis, electroless deposition) and electrochemical synthesis (e.g. electrodeposition, galvanic conversion).

NC-Ni deposits often show an initial layer of very fine-grained material close to the substrate. However, with increasing deposit thickness, a transition takes place from nucleation-controlled crystallization to growth-dominated deposition. As a consequence, there is a structural transition from fine-grained equiaxed to course grained columnar structure with strong grain shape anisotropy. The thickness of the initial fine-grained layer depends on the process parameters. On the other hand, if growth conditions are maintained to favour massive nucleation regardless of coating thickness, NC-Ni deposit showing no grain shape anisotropy can be grown to any thickness.

Upon alloying Ni with P, the grain size of Ni can be reduced down to less than 10 nm thereby achieving high hardness values. The Taber wear index went through a
minimum that corresponded to the maximum in the hardness as a function of grain size. In other words, for as-deposited Ni and Ni-P deposits, there is a one to one relationship between grain size, hardness and Taber wear index. NC-Ni has much higher abrasive wear resistance because of its lower ductility.

NC-nickel shows unique or improved properties compared to conventional polycrystalline nickel. The hardness of NC nickel has been reported to be 640 Hv at 14 nm grain size [35]. A notable increase in ultimate tensile stress (1390 Mpa) was observed for 40 nm NC nickel [36]. The wear rate of NC nickel with an average grain size of 13 nm is about half of the wear rate in polycrystalline nickel [37]. Hydrogen transportation rate and storage capacity in NC nickel have been previously shown to be significantly higher than those observed in bulk nickel [38]. The improved corrosion and fatigue properties have also been reported for NC nickel [39, 40].

NC-Ni–P alloys used as corrosion protective coatings constitute the earliest industrial applications of nanocrystalline metals [41–43]. Today such Ni–P alloys are widely used in the electronic industry as under-layer in thin film memory disks [44] and in a broad range of other evolving technological applications [45].

1.3 Electroless Nickel Deposition

Electroless plating is the deposition of metals by using chemical reducing agents on a catalytic surface [46, 47]. These reducing agents are oxidized on a catalytic surface and reduce the metal ion over there. If the deposited metal has catalytic activity, the reaction becomes continuous and one can get desired thickness of deposit. In this technique, the deposition of metal is done without the use of electrical energy on both conducting and non-conducting substrates.
A number of metals can be reduced to their metallic state by the selection of proper reducing agent and pH. However, true electroless solution should allow continuous plating of the metal to any desired thickness by catalyzing the reduction of the metal ion on the surface.

1.3.1 **Bath constituents**

Any electroless plating solution contains the following constituents [8, 48, 49].

1. Source for the metal ions to be deposited
2. Suitable reducing agent
3. Complexing agent
4. Buffer
5. Stabilizer

Mostly, soluble sulphates of the respective metal ions are used as source in electroless formulations of common metals like copper, nickel and cobalt. Chlorides of nickel, palladium and gold are used for electroless deposition of these metals. Cyanides of gold and silver are preferred in true electroless plating formulations of these metals.

Sodium hypophosphite, formaldehyde, para formaldehyde, hydrazine, amine boranes, borohydrides and glyoxal are the common reducing agents.

Acetates, hydroxyacetates, succinate, hydroxy propionates, aminoacetates, aminopropionates, malonates, glycollates, lactates, pyrophosphates, citrates, ammonia, EDTA, ethylene diamine, quadrol, ethanolamines etc., have been used as complexants in electroless plating baths.

During the course of reaction in electroless depositions, there is a rapid change in pH. To overcome this, buffers are added to maintain the pH within optimum range.
Salts of hydroxy acids and dicarboxylic acids are used as buffers in electroless plating. Some of the complexants also function as good buffers.

Life of electroless plating baths is limited. So, to prevent spontaneous decomposition of bath, thio-compounds such as cyanide, sodium ethylxanthate, divalent sulphur compounds, (dissolved oxygen) 2-mercapto benzotriazole, some heavy metal ions (lead, tin, bismuth, thallous ion in nickel bath), organic dipolar anions (oleates) and 2,2’ bipyridyl are added as stabilizers. The concentration range of many stabilizers is in ppm range (0.1 to 200 ppm).

The acid baths [8, 50] are the most popular and well investigated. The rate of deposition is as high as 20 to 25 µm/h. The compositions are more stable since there is no loss of the complexant by evaporation. The coatings obtained from acid solutions are of better quality. The properties of the electroless nickel-phosphorous alloy can be controlled easily by controlling the amount of phosphorous in the deposit.

The main disadvantages of the alkaline baths [51-65] are their high instability at temperatures greater than 90°C and loss of ammonia, which is added to raise the bath pH at that temperature. The reduction of nickel in alkaline solutions follows the same pattern as in acid solutions. Another difference from the acid solutions is that the rate of deposition of nickel increases with hypophosphite concentrations. However, very high concentrations of hypophosphite make the bath unstable due to homogeneous deposition in the bulk. Temperature influences the rate of deposition of nickel in the same way as in acid solutions.
1.3.2 Theory and mechanism of electroless plating

This oxidation-reduction reaction proceeds only on a catalytic surface. Thus the reaction of electroless metal deposition is a heterogeneous catalytic electron transfer reaction in which electrons are transferred across the interface from a reducing agent (R) to the metal ions M [8, 42, 66].

\[
\text{Catalytic surface} \quad R \rightarrow R^+ + e^- \quad \text{anodic partial reaction} \quad (1)
\]

\[
\text{Catalytic surface} \quad M^+ + e^- \rightarrow M \quad \text{cathodic partial reaction} \quad (2)
\]

\[
\text{Catalytic surface} \quad H^+ + e^- \rightarrow \frac{1}{2} H_2 \quad \text{cathodic partial reaction} \quad (3)
\]

Reaction (1) and (2) occur simultaneously at the catalytic surface. Since these cathodic and anodic sites are part of the same piece of metal, they are short-circuited and there is a flow of electrons between these sites. Each of these reactions establishes its own equilibrium with its own equilibrium potential \( E_{\text{Red}} \) or \( E_{\text{Met}} \). This leads to an establishment of a steady state with the compromised potential called mixed potential \( E_{\text{mix}} \). The equilibrium potential of reaction (1) must be more negative than the equilibrium potential of reaction (2) in order that R can function as an electron donor and M\(^{n+}\) as an electron acceptor.

Metal ions in a solution for electroless metal deposition are, in general, complexed with a ligand, L. Complexed metal ions usually involve sequence of two elementary steps;

(i) The formation of the electro active species
(ii) The charge transfer from the catalytic surface to the electro active species (electron capture).

