CHAPTER-VI
SUMMARY AND CONCLUSIONS

In this work, we studied the synthesis and surface characterization of electroless nanocrystalline Ni–P deposition on two different pretreated aluminium (zincating and anodizing) from three different acidic baths containing sodium hypophosphite as a reducing agent, nickel sulphate as the metal ion source, sodium acetate, tri-sodium citrate and glycine as the complexing agents at various bath compositions, treatment times, pHs and temperatures.

Thickness, rate of deposition, atomic percentage of phosphorus and nickel of electroless Ni–P deposits on aluminium are depending upon the concentration of sodium acetate, tri-sodium citrate, glycine, nickel ion, sodium hypophosphite, pH of the plating bath, bath temperature, surface area/volume ratio and plating time. The optimized Ni-P deposits on both zincated and anodized aluminium were characterized by EDAX, SEM, AFM, XRD, Tafel, EIS and CV studies in the as-deposited condition. Nanocrystalline Ni-P coatings after heat treatment were characterized by SEM, AFM, XRD, Tafel and EIS analysis. The following conclusions were derived from the results and discussion.

(a) **NC-Ni-P deposition on zincated aluminium**

Highly adherent, smooth, uniform, bright and pore free NC-Ni-P deposits can be successfully formed from all sodium acetate, tri-sodium citrate and glycine baths on zincated aluminium. The Ni-P deposits are having matte finish and transformed into dark gray and bright nickel finish as the deposition time increases.
For the electroless Ni-P alloy deposits, increase in concentration of sodium acetate in sodium acetate bath (low stability constant) increases the thickness and rate of deposition upto 0.2M beyond that they are found to decrease. In the tri-sodium citrate bath and glycine bath, thickness and rate of deposition increases upto 0.15 M, after that they decrease for the studied concentration range.

Increasing the concentration of nickel sulphate, sodium hypophosphite, pH value, temperature, surface area/volume ratio, increase the thickness and rate of deposition upto certain level and after reaching maximum, they decrease. For all studied baths, as the deposition time increases from 30 s to 1800 s, thickness increases and the deposition rate decreases.

EDAX results revealed that, with the increase of concentration of sodium acetate, tri-sodium citrate, glycine and the sodium hypophosphite, atomic % of phosphorus increases but atomic % of nickel decreases. As the concentration of NiSO$_4$ increases, the content of phosphorus decreases and the nickel content of the deposit increases.

Increase in the bath pH, temperature and surface area/volume ratio, increase the nickel content of the electroless Ni-P deposit but decrease the phosphorus content. Low pH value yielded higher P content of the deposit.

Increasing the plating time from 30 s to 1800 s, at.% of Ni increases and simultaneously at.% of P decreases. Initially the deposited coating contains trace amount of zinc. EDAX analysis revealed that the coating is constituted by a Ni-P alloy.

The surface morphology of the coating is uniform, spherical nodular structure is formed in the as-deposited state. After heat treatment, nanocrystalline and homogeneous grains become finer with increase in the dimension of the grain size is observed.
The AFM results show that the grains become finer, high dense and compact and form a uniform structure in the as-deposited condition. As the deposition time increases, number of grains decreases and cauliflower like morphology is observed. As the deposition time increases, roughness decreases, because of coating smoothness increases. After heat treatment, the size of the grains becomes increased. Each grain consists of larger number of smaller grains and diffused like morphology is observed.

The differences in the crystallinity of the coatings produced at low pH values with different deposition time are related to the phosphorus content in the alloy. The metallization performed in acidic bath promoted the formation of alloys with high P content, which are preferentially nanocrystalline/amorphous, as confirmed by XRD analysis. The XRD patterns of Ni–P deposits reveal that the deposit produced in shorter duration has sharp Ni and phosphorus peaks. For higher deposition time, the deposit is nanocrystalline in nature. After heat treatment, Ni-P deposits crystallized to produce Ni and different types of phosphides (Ni$_5$P$_2$, Ni$_5$P$_4$, Ni$_{12}$P$_5$, NiP and Ni$_3$P) with different plane orientations.

