Effect of pH Bath on Phosphorus Content in Electroless Nickel-Phosphorus Deposit

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Abstract - **Electroless Nickel (EN) coatings with phosphorus is preferred in many industries including chemical, mechanical and electronic industries because of their excellent resistance to corrosion and abrasion resistance. Electroless Ni-P coating was applied to the mild steel for improving its corrosion resistance. The coated samples were analysed using FESEM and X-Ray diffraction for morphological and structural analysis respectively. It was found that by varying the pH of the EN bath the phosphorus content and hence the corrosion resistance of the deposit could be greatly improved.**

Keywords – Electroless Ni-P Alloy Coating, Mild Steel, X-Ray Diffraction, pH (NaOH)

1. INTRODUCTION

Electroless process is an autocatalytic method in which the reduction of the metallic ions in the solution and the film deposition can be carried out through oxidation of a chemical compound present in the solution itself. The autocatalytic or chemical reduction of aqueous metal ions coated on a base substrate without passage of external current is referred to as electroless plating [Brenner and Riddell, 1946; Singhal et al., 2010]. Coating is a method by which an artificial surface is generated to the outer surface material to protect it from corrosion and wear. These are two areas of concern for marine applications and not only reduce the life of components but also increase the expenditure for replacement of parts. Since wear and corrosion are predominantly surface phenomena they can be addressed by surface treatment.

EN coatings improve the physical and tribological properties of coatings [Balaraju and Apachitei, 2002]. Alloys with different percentage of phosphorus, varies from 2% (low phosphorus) to up to 14% (high phosphorus) are possible [Baudrand, 1994]. EN coating have several benefits as compared to electroplating. These deposits give a low co-efficient of friction and have anti-galling properties. They have good as-plated hardness and can be further hardened by post-plating heat treatment processes and also impart a good resistance to corrosion. Hardness and corrosion properties are primarily dependent on phosphorus content.

An electroless Ni-P deposition with a hypophosphite reducer is usually represented by the following reactions [Ijeri et al., 2014]:

(i) $NiSO_4 + H_2O \rightarrow Ni^{+2} + SO_4^{-2} + H_2O$

(ii) $NaH_2PO_2 + H_2O \rightarrow Na^{+} + H_2PO_2^{-} + H_2O$

(iii) $Ni^{+2} + H_2PO_2^{-} + H_2O \rightarrow Ni + H_2PO_3^{-} + 2H^{+}$

(iv) $H_2PO_2^{-} + H_2O \rightarrow H_2PO_3^{-} + H_2$

Where, (i, ii) represent dissociation of salts, (iii) reduction of nickel cations and (iv) oxidation of hypophosphite.

The present work deals with a mild steel substrate coated with electroless Ni-P deposits to enhance corrosion resistance. The process is repeated with three different bath compositions with varied pH bath.

2. LITERATURE REVIEW

Electroless Nickel-phosphorus coatings have been used progressively in various industries since the early 1980's. Some of these coatings have better corrosion and wear resistance, good weldability, deposit uniformity and good surface lubricity. Wu Y. et al., (2006) studied the tribological behaviour of electroless Ni–P–Gr–Sic composite wear and the friction and wear of electroless Ni–P matrix with PTFE and SiC particles composite. The co-deposition of SiC particles in Ni–P coating increases the friction coefficient by almost 10% as compared to pure Ni–P coating. Also the friction coefficient showed a drastic reduction when soft particles viz. PTFE, graphite and MoS_2 are introduced in the coating. Gordani et al., (2008) have applied LASER surface alloying to obtain a good metallurgical bonding between aluminium alloy substrate and Ni–P coating. It was found that both surface hardness and corrosion resistance increase by this, moreover the best hardness and corrosion resistance is found to develop at a laser scanning rate of 37 mm/min. Sahoo P (2008-9), optimized the coating process parameters for the minimum wear process namely bath temperature, concentration of Nickel source solution, concentration of reducing agent, and

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annealing temperature. The result reveals that annealing temperature and bath temperature have the most significant influence in controlling wear characteristics.