1.3.3 Properties of electroless nickel

Electroless nickel coatings provide protection for common metal surfaces exposed to corrosion as well as to wear. The corrosion protection is due to the low porosity of the coatings and the excellent resistance of nickel to many liquids and most atmospheric conditions. Electroless nickel prevents the contamination and discoloration of plasticizers, solvents, oils, glycols, monomers and gases by metals such as iron, copper and aluminum. They possess uniform thickness high hardness, excellent wear and abrasion resistance, absorptivity, good adhesion and provides excellent base for coatings.

1.3.4 Applications of electroless nickel

Electroless nickel plating is used to deposit (a) on complex shapes; (b) on large surfaces, especially large interior surfaces; (c) on surfaces subjected to wear; (d) to replace expensive stainless steel vessels in some processing industries; (e) to repair or salvage nickel-plated machine parts; (f) for nickel depositions where electrical power is not available or possible; (g) for improving the adhesion of enamels on steel; and (h) on printed circuit boards and electronics industries for corrosion resistance and solderability.

Electroless nickel, as an engineering coating, is used in many industrial applications in aerospace automotive computers, electronics, food processing, hydraulics machinery, nuclear engineering, oil petrochemicals, plastics, power transmission, printing, pump valves, textiles, etc.
Electroless deposition in nanotechnologies allows one to produce photo masks and micro devices with nanosized adjacent elements of different thicknesses made of various materials by single conventional optical photolithography [67].

1.4 Electroless Nickel Deposition on Aluminum

Aluminium alloys have low weight, high strength to weight ratio and corrosion resistance making them of more interest for automotive and aerospace industries. In addition to low density, aluminium alloys possess high mechanical strength, excellent thermal and electrical conductance, good reflectivity and low working cost. However, severe operating conditions such as high specific pressure, high temperature, a corrosive environment or abrasive wear often limit the possibility of using aluminium alloys directly. To prolong the lifetime of components, several approaches have been adopted in industrial scale.

To reduce the structural mass of machine and equipment, the use of light aluminium alloys is widely recommended. Mass reduction is an important criterion in spacecraft design. Among the conventional structural materials used in space applications aluminium alloy are front-runners.

Aluminium is strongly electronegative metal and possesses a strong affinity for oxygen forming a very thin tenacious oxide film. Aluminium and its alloys therefore require special surface preparation for successful use in aerospace industry.

The hard PVD and electrodeposited Cr or Ni coating provide sufficient improvement in hardness and wear resistance. However, problems often arise when
complex components having internal surfaces or holes are coated. These problems are in part avoided when using electroless Ni-P coatings.

Aluminum and aluminum parts used in aircrafts or spacecrafts are coated with electroless nickel for improved wear resistance and corrosion resistance. With increased use of aluminum alloys in industrial equipment machinery, electroless nickel-plated aluminum has a bright future. Aluminum or beryllium parts coated with electroless nickel and precision turned to accuracy between 0.05 and 1.0 µm smoothness are used in paraboloid mirrors in space vehicles.

The proposed electroless Ni plating on aluminium is much more advantageous and simpler than other expensive and complicated methods such as e-beam, X-ray lithography, or production of the devices using light phase shift photo masks [83].

Many different metals are deposited on aluminium and its alloys to obtain various decorative and functional finishes such as specific metallic appearance, improved solderability, frictional properties, corrosion resistance and electrical conductivity. Nickel is deposited on aluminium and its alloys to provide high resistance to abrasion and erosion/corrosion.

1.4.1  Zincating / Stannating as pretreatment

Amongst the popular methods for the treatment of aluminium and its alloys zincating is perhaps, the most widely used process in the industry. The highly alkaline zinc or Sn immersion solutions dissolve the thin oxide film left after the deoxidizing (etching) and rinsing steps.

Zincating is an electrochemical exchange reaction between zinc complexes in solution and the aluminium substrate, depositing zinc crystallites at the expense of
aluminium dissolution [68]. The zinc deposition protects the surface, effectively providing a sound basis for subsequent deposition. During the zincating process, the aluminium oxide film is first dissolved in zincating solution as follows

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} + 3\text{H}_2\text{O} \rightarrow 2\text{NaAl(OH)}_4$$  \hspace{1cm} (4)

The oxidation of aluminium drives reduction of the zincate ion to produce a layer of zinc metal in a galvanic displacement reaction as follows

$$3\text{Na}_2(\text{ZnOH})_4 + 2\text{Al}({\text{substrate}}) \rightarrow 2\text{NaAl(OH)}_4 + 4\text{NaOH} + 3\text{Zn}({\text{deposited}})$$ \hspace{1cm} (5)

The zincating process usually consists of double dip into the zincate solution to produce a uniform layer of zinc on the aluminium surface. The double zination protects the aluminium substrate from reoxidation until it is ready to be electrolessly plated with nickel, followed by further deposition. However, the zincate pretreatment includes not only the dissolution of the thin alumina left after the etching and rinsing steps but also the dissolution of the Al substrate itself as well. The roughening of the surface may provide a better adhesion between the Ni–P plating layer and the substrate, but it has been reported [69-71] that, the Zn formed by zincate pretreatment is not active enough to facilitate the electron transfer reactions between the $\text{H}_2\text{PO}_2^-$ and $\text{Ni}^{2+}$ ions [72].

Here, if the surface of the base metal is non-homogeneous, an immersion coating of different thickness will be obtained in the matrix and on inter metallic constituents. The deposits obtained from the simple zincate solution will be thinner and more compact. The reproducibility of the coating on aluminium by zinctating is critical. In addition, special plating baths may be necessary for various alloys.
1.4.2 Anodizing as pretreatment

Anodizing is an electrolytic oxidation process, which produces an oxide film over the surface of aluminium, by passing a current at sufficient voltage through a suitable electrolyte using aluminium as the anode and lead, graphite, stainless steel or aluminium as the cathode.

During anodizing, the anion in the electrolyte migrates to the anode and the reaction occurs at the electrode. Glayman [73] suggested that in sulphuric acid anodizing, the oxide formation is by the reaction of $O_2^-$ and $H_2O$ with aluminium or by the hydrolysis of aluminium sulphate formed initially.

$$2Al^{3+} + 3O_2^- \rightarrow Al_2O_3 + \text{Energy} \quad (6)$$

According to Yoshino and Baba [74], the predominant anion causing oxidation in non-aqueous solution is $OH^-$. They suggested the following mechanism:

$$6OH^- + 2 Al \rightarrow Al_2O_3 + 3H_2O + 6e^- \quad (7)$$

As soon as the oxide film is formed on the metal surface, any further growth requires the movement of ion through the oxide film under the existing potential gradient. This occurs because, alumina is a poor electronic conductor with the result that, the ionic conductance is the predominant mode or charge transport of the field strength existing in the film. At the outer surface of primary barrier layer, by reaction with anodizing electrolyte, a secondary phase of the barrier layer is produced.

