# CORROSION BEHAVIOUR OF ELECTROLESS Ni-P COATING ON CARBON STEELS

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## Abstract

Electroless Ni-P coating treatment was applied to the mild steel substrate for improving its corrosion resistance. This work aims at studying the corrosion behaviour of Electroless Ni-P deposits were in as-coated state and furnace annealed at various temperatures. The corrosion behaviour of the deposits has been evaluated by potentiodynamic polarization studies in 3.5wt % Sodium Chloride solution. The heat treatment temperatureswere kept at regular intervals to study the corrosion performance of the coatings. The microstructures were analyzed using XRD and a scanning electron microscope used to determine the morphology of the deposits. The results showed that the corrosion and resistance of the mild steel improved after electroless Ni-P coating and the as-coating have higher corrosion resistance than the annealed samples.

***Key words*:** Electroless nickel, annealed, microstructure, corrosion resistance

## I. INTRODUCTION

The electroless nickel has an ability to coat interior surfaces of pipes, valves and other parts along with applicability on metals and non- metals [1].Due to itsease in operation, low equipment cost, and outstandingproperties in wear, corrosion, soldering, electricity, magnetismand metallization of nonmetal-materialselectroless nickel coatings are widely used in engineering industries like chemical, automotive, food and textile industries [2,3]. One of the widely used plating baths for producing electroless Ni-P coatings is based on hypophosphite as the reducing agent. A consequence of using hypophosphite is the incorporation of phosphorous in the coatings. Several investigators [4-7] have studied the as coated structures of electroless Ni-P deposits. The hypophosphite content, plating bath pH, temperature, etc. are some of the factors affecting the structure of electroless Ni-P deposits.

Electroless nickel coatings were not pure nickel deposits but rather alloys of nickel and a metalloid such as phosphorous or boron. Because of the low solubility of metalloids in a nickel matrix, these coatings were supersaturated solutions of either phosphorous or boron in nickel [8].The deposition rate, properties of coated components and the structural behavior of deposits mainly depend upon the plating bath constituents / conditions such as the type and concentration of the reducing agent and stabilizer used, PH and temperature of the bath etc., [9].Also the characteristics of the Ni-P deposits were depending on its phosphorous content and the as-plated state was a mixture of amorphous and microcrystalline nature and the deposits with high phosphorous content was a phosphorous supersaturated solid solution, exhibiting amorphous structure [10, 11].

The investigators [12-14] suggested that the EN deposits annealed at temperatures above ambient may lead to strengthen the coating and changes in the micro structure with the precipitation of Ni-P phases. The precipitation of second phases as nickel phosphides increases the hardness of the Electroless Nickel deposits. However, the hardness of the deposits degraded with excessive heating at elevated temperature due to coarsening of Nickel and Nickel Phosphide [15].In this work, electroless Ni-P coatings were deposited on the mild steel specimen and furnace heat treated at various temperatures to study the microstructural characteristics

and the corrosion resistance of the coating on 3.5% weight percentage of sodium chloride solution.

## II. EXPERIMENTAL PROCEDURE

### *A. Production of Electroless Ni-P coatings*

The mild steel samples of 20 mm diameter and 3 mm thickness were used in this process. The resulting surfaces of the samples were polished and then they were subjected to pickling treatment using 10 % Hydro chloric acid. Thereafter, the treated samples were rinsed and had subsequentcleaning by acetone. Deposits werethen prepared using the optimized bath compositions and operating conditionsas mentioned in table.1.The coated samples were heat-treated by muffle furnace for one hour at various annealing temperatures.

Table.1. Chemical composition of the electroless nickel plating bath and its operating conditions

| Chemical composition | Quantity |
|---|---|
| Nickel Chloride ($NiCl_2.6H_2O$) | 30 g/l |
| Sodium Hypophosphite ( $NaH_2PO_2H_2O$) | 40 g/l |
| Sodium Citrate ($Na_3C_6H_5O_72H_2O$) | 30 g/l |
| Ammonium Chloride ( $NH_4Cl$) | 50 g/l |
| Operating conditions | |
| Temperature | 80 °C |
| PH | 9-10 |

### *B. X-ray Diffraction Measurement*

The TheX-ray diffraction (XRD) was taken to the coatings using Siemens X-ray Diffractometer with monochromatic Cu-Kα radiation. Phases, grain size and micro strain of the coatings were yielded from the diffractograms. The scanning angles (2θ) ranged from 10° to 90°, with a step size of 0.02° and counting time of 2 S/step. The phases obtained from XRD were recognised by comparing them with the JCPDS files.