Potentiodynamic polarization studies in 3wt.% sodium chloride solution showed that all the coatings had good corrosion resistance. For as-deposited conditions, the $E_{\text{corr}}$ values had positive shift compared to the bare aluminium. However, the $i_{\text{corr}}$ value for the as-deposited condition was found to be lower for all the samples tested.

EIS studies revealed that all the coatings studied were having single time constant and the NC-Ni-P coating films were having higher polarization resistance than that of bare aluminium. The corrosion resistance of the coatings studied is increased when they are heat-treated at 400°C for 1 h.
CV investigations were carried out for electroless Ni-P deposits produced at various concentrations of solution constituents such as, nickel ion, sodium acetate, sodium hypophosphite and pH of the electroless deposition systems to study the oxidation and reduction processes involved. By increasing the above bath parameters, anodic peak potential of cyclic voltammogram move to positive direction and cathodic peak shifted to negative side.

(b) **NC-Ni-P deposition on anodized aluminium**

Effect of electroless plating parameters on the reflectance, chemical composition, morphology, structure and corrosion resistant property of electroless NC-Ni-P deposits formed on anodized aluminium from sodium acetate, tri-sodium citrate and glycine baths has been investigated by the UV, EDAX, SEM, AFM, XRD, Tafel and EIS measurements. The following conclusions were derived from the results of the investigation.

Uniform NC-Ni-P deposits have been successfully synthesized on anodized aluminum substrate by an electroless deposition after appropriate sensitization and activation pre-treatments.

Sulphuric acid anodization process produced large number of nanopores on the anodized aluminium surface. In the sensitization treatment, a continuous SnCl₂ film is formed on the AAO film surface and during PdCl₂ activation treatment crystalline Pd particles are dispersedly produced on SnCl₂ film. During electroless nickel deposition process, the nickel ions are adsorbed on the nanoporous anodized aluminium surface and reduced into the metallic nickel and they are distributed uniformly.
It was found that as the plating time increases, weight of electroless Ni-P deposits on AAO film increases.

In the NC-Ni-P coatings formed on AAO film produced in sodium acetate bath, the colour of the coating changes from matte black to jet black, nickel finish is obtained as the electroless deposition time increases. But in tri-sodium citrate bath, as deposition time increases, the colour of the coatings changes from dark brown to velvet black, nickel finish. When the deposition time was increased to more than 600 s the coatings have poor adherence and were highly brittle in nature. In the glycine bath, the colour of the coating changes from brown to black; metallic nickel finish was obtained by increasing the deposition time.

As the deposition time increases, the reflectance value of black NC-Ni-P in the visible region is decreases.

EDAX analysis reveals that as-deposited Ni-P coating on AAO at early deposition stage shows the peaks of Ni, P and S element. The Ni and phosphorus element are coming from electroless deposition process but in sulphur element comes from the sulphuric acid anodization process. As the deposition time increases, sulphur peak disappears. Atomic percentage of phosphorus in the Ni-P coating with various deposition times follows parabolic manner in the as-deposited condition for all baths.

Scanning electron microscopy analysis shows that during the initial stages of electroless nickel plating on anodized aluminium, a large quantity of nickel is deposited on palladium chloride activated surface. However, there is still a fraction of the surface area consisting of voids or gaps between nickel islands. As deposition progresses, the gaps become filled due to the self-catalytic nature of the nickel particles.
The surface morphology of the coating was changed from nodular to spherical; ripple like structure was obtained with increasing deposition time in the sodium acetate bath in the as-deposited condition. In tri-sodium citrate bath, it is noted that, nodular, granular, cauliflower like structure is obtained. In glycine bath, nodular, spherical, cauliflower like structure is observed.

SEM results showed that the coating obtained from glycine bath has nanocrystalline structure for longer duration than that of tri-sodium citrate and sodium acetate bath.