At first, during anodizing, a barrier oxide film is formed on aluminium. When the barrier oxide film is formed to the limiting film thickness depending upon the nature of the electrolyte, nucleation of pores takes place due to the solvent action of these electrolytes. Now, two opposing reactions are taking place. At each pore, one force is
dissolving the oxide film and the other force is trying to form the oxide film. When the anodizing voltage attains a steady value, the process of pore formation is complete and the porous oxide film started to form due to the action of current. The porous oxide film contains a compact array of oxide cell and each cell has a hexagonal structure with a cylindrical pore at the centre.

Thickness of the oxide film depends on temperature, current density, composition of the electrolyte, composition of aluminium alloy, duration of anodizing and on the voltage of the anodizing electrolyte. Therefore, all these factors are to be considered to get consistent anodic film. If the temperature is raised, the solubility of the oxide film also increases which will prevent the attainment of limiting thickness of the oxide film in the bath. Low current density at ambient temperature leads to the formation of soft and more porous oxide film. On the other hand, higher current density leads to quick build up of thickness and lot of heat will be evolved. Low concentration increases resistivity of the bath lead to loss of power due to voltage drop. Very high concentration leads to the dissolution of the formed of the oxide film. Longer duration after four hours, further build up will not be linear and limiting thickness will be reached because of the solubility of the oxide film in the anodizing electrolyte.

Anodizing of aluminium and its alloys has become a technology of its own because of the following advantages [75-77].

1. Anodizing increases the corrosion resistance of the light metals in severe exposure conditions.
2. It enhances the adhesion strength of paints and other organic finishes.
3. It permits production of a suitable surface for subsequent deposition.
4. It improves decorative appearance by its capability to absorb organic dyes and inorganic pigments.

5. It provides good electrical insulation.

6. It enhances the wear resistant characteristics and surface hardness properties.

7. It enhances the dielectric properties for use as electrolytic capacitors.

8. It attributes special optical properties such as reflectivity, emissivity and absorptivity in solar reflectors and collectors.

9. It provides a surface for excellent adhesive bonding with other materials.

   Anodized aluminium has been widely used as an extrusion for making doors, windows, partitions, and painting of aluminium sheets. It permits production of a suitable surface for subsequent electroplating, door winding as a substitute for copper, photolithography, printing, screw threads for hydraulic Jacks, under carriage legs for aircrafts.

   For more than four decades, aluminum anodic oxide film (AAO) has been traditionally used as a dielectric material in microelectronic applications. Recently, AAO as a template-directed method has been widely used in the fabrication of nanomaterials and nanostructures for many applications including quantum-dot arrays, magnetic materials, and photo-catalysts due to its interesting and useful features [78-81]. By filling the pores of the anodic aluminum oxide (AAO), arrays of aligned nanowires or nanotubes, uniform in diameter and length, are obtained reproducibly and economically [82]. Nanoporous anodic aluminum oxide (AAO) gained exposure for use as a membrane in applications such as gas separation, drug delivery, and bone fixation [83-86].
1.4.3 Pretreatment of anodized aluminium for electroless plating

1.4.3.1 Sensitization

The surface of the anodized aluminium is non-conducting. It behaves like a non-conductor. So direct electroless plating on anodized aluminium is impracticable. One has to follow the pretreatment process of plating on plastics, if electroless plating is to be carried out on anodized aluminium. Before electroless nickel plating, SnCl$_2$ was adsorbed on the surface of aluminium through a sensitization treatment in a solution containing SnCl$_2$ and HCl and then a layer of Sn(OH)Cl film is formed by hydrolysis of the SnCl$_2$.

$$\text{SnCl}_2 + \text{H}_2\text{O} \rightarrow \text{Sn(OH)Cl} + \text{HCl} \quad (8)$$

1.4.3.2 Activation

Activation is necessary to activate the non-conducting surface so that electroless plating is initiated. In this treatment, a replacement or exchange reaction takes place. The stannous ions are oxidized to stannic and releasing two electrons and goes into solution. These electrons are utilized for the reduction of palladium ions present in the activation solution into palladium particles. These palladium particles replace stannous ions by reduction of palladium ions into palladium. Thus formed randomly distributed palladium film is acting as a catalyst for the reduction of metal ion into metal on the palladium particles.

$$\text{Sn(OH)Cl} + \text{PdCl}_2 + \text{HCl} \rightarrow \text{SnCl}_4 + \text{H}_2\text{O} + \text{Pd} \quad (9)$$

The pictorial representation of electroless plating on anodized aluminium (non-conductor) is given in Fig. 1.1
1.5 Corrosion

Corrosion of metals may be defined as a spontaneous process of destruction in the course of their chemical, electrochemical or biochemical interaction with the environment. Electrochemical corrosion is encountered more frequently than other types of corrosion and is the most dangerous to metals. It may also occur in gaseous atmosphere when moisture condenses on the metal surface [87, 88].

Most of the metal corrosion occurs via electrochemical reactions at the interface between the metal and an electrolyte solution. A thin film of moisture on a metal surface forms the electrolyte for atmospheric corrosion.

Corrosion is both costly and dangerous. Billions of dollars are annually spent for the replacement of corroded structures, machinery, and components, including metal roofing, condenser tubes, pipelines, and many other items. In addition to replacement, costs are those associated with maintenance to prevent corrosion, inspections, and the upkeep of cathodically protected structures and pipelines. Indirect costs of corrosion result from shutdown, loss of efficiency, and product contamination or loss. To cope with the potential problems of corrosion, it is necessary to understand

- Mechanisms of corrosion
- Corrosion resistant properties of various materials
- Proper fabrication and installation techniques
- Methods to prevent or control corrosion
- Corrosion monitoring techniques.

Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is
oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often \( \text{O}_2 \) or \( \text{H}^+ \)) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs. The two reactions can take place on one metal or on two dissimilar metals (or metal sites) that are electrically connected.

### 1.5.1 Classification of corrosion processes

**(i) General Corrosion**

The metal/alloy surface area is entirely corroded in an environment such as a liquid electrolyte (chemical solution, liquid metal), gaseous electrolyte (air, \( \text{CO}_2 \), \( \text{SO}_2^- \), etc.), or a hybrid electrolyte (solid and water, biological organisms, etc.). Some types of general corrosion and their descriptions are given below.

a) **Atmospheric corrosion** on steel tanks, steel containers, Zn parts, Al plates, etc.,

b) **Galvanic corrosion** between dissimilar metal/alloys or microstructural phases (pearlitic steels, alpha-beta copper alloys, alpha-beta lead alloys).

c) **High-Temperature corrosion** on carburized steels that forms a porous scale of several iron oxide phases.

d) **Liquid-Metal corrosion** on stainless steel exposed to a sodium chloride environment.

e) **Molten-Salt corrosion** on stainless steels due to molten fluorides (\( \text{LiF} \), \( \text{BeF}_2 \), etc.,)
f) **Stray current corrosion** on a pipeline near a railroad.

