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Anticorrosion Performance of Electroless Ni-P Coated Material (Specially Steel) – A Review

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INTRODUCTION

Concrete is more widely used than any other manmade material and has been a construction staple for centuries. Thoughsteel reinforcement has been used in RCC for increasing its tensile strength (plain concrete being weak in tension), it also reduces the durability and lastingness of concrete because of corrosive nature. When steel remains corrosion free, the bonding of steel-concrete might be intact and truly unlimited with respect to durability. So, it is highly important to study the factors and mechanismby which steel gets corroded and reduces the load-bearing capacity of RCC or PSC significantly.

Corrosion is natural and familiar phenomenon associated with the chemical degradation of materials and their properties as a result of an electrochemical reaction with their environment.The mechanism of corrosion involves the flow of charges which is electrons and ions. There are some active sites gets created on the reinforcement bars which is called anodes where iron atoms lose electrons and get oxidised, further moving into the concrete surrounding the bar as ferrous ions.The process in which oxidation of iron atoms is called anodic reactionand has been represented as:

$$2Fe \rightarrow 2Fe^{2+} + 4e^{-}$$

The electrons lost by iron atoms remain in the bar and move to sites called cathodes, where reaction take place among electrons, water and oxygen present in the concrete. The reaction taking place at the cathode isa reduction reaction. The reduction reaction is represented as:

$$2H_2O + O_2 + 4e^{-} \rightarrow 4OH^{-}$$

$$4e^{-} \rightarrow 4OH^{-}$$

To be electrically neutral, the ferrous ions move through the pore water in the concrete to these cathodic sites where they react to form iron hydroxides, or rust:

$$2Fe^{2+} + 4OH^{-} \rightarrow 2Fe(OH)_2$$

These hydroxides initially precipitated have a tendency to react further with oxygen eventually forming higher oxides.The increase in volume as the reaction products react further with dissolved oxygen develops internal stress within the concrete which might be sufficient to cause cracking and spalling of the concrete cover.

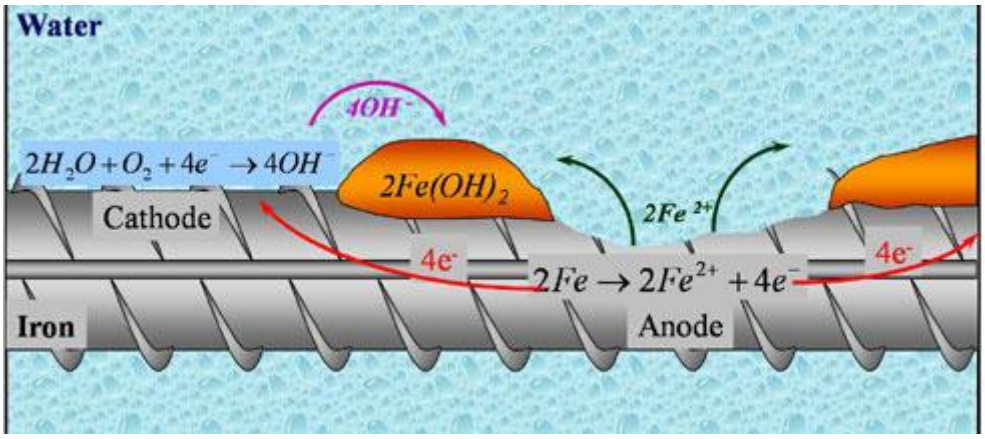

Fig.1 Mechanism of Corrosionhttps://www.cement.org/images/default-source/contech/corrosion_water_graphic.jpg?sfvrsn=361433bf_2

Common factors responsible for corrosion of reinforcement in RC structures are moisture,oxygen,pH value, chlorides and carbonation,ambient temperature and relative humidity,exposure condition,quality of concrete and other construction materials, cover to the reinforcement,initial curing conditionsand formation of cracks.

Normally, in concrete's alkaline environment, a passivating layer forms over rebar, preventing it from rusting. But chlorides or carbon dioxide can break down this protective layer. If water and oxygen are also present, steel rusts. So, *the two most common contributing factors leading to steel reinforcement corrosion are chloride attack and carbonation.*

There are some common mechanisms for controlling the corrosion of reinforced concrete. A corrosion control system is said to be effective when it either extends the time which otherwise takes in corrosion initiation or, reduce the corrosion rate of steel embedded in concrete or, do both.

