Characterization And Surface Analysis on Electroless Ni-P Coating Process on EN – 8 Steel

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Abstract- *Electroless Nickel (EN) is the major evolving surface coating technique employed in industries today. Various physical characteristics of EN coatings such as hardness, wear resistance, coating uniformity and corrosion resistance makes this coating as a choice for many engineering applications. The major advantages of EN coatings are uniform coating thickness, improved wear and corrosion resistance, hardness, ability to deposit on surface activated non conductors etc. Typical anionic surfactant and various passive chemical additives and nano additives such as ZnO, Al2O3 were added to the EN bath. In this project, Sodium Lauryl Sulphate (SLS) surfactant along with nano additives such as ZnO, Al2O3 were added to the EN bath. The effect of surfactant along with nano additives on surface properties such as surface roughness, microhardness and microstructure of electroless nickel-phosphorus (ENi-P) coating was investigated. The surface roughness of the coated specimens was measured using stylus instrument, microhardness was measured using vicker's hardness tester, microstructure was studied using Scanning Electron Microscope (SEM) and wear test was measured using Pin on disc machine. The result obtained from the above tests clearly indicates that the surfactant and passive additives improves the surface finish, microhardness, microstructure and wear rate of ENi-P coatings significantly. The complete experimental details, their results and analysis are reported in this project.*

Keywords- Electro less nickel coating; Nano Additives; Surfactants; Surface roughness; Microhardness; Microstructure; Wear.

I. INTRODUCTION

ELECTROLESS COATING

Electroless coating processes deposit metallic coating on a substrate without the use of an external voltage or current. They are commonly referred to as chemical metal deposition because the electrons required to bring about the discharge of metal ions are produced by a chemical reaction in solution. Deposition of metal is made from solutions containing reducing agents. Such deposits form only on certain catalytically active surfaces (autocatalytic deposition). The electrons needed to reduce the metal ions are provided by the reducing agents *R* which surrender *n* electrons, while getting oxidized to $R^{(n+)}$ (Fig. 1.1). The simplified form of the reaction which describes the electroless process is given as follows:

$$R \longrightarrow R^{(n+)} + ne \qquad (1.1)$$

$$M^{n+} + ne \longrightarrow M \qquad (1.2)$$

It is properly named autocatalytic, because the oxidation of the reducing agent can start or become self-sustained only at the depositing metal surface. Plating can be done on non-catalytic base materials, after suitable activation of the surfaces involved. Electroless deposits of nickel, copper, gold, silver, cobalt, palladium etc. and of alloys involving one or more of these metals have been produced in this process on various metallic and non metallic substrates.

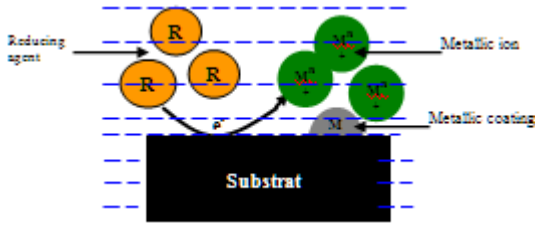

Fig. 1.1 Electroless coating with reducing agent R as the source of electrons.

In contrast to electroplating, electroless plating does not involve electric field distribution. As a consequence uniformity of coating thickness could be achieved even on intricate part geometries. A schematic comparison of electroplating and electroless plating is shown in **Fig. 1.2.**

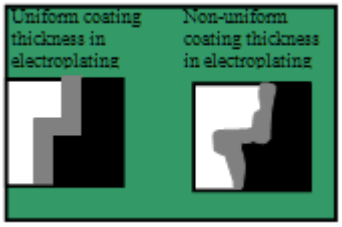

Fig. 1.2 Comparison of electroplating with electro less plating process hardness, wear, abrasion and corrosion resistance. Mainly due to this it has excellent commercial potential across a wide spectrum of industrial applications in the field of electronics, computers, aircraft parts, textile industry, automobiles, valves, dies etc.