(ii) **Localized Corrosion**

This term implies that a specific part of an exposed surface area corrodes in a suitable electrolyte. This form of corrosion is more difficult to control than general corrosion.

(iii) **Crevice corrosion** is associated with a stagnant electrolyte such as dirt, corrosion product, sand, etc. It occurs on metal/alloy surface holes, underneath a gasket, lap joints under bolts, under rivet heads.

(iv) **Filiform corrosion** is a special type of crevice corrosion, which occurs under a protective film. It is common on food and beverage cans being exposed to the atmosphere.

(v) **Pitting corrosion** is an extremely localized corrosion that causes destructive pits.

(vi) **Oral corrosion** occurs on dental alloys exposed to saliva.

(vii) **Biological corrosion** arises due to fouling organisms non-uniformly adhered on steel in marine environments.

(viii) **Selective leaching corrosion** is a metal removal process from the base alloy matrix, such as dezincification (Zn is removed) in Cu-Zn alloys and graphitization (Fe is removed) in cast irons.

1.5.2 **Factors affecting corrosion processes**

a) **Factors associated with the metal/solution interface**

   (i) Interfacial electrode potential
(ii) Presence of adsorbed ions and their concentration

(iii) Orientation of dipoles and adsorbed species

(iv) Interfacial pH

b) Factors associated with the metal

(i) Effective electrode potential of the metal in the solution

(ii) Over potential or hydrogen evolution on the metal

(iii) Chemical and physical heterogeneity of the metal surface

(iv) Ability to form an insoluble film.

c) Factors associated with the environment

(i) Hydrogen ion activity (pH)

(ii) Influence of oxygen in solution

(iii) Specific nature and concentration of ions existing in the solution

(iv) Ability of the environment to form a protective layer

(v) Temperature

(vi) Static and cyclic stress impressed on the metal

(vii) Contact between dissimilar metals or other materials affecting localized attack

(viii) Effect of flow rates.

1.5.3 Corrosion monitoring methods

Electrochemical techniques of corrosion measurements are classified into two types depending on the current used. They are DC electrochemical monitoring techniques and AC Electrochemical monitoring techniques.
**1.5.3.1. DC electrochemical monitoring technique-Tafel polarization**

In this technique, the polarization curves for the anodic and cathodic reactions are obtained by applying potentials about 300 mV against SCE well away from the corrosion potential and recording the current. Plotting the logarithms of current (log I) vs. potential and extrapolating the currents in the two Tafel regions gives the corrosion potential \( E_{corr} \) and the corrosion current, \( i_{corr} \). A hypothetical Tafel plot is shown in Fig. (1.2). Knowing \( I_{corr} \), the rate of corrosion can be calculated in desired units by using Faraday's law. The modern techniques for measurement of corrosion rates are based on the classical work of Stern and Geary [89].

Polarization method involves changing the potential of working electrode and monitoring the current, which is produced as a function of time or potential.

Electrochemical reactions either produce or consume electrons. The rate of electron flow is the measure of reaction rate. Faraday’s Law gives the proportionality between the corrosion current, \( I_{corr} \) and mass reacted \( m \), in an electrochemical reaction: [90]

\[
m = I_{corr} \cdot t \frac{(a/n) F}{\text{Faraday’s constant}}
\]

where ‘F’ is Faraday’s constant, ‘n’ is the number of equivalents exchanged, ‘a’ is atomic weight and ‘t’ is time. Dividing Equation 1.1 by ‘t’ and surface area \( A \), we get corrosion rate (CR) as:

\[
CR = \frac{m}{At} = I_{corr} \frac{(a/n) F}{\text{Faraday’s constant}}
\]

where \( i_{corr} = I_{corr}/A \), is the corrosion current density. Units of penetration per unit time result from dividing Equation 1.2 by density ‘D’ of metal or alloy and substituting the value of F, we get,
Equivalent weight (gm) 

\[ CR \text{ (mpy)} = \frac{0.129 \times i_{\text{corr}} \text{ (μA/cm}^2\text{)}}{\text{Density (gm cm}^{-3}\text{)}} \]

Corrosion rates are generally expressed as either a rate of metal penetration or a rate of weight loss per unit area. As a result, we have corrosion rate units such as mills per year (mpy) or millimeter per year (mm y\text{-1}) or milligrams per square decimeter per day (mdd) or micrometer per year (μm y\text{-1}). The proportionality constant 0.129 becomes 0.00327 for mmy\text{-1} and 3.27 for μm y\text{-1} respectively.

The potential-current density plot is approximately linear in the \pm 0.1V of the corrosion potential. The slope of this linear portion will give the polarization resistance, which is further related to the corrosion current density.

\[ R_p = \frac{b_a \times b_c}{2.303 \ (b_a + b_c) \ i_{\text{corr}}} \]

where \( R_p \) is polarization resistance, \( b_a \) and \( b_c \) are the magnitude of the Tafel slope of the anodic and cathodic Tafel lines respectively.

1.5.3.2. AC electrochemical monitoring technique – Electrochemical Impedance Spectroscopy (EIS)

The AC impedance technique has been extensively used to study corrosion phenomena. By applying a low-amplitude oscillating potential to the working electrode, the perturbation of the electrode is minimized and useful information about the electrochemical characteristics of the corrosion process on the surface is obtained. This technique is a powerful tool for characterizing coated metal surface.

To make an EIS measurement, a small amplitude signal, usually voltage between 5 and 50 mV, is applied to a specimen over a range of frequencies of 0.001 Hz to
1,00,000 Hz. The EIS instrument records the real (resistance) and imaginary (capacitance) components of the impedance response of the system. Depending upon the shape of the EIS spectrum, a circuit description code and initial circuit parameters are assumed and input by the operator. Fig.1.3a represents the equivalent circuit for corroding electrode. A typical Nyquist (cole-cole) plot for the Randles cell is illustrated in Fig. 1.3b.

The Bode plot (Fig. 1.3c) is a useful alternative to the Nyquist plot to avoid the larger measurement times associated with low frequency $R_{CT}$ determinations. Sometimes allows a more effective extrapolation of data from higher frequencies. The Bode format is also desirable when data scatter precludes adequate fitting of the Nyquist semicircle. In general, the Bode plot provides a clear description about the frequency-dependent behaviour of electrochemical systems than does the Nyquist plot, where the frequency values were implicit.