### *C. Corrosion Test*

The Electrochemical analysis was done using ElectrochemicalAnalyser. The Tafel electrochemical measurements were obtained to study the corrosion resistance of the coatings. The criteria to evolve thelinear polarization curves for the specimens were exposed to a 3.5% Sodium Chloride aqueous solution at room temperature with a constant scan rate of 2mV/s. The cell configuration consisted of a reference saturated calomel electrode, a counter platinum electrode and the testing specimen was acting as the third electrode.

## III. Result and Discussion

The corrosion testing was carried out on the as-plated and furnace heat treated samples in the electro chemical analyzer. The most commonly used corrosion medium for the electrochemical analysis is Sodium chloride solution. It could be significantly accelerated the pitting corrosion by replacing oxygen molecules in water molecules to prefer initially adsorb on the Ni-P coating surface and to form a soluble NiCl2 (Ni2+ + 2Cl2 ←→NiCl2). The adsorbed chlorine ions can easily penetrated through the voids present in the coating surface causing pitting corrosion [16].Figure.1 shows the electrochemical polarization curvesfor furnace annealed electroless Ni-P coatings in 3.5 Wt% NaClsolution. The corrosion potential (Ecorr) and corrosion current density (Icorr) were calculated using Tafel extrapolation method and the corrosion resistance was calculated by the following equation.

$$CR\ (mpy) = \frac{0.13\ Icorr(\ Eq.wt.)}{d} \quad \ldots\ldots\ldots\ldots (1)$$

where,Eq.wt is the equivalent weight,d is the density of the coating in g/cm3and Icorr is the corrosion current in µA/cm2.

The corrosion rate of the base metal is high with a value of21.85 mpy for which Icorr value is 47.26µA/Cm2. The as-coated samples corrosion current density Icorr was much lower than that of the substrate and its corrosion resistance was found to be the highestvalue of 0.427 mpy withIcorr being 0.25µA/Cm2. The X-ray diffraction pattern of plain electroless Ni-P coating in it's as–coated condition exhibits only a single broad peak around 2θ = 45° as shown in fig 2.

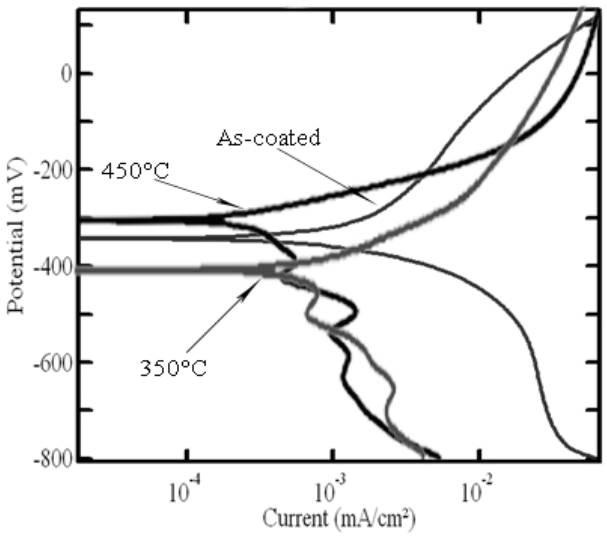


Fig.1polarization curves for the as-coated and annealed electroless Ni-P coatings