II. ELECTROLESS NICKEL COATING

As already mentioned, a number of metals like nickel, copper, gold, cobalt, palladium, silver etc. can be deposited by electro less process. However, the bulk of the deposits produced today are based on nickel. It has excellent mechanical and electrochemical properties such as

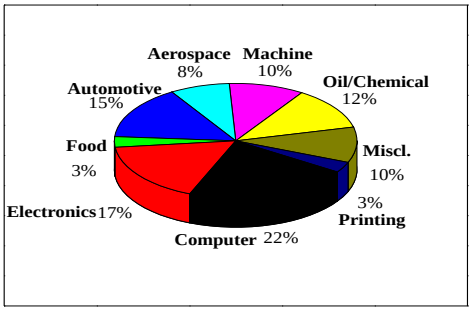

Fig. 1.3 Electro less nickel applications in various fields (Parkinson, 1997).

Major advantages of electro less coatings over the electro deposition process include:

- Formation of a uniform deposit on irregular surfaces
- Direct deposition on conductors and surface activated non – conductors
- Formation of less porous deposits
- Good wear resistance
- Good corrosion resistance.
- Wastage in the form of nickel bearing sludge (Fig. 1.4)

Electroless nickel bath decomposition (Fig. 1.5)

Due to these reasons, the EN coating process efficiency is reported to be poor and is of the order of only 50%.

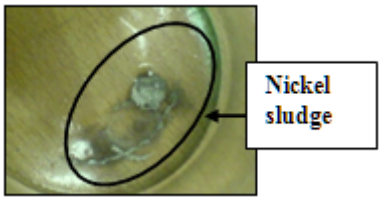

Fig. 1.4 Wastage in the form of nickel bearing sludge

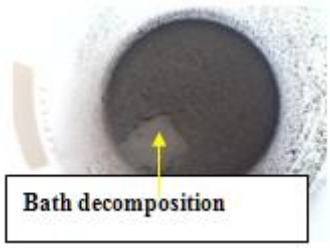

Fig. 1.5 Electro less nickel bath decomposition

III. OBJECTIVES AND SCOPE OF THE PRESENT STUDY

Several investigations have been carried out to tackle the problem of high wastage through modifications in the chemistry of the bath. However almost all such attempts were based on altering the basic chemistry of the process. Hence it is felt that a detailed investigation on the possibility of improving the coating efficiency of electroless coatings by modification to the surface energies of hydrogen/nickel/electrolyte system without altering the basic chemistry of the electrolyte bath would be a worthwhile attempt. Accordingly, the specific objectives of the present research work are as follows:

- To explore the possibility of improving the efficiency of electroless nickel coatings by modifying the surface energies of hydrogen/nickel/electrolyte system by addition of suitable surfactants, stabilizers and accelerators.
- To investigate the influence of nano additives during the coating process in the above context.
- To investigate the properties of the coating to understand their influence on the efficiency and performance as whole

The scope of the work is limited based on the following:

- The type of coating selected for the study is electroless Ni-P coatings. The basic composition of the bath is kept the same in all cases involving comparative studies.

- The operating conditions employed for deposition like pH, bath temperature etc. are kept at reported optimum constant values for facilitating easy comparis on.
- Passive additives viz. Surfactant (sodium lauryl sulfate), Stabilizers (Thiourea, Glycine) and Accelerator (Succinic acid) have been employed in this investigation.

ELECTROLESS NICKEL - PHOSPHORUS COATING

Electroless Nickel-Phosphorus (EN) coatings have been used either as protective or decorative coatings in industries such as electronics, computer, aerospace, printing, automotive, textile, plastics, optics, paper and food (Parker, 1972). Some of the outstanding characteristics of EN coatings are superior corrosion and wear resistance, excellent uniformity, wide range of thickness, good solderability, improved mechanical and physical properties (Baudrand, 1978). EN deposition is carried out with:

a) nickel chloride and/or nickel sulfate as the source of nickel
b) sodium hypophosphite or sodium pyrophosphate as the reducing agent
c) a salt of an organic acid as a buffer
d) a mild complexing agent for nickel.