1.6 Characterization Techniques

1.6.1 Scanning electron microscopy (SEM)

SEM is one of the most widely used techniques used in characterization of nanomaterials and nanostructures. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications that are easily adjusted from ~10 to over 300,000. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface. In a typical SEM, a source of electrons is focused into a beam, with a very fine spot size of ~5 nm and having energy ranging from a few hundred eV to 50 KeV that is faster over the surface of the specimen by deflection coils. As the electrons strike and
penetrate the surface, a number of interactions occur that result in the emission of electrons and photons from the sample, and SEM images are produced by collecting the emitted electrons on a cathode ray tube (CRT). Various SEM techniques are differentiated based on what is subsequently detected and imaged, and the principal images produced in the SEM are of three types: secondary electron images, backscattered electron images and elemental X-ray maps. An additional electron interaction occurs in the SEM when the primary electron collides with and ejects a core electron from an atom in the sample. The excited atom will decay to its ground state by emitting either a characteristic X-ray photon or an Auger electron, both of which have been used for chemical characterization. Combining with chemical analytical capabilities, SEM not only provides the image of the morphology and microstructures of bulk and nanostructured materials and devices, but can also provide detailed information of chemical composition and distribution.

1.6.2 Energy dispersive atomic X-ray analysis (EDAX)

Another possible way in which a beam of electron can interact with an atom is by the removal of an inner shell electron. The resultant vacancy is filled by an outer electron, which can release its energy either via an Auger electron or by emitting an X-ray. This produces characteristic lines in the X-ray spectrum corresponding to the electronic transitions involved. Since these lines are specific to a given element, the composition of the material can be deduced. This can be used to provide quantitative information about the elements present at a given point on the sample, or alternatively it is possible to map the abundance of a particular element as a function of position.
1.6.3 Atomic force microscopy (AFM)

The atomic force microscope (AFM) or scanning force microscope (SFM) is a very high-resolution type of scanning probe microscope, with demonstrated resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit. Block diagram of AFM is given in Fig. 1.4. The AFM consists of a microscale cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature about nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, Van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, solvation forces etc. The deflection is also measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes.

1.6.4 X-ray diffraction (XRD)

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. In XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 A, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law:

\[ \lambda = 2d \sin \theta \]
where $d$ is the spacing between atomic planes in the crystalline phase and $\lambda$ is the X-ray wavelength. The intensity of the diffracted X-rays is measured as a function of the diffraction angle and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties.

Diffraction peak positions are accurately measured with XRD, which makes it the best method for characterizing homogeneous and inhomogeneous strains. Homogeneous or uniform elastic strain shifts the diffraction peak positions. From the shift in peak positions, one can calculate the change in $d$ spacing, which is the result of the change of lattice constants under a strain. Inhomogeneous strains vary from crystallite to crystallite or within a single crystallite and this causes a broadening of the diffraction peaks that increase with $\sin \theta$. Peak broadening is also caused by the finite size of crystallites, but here the broadening is independent of $\sin \theta$. When both crystallite size and inhomogeneous strain contribute to the peak width, these can be separately determined by careful analysis of peak shapes. If there is no inhomogeneous strain, the crystallite size, $D$, can be estimated from the peak width using the Scherrer's formula.

$$D = \frac{K\lambda}{\beta \cos \theta}$$

where $\lambda$ is the X-ray wavelength, $\beta$ is the full width at half of maximum (FWHM) of a diffraction peak, $\theta$ is the diffraction angle, and $K$ is the Scherrer’s constant of the order of unity for usual crystal. However, one should be alerted to the fact that nanoparticles often form twinned structures; therefore, Scherrer’s formula may produce results different from the true particle sizes. In addition, X-ray diffraction only provides the collective information about the particle sizes and usually requires a sizable amount of powder. It should be noted that, since the estimation would work only for very small particles, this
technique is very useful in characterizing nanoparticles. Similarly, the film thickness of epitaxial and highly textured thin films can also be estimated with XRD.

1.6.5 Cyclic voltammetry

Cyclic voltammetry is a technique that allows one to scan the potential of working electrode either in anodic or cathodic direction and observes peaks due to oxidation or reduction. It is a simple technique, which provides a great deal of information about electrochemical behaviour. Hence, it is considered as one of the most powerful electrochemical diagnostic tools. The shape of the voltammogram depends strongly on the mechanism of the electrode process. Cyclic voltammetry can provide information about the number of electrons transferred in each peak. The potential may be swept anodically or cathodically and unlike polarographic waves, the curves obtained are peaks. The chief strengths of cyclic voltammetry are:

- Applicability to a wide range of electrode materials.
- A range of five orders of magnitude in scan rates.
- Great flexibility in setting up scan limits and reversal conditions.
- An intrinsic facility for highlighting the chemical conditions between various electroactive species present in the voltammogram.
- Highly developed theory.

The criteria for important systems are presented in Table 1.1

1.7 Review of Literature

Nanocrystalline nickel was synthesized by number of methods on different substrates. E. Moti et al. [91] synthesized NC-Ni (14-25nm) by electrodeposition using
rotating cylindrical electrodes in a modified Watts bath. In this method, the effect of cathode rotation speed and saccharin concentration on the grain size was studied by transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis.

U. Klement and M. Silva [92] have determined the grain orientation of abnormally grown grains in nanocrystalline Ni electrodeposits upon annealing using the electron backscattered diffraction technique. They found that the preferred alignment of the abnormally growing grain changes from (311) to (111) upon annealing.

S.C. Mehta et al. [93] studied the microstructural evolution of electrodeposited NC Ni-1.2wt%P and pure nickel during heating experiments. They found that grain structure of the Ni-1.2wt. %P alloy was stable up to a temperature of 360°C. The grain growth was concurrent with Ni₃P precipitation, suggesting the important role of phosphorus in supersaturated solid solution in imparting the thermal stability to the microstructure.

F. Ebrahimi and Z. Ahmed [94] studied the effect of current density on properties of electrodeposited NC nickel from a sulfamate-based electrolyte. The crystalline size of the deposit was evaluated by XRD technique and their mechanical properties were characterized by tensile testing. They suggested that the enhanced evolution of hydrogen at high current densities is responsible for the formation of larger crystals and the unusual low tensile elongation.

A.M. Rashidi and A. Amadeh [95] have investigated nanocrystalline nickel coatings from a Watts bath containing 5 g/l sodium saccharin as an additive, by direct current electroplating at different current densities. X-ray diffraction analysis and modified Williamson–Hall relation were used to determine the average grains size of the coatings.
S. Kobayashi and Y. Kashikura [96] examined the grain growth and mechanical properties of electrodeposited nanocrystalline Ni-4.4mass% P alloy.

G.A. Walker and C.C. Goldsmith [97] have studied the structural comparison of electroless and electrolplated NC-Ni by XRD and scanning electron microscopy.