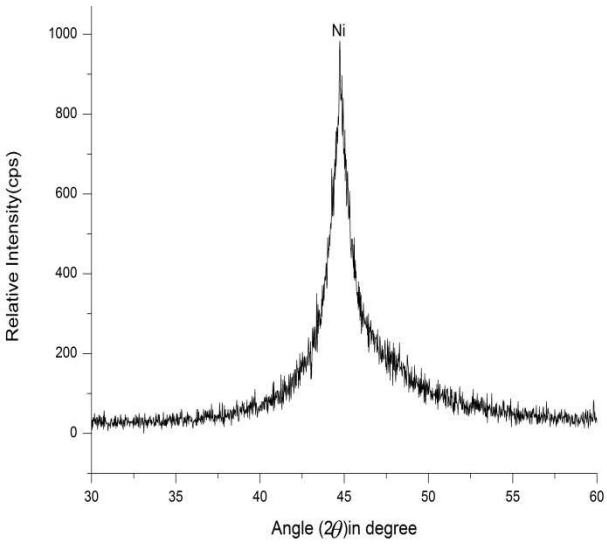


Fig. 2 XRD for the as-coated electroless Ni-P deposits

During deposition, phosphorous atoms were randomly captured on nickel atoms and its segregation determines the crystallinityof the resulting coating and the rate of diffusion of phosphorous is relatively small as compared to nickel. But Balaraju.et.al.[2006] suggested that the weight percentage of P greater than 7 is in the as-coated deposits exhibits amorphous nature. The amorphous alloys have higher corrosion resistance compared with furnace annealed deposits. This isdue to the non-existence of grain boundaries which give glassy film structure that is conducive for corrosion resistance in the surfaces.

Table.2. the corrosion current density and corrosion rate for the electroless Ni-P deposits in 3.5% sodium chloride solution

| Sl. No | Annealed temperature (°C) | Corrosion current $I_{corr}$ (µA/Cm2) | Corrosion rate (mpy) |
|---|---|---|---|
| 1 | As-coated | 0.25 | 0.427 |
| 2 | 250 | 2.2299 | 3.808 |
| 3 | 300 | 2.045 | 3.492 |
| 4 | 330 | 1.71 | 2.92 |
| 5 | 350 | 1.178 | 2.012 |
| 6 | 370 | 3.4546 | 5.9 |
| 7 | 400 | 3.6528 | 6.239 |
| 8 | 420 | 3.912 | 6.681 |
| 9 | 450 | 4.361 | 7.448 |

The corrosion resistances of the furnace annealed coatings were lower than as-plated Ni-P depositwhich could be attributed to the changes in crystallinity from amorphous to crystalline. Table.2 depicts the effect of heat treated temperatures on the current density and corrosion rate. The corrosion rate of the furnace annealed coatings decreases for lower heat treatment temperatures. The lowest values of Icorrand corrosion rate were obtained when the coating was heat treated at 350°C. For the temperatures above 350°C, corrosion current and corrosion rate were found to be increased which could be due to the absence of amorphous phosphorous content. Besides at lower annealing temperatures, the phosphorus content in electroless Ni-P coatings was enriched on the surface layer. The enriched phosphorus surface reacted with the water molecules in the Sodium Chloride solution to form an adsorbed film of hypophosphite, which in turn blocked the water molecules to the electrode surface, thereby preventing the hydration of nickel.