3. EXPERIMENTAL DETAILS

An electroless Ni-P bath with sodium hypophosphite as reducing agent was used to coat marine based applications of Mild Steel. A mild Steel substrate with circular cross section of 20 mm diameter and 5 mm thickness with a pin hole drilled close to the circumference (so as to suspend the substrate in the chemical bath) was used. The bath composition and operating conditions of electroless Ni-P coatings were as given in Table 1. The following surface preparation of the work-piece was carried out prior conduct of the experiment: (a) mechanical cleaning for removal of corrosion, (b) degreasing using Acetone, (c) cleaning with a NaOH solution, (d) etching process in 10 ml of 40 percent by volume HCl for 02 minutes and (e) cleaning with 50 gm/lit NaH_2PO_2 for 10 minutes with rinsing in distilled water between consecutive steps.

Table 1 Bath compositions and operating conditions of electroless Ni-P coatings

Bath constituents and operating conditions	Bath A	Bath B	Bath C
Nickel sulphate hexahydrate (g/l)	30	30	30
Sodium hypophosphite monohydrate (g/l)	28	28	30
Sodium succinate hexahydrate (g/l)	16	-	-
Citric acid monohydrate (g/l)	-	12	12
Lactic Acid (g/l)	28	-	-
Propionic Acid (ml/l)	-	2.2	2.2
Lead acetate (g/l)	0.003	0.003	0.003
pH	5	8	11
Temperature (^{o}C)	80±1	80±1	80±1
P content (wt. %)	16.94	12.91	4.51

Scanning electron microscope [Model: Σigma, Carl Ziess] was used to evaluate the surface morphology and distribution of Ni-P particles in the deposits obtained from different bath compositions. EDX (energy dispersive X-Ray) analysis was used to evaluate the percentage content of Nickel and phosphorus in the deposit. The crystalline structure of the deposit was analyzed using the X-ray diffractometer.

3.1 Selection of Electroless Ni-P coating bath

Bearing in mind Marine applications, high corrosion resistance is required, an EN bath covering the complete acidic and alkaline range was chosen for experimental analysis and study. Hot acid electroless nickel baths are used almost exclusively for the deposition of relatively thick coatings onto metals. The phosphorus content can be easily controlled by varying the bath constituents. Depending on the phosphorus content they EN deposits can be sub-classified into:-

(i) 3-5 % P (low phosphorus) – these coatings have excellent wear resistance. They have excellent corrosion resistance in concentrated caustic soda.

(ii) 6-9 % P (medium phosphorus) – corrosion protection and abrasion resistance are good enough for most applications. The plating bath works economically.

(iii) 10-14 % P (high Phosphorus) – coatings are very ductile and corrosion resistant. Particularly, they have corrosion resistance against chlorides and simultaneous mechanical stress [Sudagar J. et al., 2013].

4. RESULTS AND DISCUSSION

EN deposit with low content was obtained using bath C while bath A, B resulted in high Phosphorus deposit (Table 1). On analysis of surface morphology and EDX, the presence of nickel and phosphorus elements in the deposit was strongly indicated (Fig. 4.1).

Figure 4.1 compares the surface morphologies of Ni-P coatings of different compositions deposited under varying pH. The Phosphorus content in Ni-P deposit was optimized for marine applications by varying the bath pH from acidic to alkaline, using NaOH (Table 1). A comparison of the surface morphologies of deposits obtained from different bath compositions revealed that the best morphology (corresponding to marine applications) is attained from bath B. The deposit from this bath displayed a globular form, good homogeneity and high density of deposition. This in turn implies uniformly distribution of phosphorus particles with highly adherent property thereby increasing the amorphous nature of the coating [Narayanan et al., 2006]. Sudagar J. et al., 2013 studied the effect of phosphorus content in electroless Ni-P deposits and surmised that high phosphorus content (10-14 %) significantly increases the corrosion resistance of the deposit.