Deposits from these reducing agents contain a maximum of 14 wt. % phosphorus. Hydrazine hydrate is also used as a reducing agent for production of high purity nickel deposits. For the controlled deposition of the metal, number of parameters like temperature of deposition, pH of the bath, concentration of the reducing agent etc. are to be monitored closely during deposition. Improper control of one or more of these parameters might result in deposits with widely fluctuating properties. For better stability and utility of the plating bath, specific stabilizers and complexing agents are employed.

Formulation of Electroless Ni-P Coating Baths

Brenner and Riddell in 1946 during their experimentations on electrolytic nickel plating were trying to prevent the undesirable oxidation of bath constituents at the inert anode by making additions of reducing agents to the bath. The reducing agent used was sodium hypophosphite. Surprisingly, the amount of nickel deposited exceeded the amount theoretically predicted by Faraday's law. This led to a series of experiments and electroless deposition was discovered. The initial formulation used contained nickel chloride, sodium citrate and/or ammonium chloride and sodium hypophosphite. These were alkaline baths. The acidic bath formulated was consisting of either hydroxyacetate (glycolate) or citrate as nickel complexent (Brenner and Riddell, 1946). During 1950s and '60s various attempts were made to study the influence of additives on plating performance. The 'Kaningen' process developed by Gutzeit (1956) consisted of lactic acid as the complexing agent, propionic acid as the exalt (additive to increase the deposition rate) and a trace to lead as the stabilizer. The selection of specific plating bath depends upon many factors including the composition of the deposit, deposition rate, life of the bath etc.

ADDITION OF ACCELERATOR

Accelerators increase the plating rate without causing bath instability. In our study accelerator namely succinic acid (A) is introduced into the electrolyte bath.

EXPERIMENTAL DETAILS

INTRODUCTION

This chapter deals with details of experimental procedure adopted, relevant parameters and equipments employed during the course of the present investigation.

The specific details covered pertain to:

- Preparation of the substrates
- Pretreatment of the substrates
- EN Coating bath and Operating conditions
- Production of Electroless coating
- Influence of additives on the Electroless Ni-P process

PREPARATION OF THE SUBSTRATES

Substrate material chosen for coating is Mg AZ91D Alloy. Mg alloy is turned to the dimensions 10 mm X 10 mm. Finally the samples were surface finished by grinding followed by disc polishing the typical surface finish value measured using a stylus instrument of the finished samples are as follows: Average roughness value(the average of the peak and valley distances measured along the center line of one cutoff length (Ra)) = 0.57µm.

PRETREATMENT OF THE SUBSTRATES

Prior to the coating it must be ensured that the substrate is free from any impurities. So pretreatment is very important to achieve efficient coating. The pretreatment procedure consists of alkaline cleaning to remove soils or greases in the substrate with NaOH 4.5g/ 100ml, Na3P04.H2O

1g/100ml at 65 C temperature, Acid Pickle to remove oxide layer CrO3 12.5g/100ml, HNO3 10ml/100ml time 40 seconds. Flouride activation to create an equipotentialized film (MgF2) HF 35ml/100ml time 10 seconds.

PRODUCTION OF ELECTROLESS COATINGS

The electrolyte bath was heated indirectly through an electrically heated oil bath. The temperature of the oil bath was controlled by an ON/OFF relay and Proportional Integral Derivative (PID) controller. Temperature of the electrolyte bath was monitored using a thermometer.The pH of the electrolyte bath was maintained between 6 and 8 by adding sodium hydroxide solution. The total initial volume of the plating bath restricted to 150 ml (unless otherwise mentioned). The coating duration is 2 hours after which the bath decomposes as shown in Fig.3.2.