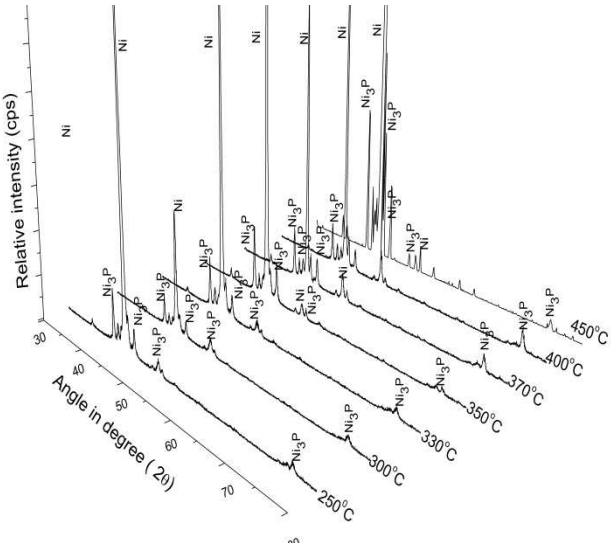


Fig.3 XRD for the furnace annealed samples

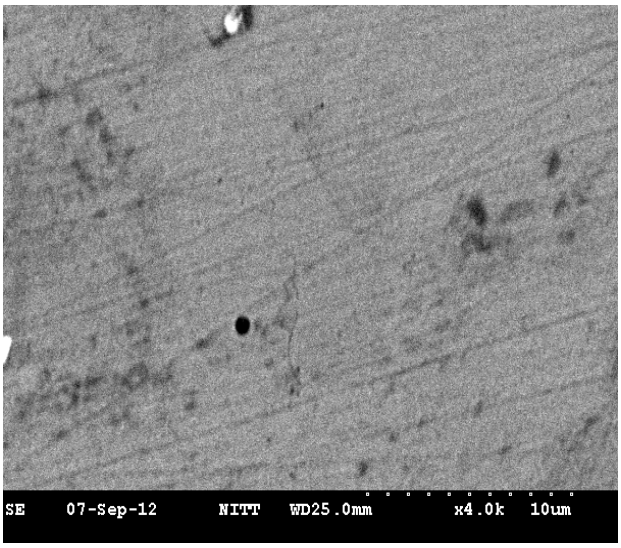


Fig. 4 SEM image for the electroless Ni-P annealed at 400°C

Fig.5a. optical image for electroless Ni-P annealed at 350°C

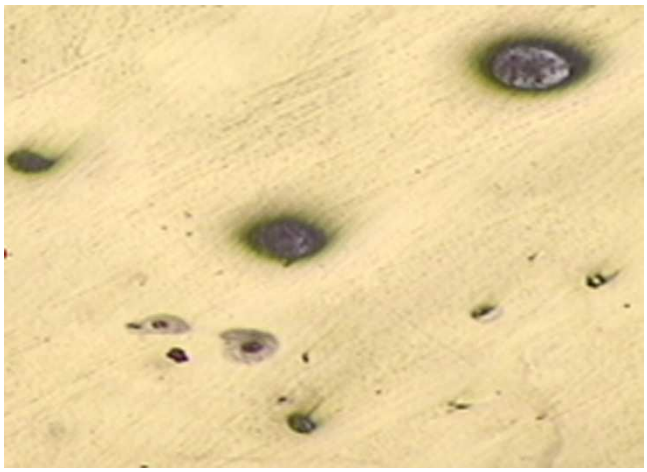

Fig.5b. optical image for electroless Ni-P annealed at 450°C

At the elevated heat treatment temperature above 350°C, coarsening of Ni3P phase occurred which in turn reduced the phosphorus content of the remaining material and to form Ni and Ni3P phases which could be clearly seen in the corresponding XRDalso the numbers of Ni and Ni3P peaks were increased and the widths of theses peaks were narrowed as shown in fig. 3. This indicates that the amorphous nature decreased to increase the crystalline nature. The formation of these two phases enhanced surface inhomogeneity. The two phase mixture could beincreasing the number of grain boundaries within the coating, resulting in severe chemical attack which in turn caused a decrease in corrosion resistance. The numbers of black dots (voids) present in the coating surface are shown in fig. 4. Through these voids chlorine atoms penetrated in to the substrate to cause a pitting corrosion. The optical microscopic images for the samples annealed at the temperatures 350°C and 450°C are shown in figure.5 (a&b). From these figures it is clear that, the number of voids present in the sample and the size of the voids were more at the annealing temperature 450°C. The chlorine ions first attack the mouths of the voids then penetrate into the substrate could be clearly visible in figure. 5(b).thus caused pitting corrosion in the annealed coatings.

## IV. CONCLUSION

The electroless Ni-P coating can be successfully coated on the surface of mild steel (substrate). The coating was compact and had a uniform thickness of 25µm and showed the amorphous nature at the as-coated state. The as-coated deposits had higher corrorsion resistance than the annealed deposits. This isdue to the non-existence of grain boundaries which give glassy film structure that is conducive for corrosion resistance in the surfaces. The annealed deposits were micro crystalline in nature and it consists of Ni and Ni3P phases. The two phase mixture could beincreasing the number of grain boundaries within the coating, resulting in severe chemical attack which in turn caused a decrease in corrosion resistance.

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