Some of the traditional measures used to combat the corrosion of reinforced concrete are:

- Cathodic protection;
- Corrosion inhibitor admixtures; and
- Anti-corrosion coating

Unfortunately, these traditional methods meant for tackling concrete corrosion have proven to be less effective than desired considering the current state of deteriorating infrastructure. Thick or dense concrete cover over reinforcing steel will help, but still leaves the concrete vulnerable to cracking and a whole new set of issues. Corrosion inhibitors provide only temporary protection. Cathodic protection is expensive and has its own downsides, and repair procedures often have short service lives and may be continuously reinstalled. So there has been discussion of some alternative methods or technique by which steel can be made corrosion (due to carbonation, chlorides) resistant so that RCC and STEEL structures can be made serviceable for long period and economicallywe can bebetter placed by preventing failure of such structures causing huge loses.

One such alternative is electroless plating which has firmly established as a functional coating in the electronics, oil and gas, chemical, aerospace and automotive industries. It is also recognized and used effectively in many others and the number of applications continues to grow. Some of the unique properties of electroless nickel, such as thickness uniformity, wear resistance, hardness, corrosion resistance and magnetic response have resulted in its use in many different industries.So,this paper critically reviews for corrosion resistance behaviour of electroless coated materials with or without using nano particles.

Electroless coating

Elecroless plating is a very famous method widely used in coating of metal substrate without any electrical means. This plating method is done by immersing the substrate in a bath which containing reducing agent. The coating is done by the process that the changes metal ions to metal that forms a deposit on the substrate when catalyzed by certain materials.Thuselectroless plating can be defined as a controlled autocatalytic deposition of a continuous layer on a catalytic surface by the reaction of a complex compound and a chemical reducing agent. This method of electroless deposition provides a easy and well preparation of film on different types of substrate by using some simple and very easily available equipments and any type of support with low thickness.

This definition of electroless plating may include each of the techniques which are described below-

1.Immersion Plating- This is the process in which the deposition of a more noble metal takes place onto the surface of a less noble metal by the means of electrochemical series. Eg- when steel (iron) is immersed in a solution of copper ions, and the copper is deposited onto the steel substrate. Due to the thin, nonadherent coatings that are typically produced, this technique has few applications.

2. Homogenous Chemical Reduction- In homogenous chemical reduction, a chemical reagent provides electrons for the reduction of metal ions for deposition onto a substrate. Thicker coatings can be deposited by this method, but adhesion issues still exist. Another disadvantage of this process is that the metal ion solution and the chemical reducer must be kept separate, otherwise they will immediately react.

3. Autocatalytic Deposition -Autocatalytic deposition utilizes chemical reducing agents to provide the electrons for plating, but the treatment solutions are formulated to deposit onto naturally catalytic surfaces, or ones which can be rendered catalytic. The deposit itself is catalytic, thus the reaction is selfperpetuating. As a result, the coating can be built up to a significant thickness and is highly adherent.

Electroless nickel coatings can be categorized into following sets like

(i) Alloy coatings - it may be binary alloys (Ni-P, Ni-B, etc.), ternary alloys (Ni-P-B, Ni-W-P, Ni-Co-P, etc.) or quaternary alloys (Ni-W-Cu-P)

(ii) Composite coatings – it may be combination of binary alloy and nano particles (Ni-P-SiO2, Ni-P-Al2O3, Ni-P-PTFE, Ni-P-SiC, etc.) and

(iii) Metallic coatings.

Uniformity in coating composition is one of the primary advantages of autocatalytic reduction reaction. Reducing agents popularly employed in electroless bath are listed in Table below-

Table-1

Reducing agents

Deposit	Reducing agent
Ni-P	Sodium hypophosphite (NaH2PO4)
Only Ni	Hydrazine (NH2NH2)

Table- 2

Classification of different electroless coatings on number of substrates-

Coatings	Substrate	Solution properties (pH)
Ni-P	Brass substrate [2]	4.7-4.8
	Fe-600 grade steel[5]	-
	Mild steel bar[10]	5.5-5.8
	APIX70steel[23]	2-4
Ni-P-SiC	Mild steel [4]	4.5
	Low carbon steel and brass[6]	2.15
Ni-P-PTFE	Low carbon steel disc[3]	2.15
	Mild steel bar[10]	5.5-5.8
Ni-P-W	Fe-600 grade steel[5]	-
	SAE100 carbon steel[22]	9.0
Ni-P-Cu	Fe-600 grade steel[5]	-
Ni-P-TiNi	APIX100 carbon steel[9]	4.5
Ni-P-CNT	Low alloy of carbon[11]	-
Ni-P-C3N4	APIX100 carbon steel[12]	4.7-4.8
Ni-P-Al2O3	Mild steel[14],[15],[25]	5.5,4.5,6.5-7.2
Ni-P-Zn	Mild steel [16]	5.0
	Low carbon steel(st37)[21]	10.5
Ni-P-Si3N4	Low carbon[17]	5.0
Ni-P-Talc	Low alloy substrate[18]	10
	Cu-plate[20]	-
Ni-P-SiO2	St37 steel	
Ni-P-rGO(graphene)	AISI1018 low steel carbon[24]	5.5-6.0
Ni-P-TiO2 sol-RGO	Mild steel[13]	4.5