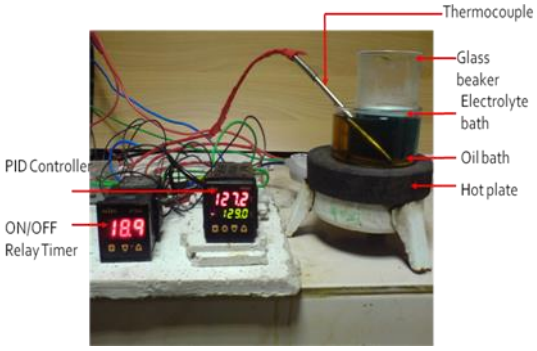

Fig.3.2. Experimental set up used for EN deposition

Table 3.2 Features And Specifications

Parameter	Unit	Min	Max
Pin Size	mm	3	12
Ball Diameter	mm	10	12.7
Disc Size	mm	165 x 8 mm Thick	
Sliding Speed	M/s	0.05	10
Disc Rotation	RPM	200	2000
Normal Load	N	0	200
Frictional Force	N	0	200
Wear	mm	0	2
Track Radius	mm	to be set manually	

IV. EXPERIMENTAL STUDIES

4.1 SEM TEST FOR FOLLOWING MODULES

- Without surfactant
- With surfactant

(i) CTAB (Cetyl Trimethyl Amonium Bromide)

(ii) SLS (sodium lauryl sulphate)

- Nano additives

(i) Al_2O_3

(ii) ZnO

4.2.1 WITHOUT SURFACTANT

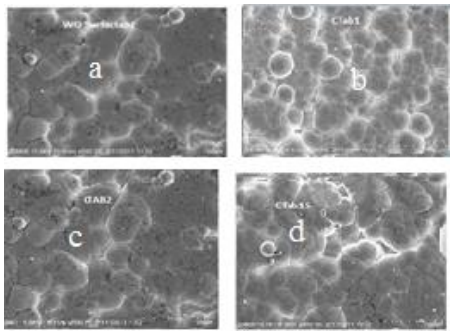

Fig 4.1 SEM micrograph of AZ91D magnesium alloy a) without surfactant (magnification 500x) b)with surfactant C-TAB (1g) c)with surfactant C-TAB(2g) d)with surfactant CTAB (3g)

INFERENCES:

- There is no visible difference among the three quantities of c-tab used Ni-P coating is evenly distributed over preferentially nucleated on the $\beta Mg_{17}Al_{12}$ phase due to the usage of surfactants influencing Ni-P Deposition over the $\beta Mg_{17}Al_{12}$ phase.
- Agglomeration of Ni-P matrix over $\beta Mg_{17}Al_{12}$ phase without the usage of surfactants.

4.2 IMPLEMENTATION OF EXPERIMENT

- prepartion of specimen (surface prepartion with 2000 sic emery paper)
- pretreatment process as per procedure mentioned
- bath composition prepared
- coating the pretreated specimen in the coating bath as per conditions mentioned
- following modules were used to coat the specimen along with the bath
- with surfactants sls and c-tab with nano additives zinc oxide,silicon dioxide and alumina nano particles

4.3 ROLE OF ADDITIVES ADDITION TO ELECTROLYTE ON MECHANICAL PROPERTIES OF THE COATING

4.3.1 Surface roughness of electroless Ni-P coating

The variation in Average Roughness of ENi-P coating as a function of Reducing agent concentration is presented in Figure 4.1. At lower concentration of Reducing agent(25% excess), the average surface roughness value is lower 1.986µm (RA added at Middle of reaction) & 2.131µm (RA added at End of reaction). But for all other higher concentrations (50%, 75%, 100% &125% excess RA), average roughness values ranges from 3.138µm to 0.165µm. The mean average roughness value of ENi-P deposit with addition of Reducing Agent (RA) is 2.0755µm which is greater than the average roughness value of ENi-P deposit without addition of RA (0.423µm). Figure 4.2 shows the surface morphology of SEM images of ENi-P deposited with various RA concentrations. In Figure 4.2(c)–(j) the Ni-P deposits changes the surface topography from a smooth state to non-smooth state as the amount of nickel particles deposited on the coating surface is increased. As the concentration of RA increases, the amount of Ni ions in the bath increases which leads to increase in deposition of ENi-P. It is apparent that RA addition during Ni–P deposit can improve the roughness.