The Young’s modulus of electrodeposited amorphous and nanocrystalline Ni–P with grain sizes ranging from 4 to 29 nm was examined by Y. Zhou et al. [98] using the nanoindentation technique.

A. Malecki and A. Micek-Ilnicka [99] proposed the mechanism of electroless nickel plating in acid bath. The kinetics of this reaction has been investigated and an empirical rate equation for the bath has been developed.

P. Sampath Kumar and P. Kesavan Nair [100] have studied electroless nickel-phosphorus deposits with 4.35, 5.45, 6.80, 8.10 and 9.12 wt.% P. The deposits were annealed at 60, 100, 200, 300, 330, 360, 400 and 600°C for 2 h. The crystallization process of these deposits was studied using X-ray line profile analysis and differential scanning calorimetry.

J.X. Kang et al. [101] have prepared nanocrystalline nickel coatings by a direct current electrodeposition technique and their microstructure and microhardness were investigated by high-resolution transmission electron microscopy and microhardness tester.

G. Yue et al. [102] prepared nickel nanowire (NW) arrays on the inside nanochannels of anodic aluminum oxide (AAO) templates via direct current electrochemical deposition. They synthesized single-crystal and netlike poly-crystal Ni nanowires by controlling electrolyte composition and electrodeposition parameters.
L. Qin et al. [103] have examined the electrodeposited nanostructured Ni coating on steel sheet using X-ray diffractometer analysis. They found that, on gradually increasing the grain refiner concentration, the grain size vary from 22 nm on surface to about 586 nm near the coating–substrate interface. Hardness and electrochemical measurements in NaCl solution were carried out. They found that nanostructured nickel coatings had high hardness and high corrosion resistance properties as well as excellent adhesion to substrate.

T. Asada in Japan [104] developed a process in which very light fast shades of bronze or black were obtained from electrolyte system containing either Ni or Tin salts by AC electrodeposition of fine Ni or Tin particles in the pores of the anodized aluminium.

Nanocrystalline (50-μm-thick) Ni films with controlled surface morphology were synthesized by F. Sansoz et al. [105] using direct-current electrodeposition of Ni on Si substrate under different electrochemical conditions. A relationship between spatial roughness scaling and mean grain size in electrodeposited Ni was established using X-ray diffraction and atomic force microscopy. A non-destructive method was demonstrated to estimate the grain size distribution of ultra smooth NC-Ni surfaces by atomic force microscopy with high-resolution probes.

N. S. Qu et al. [106] studied the synthesis of pulse electrodeposition of nanocrystalline nickel using ultra narrow pulse width and high peak current density.

C. Wang et al. [107] prepared the NC-Ni powders in aqueous solution through a thermal-reduction process. XRD, (TEM) and chemical analysis were employed to characterize the products.
L. Ajdelsztajn et al. [108] studied the synthesis and mechanical properties of nanocrystalline Ni coatings produced by cold gas dynamic spraying (CGDS) technology. The resulting coatings were evaluated using SEM, TEM, XRD and micro and nanoindentation techniques.

X. F. Qian et al. [109] successfully prepared nanocrystalline Ni$_2$P by the solvent–thermal method at 150°C.

Y. Mi et al. [110] synthesized NC-Ni by thermal reduction process using nickel chloride by KBH$_4$ in ethylenediamine at 300°C. X-ray powder diffraction and selected-area electron diffraction showed that the nanocrystalline nickel has a hexagonal close-packed structure. Transmission electron microscopy indicated that the products were nanoclusters, which consist of nickel nanoparticles.

A.M. Rashidi and A. Amadeh [111] have studied the optimum conditions for electroplating nanocrystalline nickel coating from Watts-type bath. Effect of some process parameters namely, bath temperature, current density, and saccharin addition on grain size and texture coefficient (TC= $I_{(200)}/I_{(111)}$) of the deposits were investigated by X-ray diffraction (XRD).

L.Y. Qin et al. [112] have fabricated nanocrystalline (NC) and coarse-grained Ni with different grain sizes (from 16 nm to 2 μm) by direct current electrodeposition. They studied the effect of grain size on the electrochemical corrosion behaviour of these Ni deposits in different corrosion media and characterized by using potentiodynamic polarization test, electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS) and immersion corrosion test. They found that in the NaOH or NaCl
solution, the NC-Ni exhibits improved corrosion resistance with the decrease of grain size.

H.T. Zhang et al. [113] synthesized nickel nanocrystals by the decomposition method. The resulted nanoparticles were characterized to be single-phase nanocrystalline nickel with a face-centered cubic type. They studied the mechanism of the size-controlled nanocrystals formation and found that, relative monodispersed nanocrystals could be formed by the separation of nucleation and growth process while the size could be controlled through modulating growth period.

A new electrolytic process was presented by T. Moller and D. Honicke [114] to grow solar selective layers on aluminium. By this process, anodization of aluminium and the pigmentation of the Al₂O₃ can be done in a single electrolysis bath. They investigated the optical properties of these layers and the scale-up of the process and to improve the corrosion resistance of these layers, a hydrophobic procedure was used.

Z. Wu et al. [115] studied the synthesis of nickel nanoparticles supported on metal oxides using electroless nickel-plating method. The process and mechanism of electroless nickel plating were studied by changing the active metal (Ag) loading, acidity, and surface area of metal oxides and were characterized by UV–Vis. spectroscopy, transmission electron microscopy, scanning electron microscopy and H₂ chemisorption.

S. Kodama et al. [116] investigated the absorbance of ultra black films of electroless nickel-phosphorus alloy. Results of varying the plating and etching bath components and conditions were studied. They observed that the coating was a superior optical absorber, which has a spectral reflectance of about 0.1-0.2%.
N. Backović et al. [117] found that electroless Ni-P deposition on aluminium starts by nucleation of nickel primarily at grain boundaries and at defects present on the aluminium surface. They found that, after heat treatment, the deposits have a well-defined crystal structure and it was confirmed that two crystalline phases of nickel and Ni$_3$P were present.

S. John et al. [118] have reported a method for immersion blackening of galvalume coatings for use as a selective surface for solar collectors. They found that such coatings have a solar absorbance ($\alpha$) of 0.90–0.92 and thermal emittance ($\epsilon$) of 0.25–0.40 and moderate corrosion resistance. They observed that, post-treated coatings in dichromate solution offered good corrosion resistance, thermal cycling tests showed that the coatings were stable upto 220°C and the tape tests showed that the coating was strongly adherent.

S. John et al. [119] reported the solar absorber coatings formed by blackening of electroless nickel deposits. Such coatings have an absorbance $\alpha$ of 0.94 and an emittance $\epsilon$ of 0.15. Electroless nickel was deposited at room temperature and then blackened in dilute HNO$_3$ solution. The coatings were tested for thermal stability and compared with standard black chrome panels.