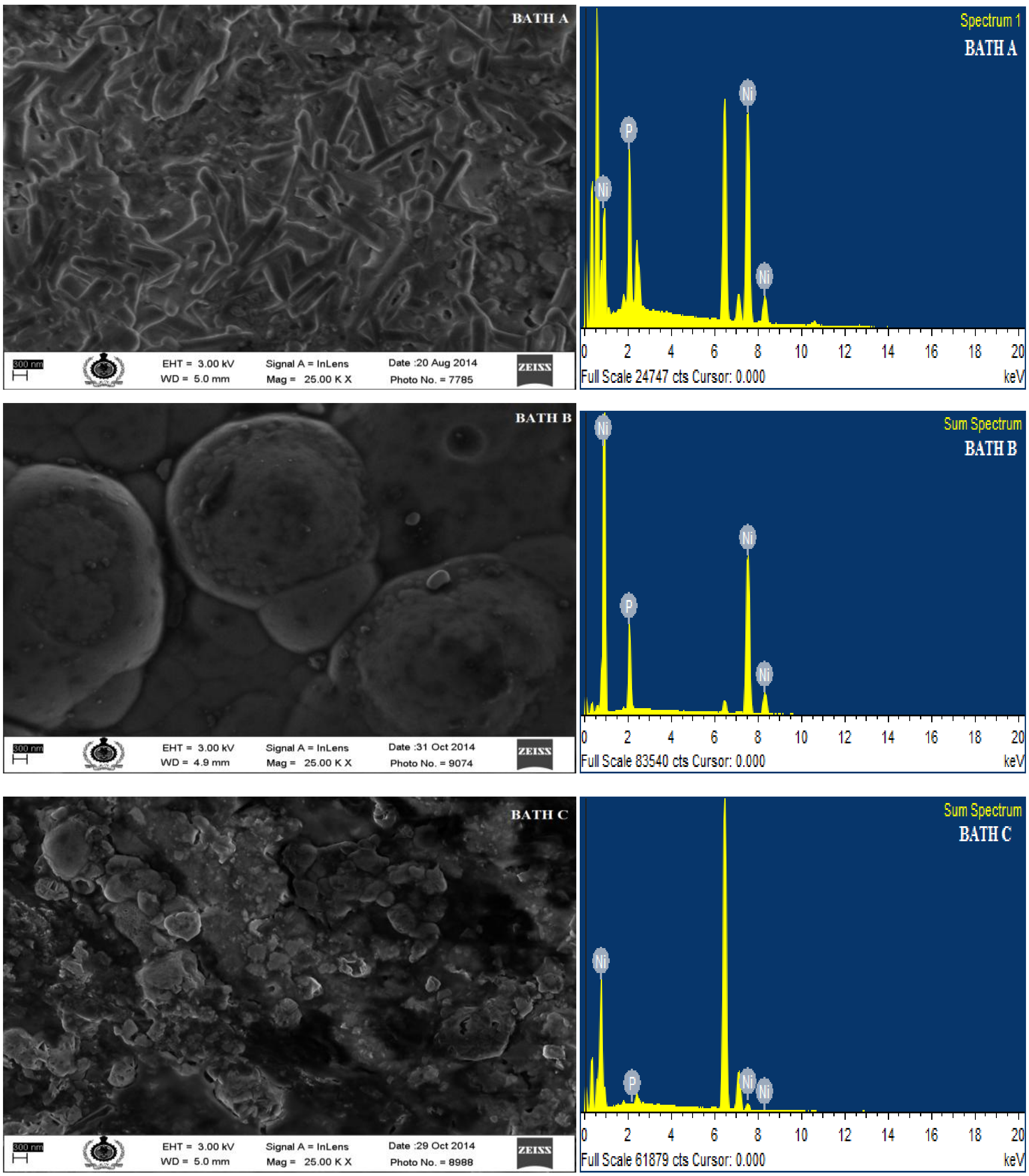

Figure 4.1: Bath A, B and C of FESEM morphologies as-deposited condition under high magnification and EDX analysis of electroless Ni-P coatings