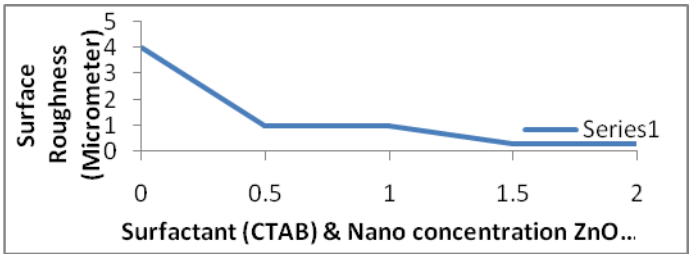

Fig 4.1 Surface hardness of CTAB

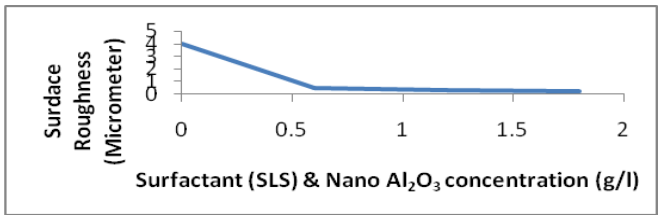

Fig 4.2 Surface hardness of SLS

Variation in average roughness of EN coating as a function of reducing agent concentration

4.3.2 SEM micrographs

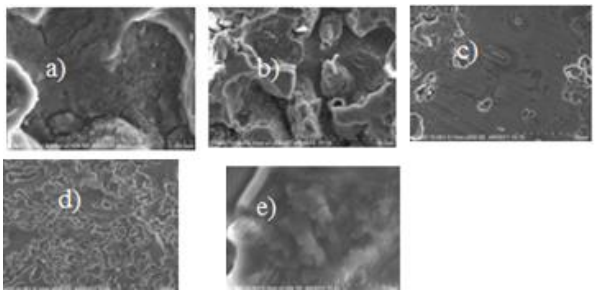

Fig 4.3 SEM micrographs (1000X) of ENi-P deposited : (a) without SLS addition (b) with SLS; (c) with 25% excess RA added at middle; (d) with 25% excess RA added at End; (e) with 50% excess RA added at middle

4.3.3 Hardness of electroless Ni–P deposits

The micro hardness of ENi-P deposits increase with addition of SDS. In the as plated condition, hardness is 450 VHN200. In the presence of SDS the hardness increased upto 580 VHN200. The reason for this is due to the change in phosphorus content on the ENi-P deposit. In the as plated condition, without addition of surfactant the amount of phosphorus alloyed in the deposit is 3 to 4%. When SDS is added into the electrolyte bath the phosphorus content is increased from 6% to 7.5%. Mukherjee and Rajagopal (1992), Carbajal and White (1988) and Lashmore and Weinroth (1982) have reported that high phosphorus amorphous EN coatings have outstanding corrosion resistance, but their hardness and wear resistance are lower than their low phosphorus counterparts. In the present study, a similar trend has been observed as well.

Figure 4.4 shows the variation of microhardness of ENi-P deposit with respect to reducing agent (RA) concentrations. The microhardness values for different RA concentrations ranges from 580 VHN200 to 600 VHN200 which is nearer to microhardness value of SLS added ENi-P deposit.

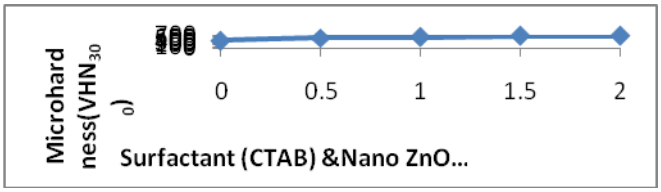

Fig 4.4 Microhardness of CTAB

Fig.4.5 Microhardness of SLS

Variation in microhardness of EN coating as a function of reducing agent concentration

Figure 4.5 shows the variation of microhardness of ENi-P deposit with respect to different stabilizers. It is observed that microhardness values 400 (VHN200 & 600 VHN200) with CTAB and with SLS (400 VHN200 & 500 VHN200).