H. Jha et al. [120] demonstrated the formation of palladium nanoparticles on aluminum and aluminum oxide surface. They used as-received, boiled, electropolished and anodized aluminum as substrate. The specimens were first immersed in palladium (II) acetate solution followed by immersion in electroless nickel plating solution. Using the technique, about 6 to 8.5 $\mu$m thick Ni–P metallic layer was deposited on the specimen surface.
Electroless Ni-7.4 to 10% P deposits obtained from acidic nickel sulphate baths with sodium hypophosphite as a reducing agent were analyzed by S.H. Park and D.N. Lee [121] using electron microscopy, X-ray diffraction and thermal analysis. The deposits have a microcrystalline structure composed of 4 to 5 nm fcc Ni-P solid-solution grains rather than an amorphous structure. The deposits also had the (111) texture, which persisted in nickel grains even after phase separation of nickel and Ni₃P by heating in the case of the low nickel content, whereas the texture approached the random orientation with increasing phosphorus content. The phase transformation temperature was independent of the phosphorus content.

S. N. Kumar et al. [122] have developed low cost electroless nickel black coatings for photothermal conversion.

Á. Révész et al. [123] have analyzed the nanocrystalline structure of an electroless plated Ni-P amorphous alloy using Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements.

B. Farber et al. [124] investigated the microstructure of electroless plated and thermally aged nanocrystalline Ni±3.6 at.% phosphorus on an atomic scale with a tomographic atom probe (TAP) method.

The transformation sequence of electroless plated nanocrystalline Ni±3.6 at.% P layers upon different heat treatments were studied by Hentschel et al. [125] using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and atom-probe field-ion microscopy (APFIM) methods.

L. Li [126] examined AC anodization of aluminium in phosphoric acid modified by a small number of intention alloy added species such as iron species, followed by
electrodeposition of Nickel. They developed a cheap and best method for preparing selective solar absorbing surface of nickel pigmented anodic films of aluminium. They also calculated the solar absorbance and thermal emittance.

Crobu et al. [127] studied the corrosion resistance of electroless deposited nanocrystalline Ni-P alloys using potentiostatic polarization method.

J. G. Jin et al. and co-workers [128] have investigated the electroless plated Ni layer by ultrasonic agitation during zincating process. Adhesion strength was evaluated by a pull-off test and scratch test. They found that ultrasonic agitation during zincating increased the nucleation density of Zn particles and refined Zn particle size.

The Ni–P coatings with different contents of nanocrystalline phase were prepared by Y.H. Cheng et al. [129] using electroless plating method. Crystallization fouling adhering experiments indicated that these electroless Ni–P coatings have better anti-fouling property than that of uncoated sample. They found that the adhering amount of crystallization fouling increased with the increasing of nanocrystalline phase.

M. Yan et al. [130] reported that, the coatings with different phosphorus contents were obtained by varying the ratio of lactic acid to acetic acid in the electroless plating bath. They found that, with the increase of phosphorus content, the structure of the electroless Ni–P coating was transformed from nanocrystalline to a mixture of nanocrystalline and amorphous phases, then to amorphous phase. The refined nanocrystalline grains with an average size of ~ 4 nm were found to be responsible for the record high hardness and improved wear resistance of the as-deposited Ni–P coating.

F. Wang et al. [131] reported the synthesis of carbon nanotube supported nickel-phosphorus nanoparticles by an electroless process.
J.N. Balaraju and K.S. Rajam [132] have studied the synthesis, structural characteristics and phase transformation behaviour of plain electroless Ni–P and Ni–P–Si$_3$N$_4$ composite coatings formed from a low phosphorus electroless nickel bath containing 1 to 5 g/l submicron silicon nitride particles at pH 6.5 and temperature 85 ± 2°C by SEM, XRD, EDX and DSC.

I. Petukhov [133] studied the electroless deposition of nickel-phosphorus coatings from acetate solutions. The morphology and microrelief of the coatings surface were defined by the nucleation and growth of spheroids. The spheroids form probably via a layered-growth mechanism and are markedly extended in the substrate's plane.

X.C. Wang et al. [134] obtained electroless Ni–P deposits with a wide range of phosphorus contents (from; 2 to 13 wt.%) at higher deposition rates from alkaline solutions containing tri-sodium citrate and ammonium chloride. X-ray fluorescence analysis, XRD, SEM and polarization curves were used to characterize the compositions, structures, morphologies and anti-corrosion properties of these Ni–P coatings respectively.

The effect of continuous heating on the crystallization kinetics and the phase transformation behaviour of electroless nickel–phosphorus deposits with high phosphorus contents of 12 and 16 wt.%, were studied by K. G. Keong et al. [135]. They found that the crystallization temperature of the deposits increased with decreasing phosphorus content, and increasing heating rate. The activation energies during the crystallization processes were calculated from the differential scanning calorimetry (DSC) curves.

Manufacture of nickel–phosphorus black surfaces by chemical etching of electroless deposited Ni–P alloy has been achieved by R.J.C. Brown et al. [136] They
examined the influence of pre-etch phosphorus composition on the resulting morphology, composition and reflectance of the black surface produced. AFM studies have also provided information about the phase structure of the as-deposited Ni–P alloy.

X. Haowen and Z. Bangwei [137] have studied systematically the fabrication technology and its effects on the structure and amorphous forming region (AFR), and theoretical description of the AFR for electroless Ni–P alloys. It has been found that the deposition rates increase and approach a maximum value and then decrease with the increase in the concentration of nickel chloride, sodium hypophosphite and pH value respectively. However, the deposition rates decrease with the increase of sodium citrate.

S.Z. Chu et al. [138] described the fabrication and characteristics of nanostructures on glass by Al anodization and electrodeposition. An aluminium film was sputter deposited on a glass substrate coated with a tin-doped indium oxide (ITO) film. The film was then anodically oxidized to obtain a porous alumina template with pore diameters ranging from 5 to 120 nm. They found that, in nickel electrodeposition, the porous alumina films not only define the dimension of the nickel nanowires but also influence their crystalline orientation, showing a textured (2 2 0) orientation for 18 nm nanowires.

The highly ordered Ni–P alloy nanotube and nanowire arrays with high aspect ratio have been successfully synthesized inside porous anodic aluminum oxide (AAO) membranes by J. Liu et al., [139] by self-assembly electrodeposition at different current densities. The as-synthesized Ni–P alloy arrays have amorphous phase structure with nanograins of crystalline Ni. The formation of nanotubes or nanowires during
electrodeposition mainly depends on the current densities, deposition time and phosphorous acid concentration in the electroplating bath.