After heat treatment the dimension of the crystal size increases compared to as deposited Ni-P coatings. As expected, the crystallization of the films changes their surface topography.

From the AFM observation, it can be found that, in the electroless Ni-P deposits obtained from sodium acetate bath, surface topography of the as-deposited coating consists of nanocrystals which become finer, dense, compact and uniform square like boxes. These Ni-P crystals joined to each other in the direction parallel to the substrate surface to form the columnar structure at 30 s. The crystal size is less than 50 nm. As the deposition time increases to 1800 s columnar deposits coalesced to larger mounds and the crystal size is less than 250 nm. As the deposition time increases the number of nanocrystals present on the surface decreases.

After heat treatment, the surface of the coating at 30 s deposition times is orange peel shape structure, crystal size is in the range of 250-1000 nm and for 1800 s deposition time, the surface of the nanocrystalline coating is uniform, layered like nodular structure with crystal size in the range of 500-750 nm.
In the tri-sodium citrate bath, at 30 s deposition time, the coating is composed of box like Ni-P nanocrystals coalesced to the columnar structure. The columnar structure in the vertical direction is continuous and denser. There are no vacant places for the growth of the as-deposited Ni-P crystals in the horizontal direction of the columnar structure. The grain size is in the range of 10-60 nm. The electroless nickel deposition at 600 s produces larger nodular cauliflower structure and the grain size is in the range of 90 to 250 nm.

After heat treatment the surface of the coating at 30 s deposition time produce a uniform thicker columns and the crystal size is 10-100 nm, and at 600 s deposition time the crystal size is 150-250 nm.

In the glycine bath, the electroless nickel deposits formed in 30 s are composed of uniform layer of black Ni-P nanocrystals, the nanoporous AAO film without any cracks or pits. At 1800 s deposition time, larger number of Ni-P nanocrystals combined to form almost uniform like morphology. For both of these deposition times, the crystal size is less than 100 nm.

After heat treatment, surface of the coating at 30 s deposition time, is having wave like uniform layer structure and the crystal size in the range of 75-150 nm. At 1800 s deposition time, coatings have a larger nodular structure with the grain size is less than 700 nm.

From the AFM analysis, it can be concluded that, surface roughness is higher for lower deposition time. The number of pores per unit area is high. However, in higher deposition time, the roughness values decreases due to the increase in the smoothness. This is because, bright finish with smooth surface is formed in the higher deposition time.
and the black finishes are formed at lower deposition time. After heat treatment, the roughness value is decreases than that of as deposited coatings.

X-ray diffraction pattern of the electroless Ni-P coating in the as-plated condition exhibits a sharp nanocrystalline peak at different positions in the initial deposition time. The coating shows only nickel and phosphorus peak. Ni-P coating occurs on the surface of the anodized aluminium sample with the same plane orientation indicating that crystal growth occurs in the same plane orientation. For increasing the deposition time, peak at lower angle disappears and the sharp nickel peak at 2θ of around 44° is transformed into broad peak. It indicates the amorphous nature of the coating.

It has been found that, after heat-treatment, the amorphous Ni–P phase present in the as deposited coating at 600 s to 1800 s convert into multiple peaks i.e. nanocrystalline Ni, meta stable peak and to the Ni$_3$P peak with different plane orientations. However, after annealing (at 400°C for 1 h), the degree of crystallinity increases and leads to the formation of nanocrystalline Ni-P. The dimension of crystallites is in the range of nanometer. It is strongly dependent on the chemical composition of the amorphous alloy and heat treated condition.

The corrosion potentials of as-deposited samples decreases (become less noble) with increase of coating time (i.e. decrease of phosphorus content). The heat treatment of electroless specimens (obtained at various coating times with different phosphorus content) at 400°C for 1 h, significantly decreases their $i_{corr}$ values, and hence their corrosion rates, with respect to the as-deposit specimens produced under similar conditions.
The NC-Ni-P deposits on AAO film using three different complexing agents exhibited high polarization resistance and lower double layer capacitance than those that of bare aluminium.