4.3.4 Wear test is done using Pin On Disc test.

Fig 4.6

Disc – Hardened Steel Time- 33.33 mins
Speed- 135.8 rpm Load applied – 30N
Sliding Distance – 1 km

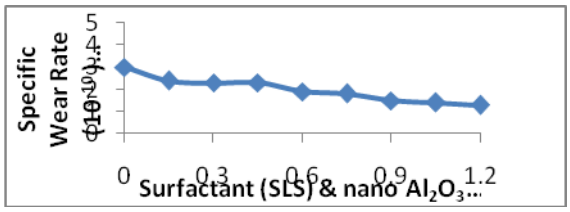

Fig.4.7 Specific Wear Rate of SLS

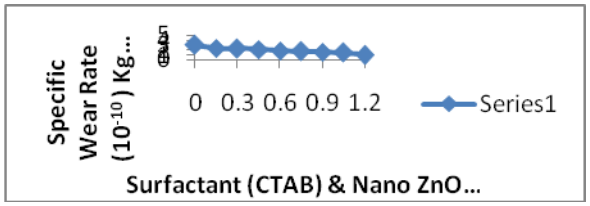

Fig.4.8 Specific Wear Rate of CTAB

4.3.5 SEM IMAGES OF WEAR TRACK:

Fig a. Nano additive Al_2O_3 0.5g

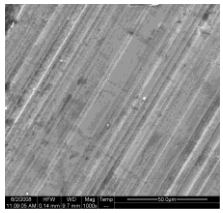

Fig b. Nano additive Al_2O_3 0.6g

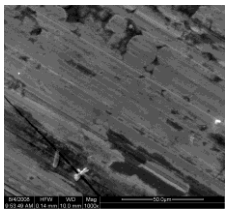

Fig c. Nano additive ZnO 0.5g

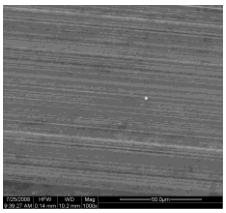

Fig d. Nano additive ZnO 0.6g

V. CONCLUSION

A comprehensive experimental study under specific coating conditions on the influence of addition of various additives to the electroless nickel bath on the mechanical properties of the coatings so produced have been carried out and the results are presented and analysed. In general, it has been observed that the surface finish, and microhardness of the EN coated layers improved significantly with the addition of various additives.

Based on the present investigations, the following specific conclusions could be drawn.

A. On Surface Roughness of Coatings

- There was an improvement in the surface roughness (upto 46% in Ra values) of the coatings due to addition of additives to the bath. Addition of additives to the EN bath prevents the floatation of nickel particles generated at the substrate surface. Since the nickel particles do not float and move to the top surface of bath, more percentage of them get deposited as a fine layer thus improving the surface roughness. This has been proved by the increase in nickel recovered.
- With the above additives added, the average surface roughness of ENi-P deposits have been increased which could be reduced by selecting optimum additives. 3.037

B. On Hardness of Coatings

- There was a considerable improvement in the hardness of the coated layers. With the addition of selected stabilizer (thiourea), accelerator (Succinic acid), surfactant(SDS)& nano additives the improvement was 47% (602 VHN200).

- By adding the above additives during deposition of ENi-P, the phosphorus content had gone up resulting in improved quality of the deposits.

C. On Wear of coatings

- There was a considerable improvement in wear of the coated layers. With the addition of selected surfactant (SDS), & Nano additives (SiO2, Al2O3, ZnO2) the improvement is 2.886 micrometers to 1.068 micrometers.

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