1.8 Current Status, Scope and Objectives

Materials with grain sizes of around 5 to 100 nm are termed as nanocrystalline. Grain sizes greater than 100 nm are normally considered as polycrystalline materials. Grain sizes of this order leads to have different properties from those in crystals. These properties include very high mechanical strength, magnetic, electrical and high corrosion resistance [1, 140]. There are several methods to prepare nanocrystalline materials [1]. Among which electrochemical method is one thereby, one can deposit nanocrystalline coating over a base material in order to get good properties. Electroless deposition is one of the best methods to form coating of nanocrystalline in nature. Electroless nickel phosphorus is well known for its amorphous/nanocrystalline alloy considered to be closed to commercial applications [8, 41, 141-143].

Review articles on chemical reduction of nickel alloys with hypophosphite [47], electroless plating [144], electroless alloy/composite coatings and an over all aspect of electroless nickel – phosphorus [49] deal with general electroless plating with special reference to nickel. Various complexing agents have been reported in the literature such as acetate [145, 146], citrate [50, 147-154], lactate [155, 156], succinate [157, 158], glycine with citrate [159] and glycine with acetate [160]. Among which, acetate, citrate and lactate are widely used as complexing agents for the deposition of nickel-phosphorus alloy. In the citrate-based electrolyte, the effect of ultrasonic radiation on the rate of deposition of Ni-P alloy and their properties were reported [154, 161]. Effect of agitation
in the citrate based electrolyte on its rate and alloy composition has been studied by K. Sevugan et al. [162].

Electroless nickel depositions on different substrate materials have also been reported. Ni-P coating on various substrates such as aluminium [144, 120], anodized aluminium [163-167], porous anodic aluminium oxide [168], carbon fibre [169], steel [145, 170-172], rebar surface [173], silicon [174, 175], silicon carbide/aluminium composite [147], copper [176], Fe/Si [177], graphite [178], magnesium alloy [179-181] and Al/Si [182] substrates have been reported.

From the thorough literature survey, it was noted that, no detailed work has been reported on the formation of NC-Ni-P deposits directly on anodized aluminium in electroless nickel baths containing complexing agents sodium acetate, tri-sodium citrate and glycine. Hence, it was decided to study the electroless NC-Ni-P deposition on aluminium from sodium acetate, tri-sodium citrate and glycine baths and to find out the feasibility of developing these bath solutions for industrial applications.

In the present work zincated and anodized aluminium were used as the substrates for the synthesis of nanocrystalline nickel. Sodium acetate, tri-sodium citrate and glycine were used as complexing agent. First investigation is on studies on electroless nickel deposition from sulfate bath containing only sodium acetate as the complexing agent. Effect of bath parameters on the rate of deposition, alloy composition, morphology, spectral characteristics, corrosion and structure before and after heat treatment were studied. The above studies were also carried out on the electroless Ni-P deposition from tri-sodium citrate and glycine based electrolytes separately. Sodium hypophosphite was
used as the reducing agent for all the three systems viz., electroless Ni-P from (i) Sodium acetate bath, (ii) Tri-sodium citrate bath and (iii) Glycine bath.

In the present investigation, we have demonstrated a new approach to the synthesis of nanocrystalline Ni-P on aluminium by electroless plating. The main aim and objectives of the present investigation are given below:

- To find out suitable pretreatment method for formation of nanocrystalline electroless Ni-P deposition.
- To optimize the conditions of pretreatment (zincating and anodizing) and electroless Ni-P plating.
- To form nanocrystalline Ni-P coatings by electroless nickel deposition on zincated and anodized aluminium from three different plating baths.
- To evaluate the plating parameters such as rate of deposition and thickness of the coating.
- To characterize the surface morphology of the NC-Ni-P coatings.
- To analyze the phase and elemental composition of the coatings.
- To analyze the nanostructure and texture of the electroless nickel coating.
- To study the electrochemical behaviour of the NC-Ni-P deposit.
- To study the corrosion resistance behaviour of the NC-Ni-P coated aluminium.
Anodized Aluminium

Sensitisation → (SnCl₂ + HCl)

Sn²⁺ + Sn⁴⁺ + Pd²⁺ → Sn⁴⁺ + Pd⁰

Activation → (PdCl₂ + HCl)

Electroless Plating

Fig. 1.1. Pictorial representation of electroless plating on anodized aluminium
Fig. 1.2. A hypothetical Tafel plot
Fig. 1.3. AC impedance profile for a simple electrochemical system

a) Equivalent circuit model

b) Typical Nyquist plot

c) Typical Bode plot
Fig. 1.4. Block Diagram of Atomic Force Microscope
<table>
<thead>
<tr>
<th>System</th>
<th>Diagnostic criteria</th>
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</table>
| **Reversible** | $E_p$ is independent of $\nu$; $E^o = (E_p^a - E_p^c) / 2$  
$E_p^c - E_p^a = 59/n \text{mV at 25}^\circ \text{C}$ and is independent of $\nu$  
i_p/\nu^{1/2}$ is independent of $\nu$; $i_p^a/i_p^c$ is unity and independent of $\nu$  
Wave shape is independent of $\nu$ |
| **Quasi reversible** | $E_p$ shifts with $\nu$  
$E_p^c - E_p^a$ may approach $60/n \text{mV}$ at low $\nu$ but increases as $\nu$ increases  
i_p/\nu^{1/2}$ is virtually only for $\alpha = 0.5$ |
| **Irreversible** | No current response in reverse scan  
$E_p$ shifts cathodically by $30/\alpha n \text{mV}$ per tenfold increase in $\nu$  
The wave shape is determined by $\alpha$ [49] and is independent of $\nu$ |
| Preceding reversible chemical reaction | $E_p$ shifts anodically with an increase in $\nu$  
i_p/\nu^{1/2}$ decreases as $\nu$ increases |
| Following reversible chemical reaction | $E_p$ shifts cathodically with an increase in $\nu$  
i_p/\nu^{1/2}$ virtually constant with $\nu$  
i_p^a/i_p^c$ decreases from unity as $\nu$ increases |
| Charge transfer with catalytic regeneration | $E_p$ shifts anodically by a maximum of $60/n \text{mV}$  
i_p/\nu^{1/2}$ increases at low values of $\nu$ and becomes independent in higher $\nu$  
i_p^a/i_p^c$ is unity |
| Following irreversible dimerisation reaction | $E_p$ shifts cathodically by $20/n \text{mV}$ per tenfold increase in $\nu$ and per tenfold decrease in initial concentration, $C_{ox}^*$  
i_p/\nu^{1/2}$ decreases a maximum of $20\%$ from low to high $\nu$  
i_p^a/i_p^c$ increases with $\nu$ and decreases as $C_{ox}^*$ increases. |