In the study it was observed that in bath A and B, (where the pH was maintained at 5 and 8 respectively) produced deposits with high phosphorus content, however in bath C (pH maintained at 11), the phosphorus content was observed to be low. Additionally the phosphorus content of bath A was above the desirable limit of 14%, because beyond this limit the amount of β-phase decreases while the amount of the γ-phase increases thereby causing a reduction in the overall hardness of the deposit (since the γ-phase is a softer phase as compared to the β-phase) [Taheri, 2003].

The X-Ray diffraction (XRD) [Model Name: Bruker AXS, Germany (D8 Advanced)] pattern of deposits, obtained from bath A, B and C in their plated condition, are given fig. 4.2. The deposit is amorphous in nature for bath B while in the case of bath A and C, they are microcrystalline and crystalline. In bath B, the peak point of XRD is found to be lower than the peaks of bath A and bath C, which indicates an amorphous nature whereas in bath A and C the peak gets progressively sharper which indicates microcrystalline and crystalline nature respectively.

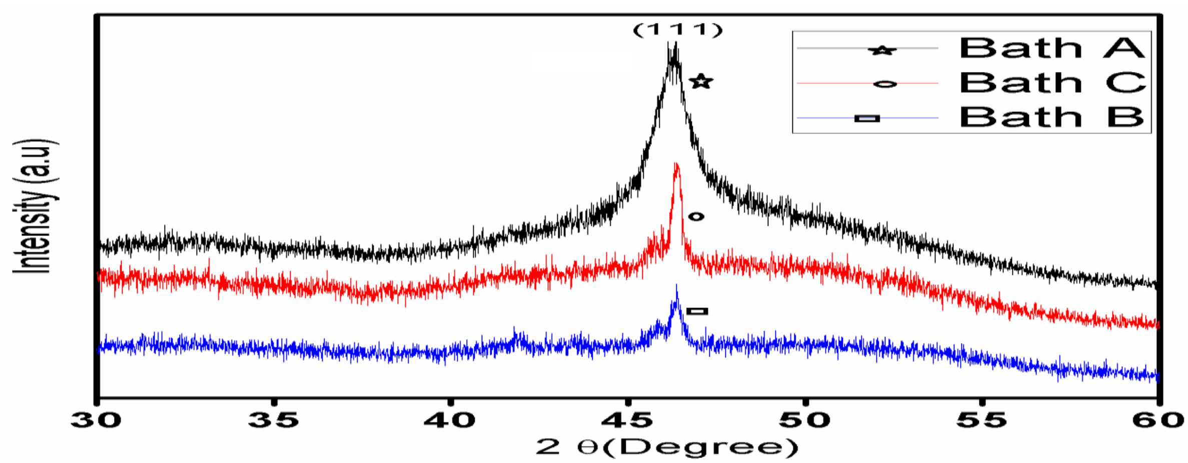

Figure 4.2: X-Ray diffraction pattern of as-deposited condition electroless Ni-P coatings obtained from bath A, B and C

5. CONCLUSIONS

In Electroless Ni-P coatings, optimum phosphorus content can be obtained by maintaining a pH between 7 and 8. A high phosphorus deposit ensures good corrosion resistance in the substrate. FESEM study shows that deposits have smooth finish, uniformity of deposition and low porosity; consequently they can be used for components with complex geometries. The XRD analysis shows that the films contain Nickel as primary component of the coating. Electroless Ni-P coatings have been found to have high corrosion resistance, abrasion resistance and hence are suitable for marine applications. Some of the marine components which can be coated with electroless Ni-P are: internal components of pumps and valve seat of marine diesel engines.

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