2.1. Bath characteristics

A schematic diagram of the experimental bath set-up which is used for the process of electroless plating is shown in Fig-1. A magnetic stirrer with pH and temperature variation is the main component of this bath setup. It also comprises beaker, pH sensor and temperature sensor. In the coating process 500-mL beaker is filled with the electroless Ni–P plating and the metallic substrate is dipped in it with the help of a wire which is clenches by the wire holder. A pH cum temperature sensor has been used to monitor pH and temperature throughout the experiment since the temperature and pH of the electroless solution play a major role in coating process[26].

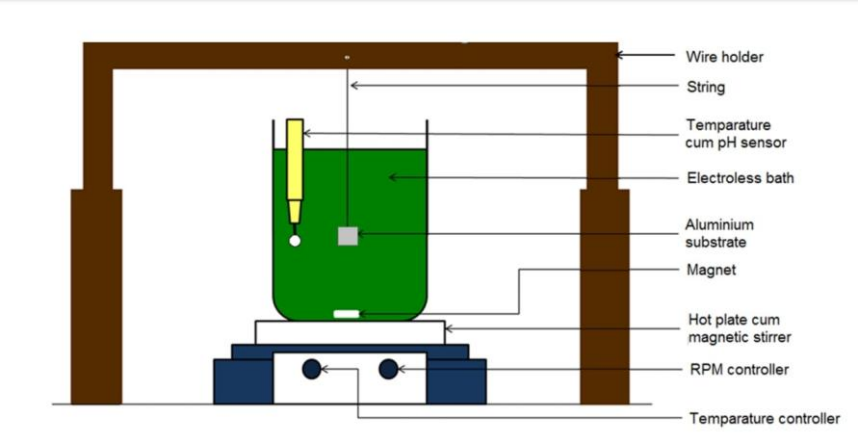

Fig. 2 Experimental setup for electroless plating

Major uses for electroless nickel deposits is represented by pie chart as shown below-

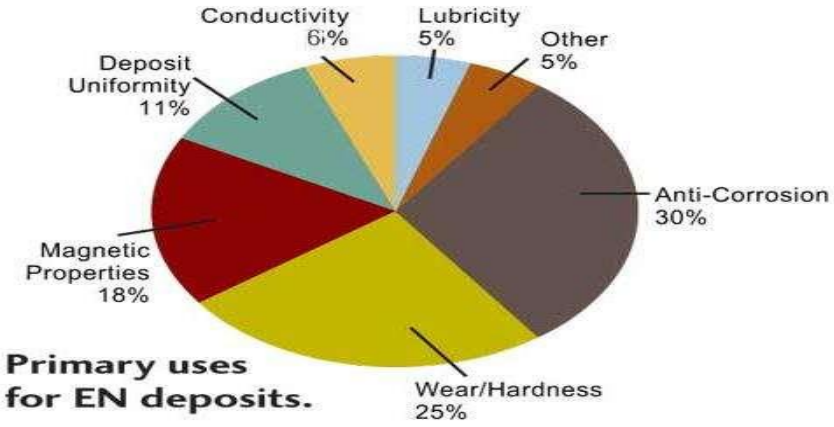

Fig. 3 https://www.researchgate.net/figure

TABLE-3
Electroless Ni-P plating observation found out from several papers after experimentation and has been listed as-

Reference	Type of composite	Characterization techniques	Major findings
B.-H. Chen et.al (2002) [2]	1.Nickel-phosphorus (Ni-P) 2. Acidic hypophosphite as surfactants 3. Brass substrates	1. Reflective optical microscope 2. Scanning electron microscope 3. X-ray spectroscopy	1. Addition of suitable amounts of surfactants can increase the deposition rate up to 25% and reduce the formation of the pores on the surface of Ni-P alloys, as well as enhance the corrosion resistance of the deposits. 2. The corrosion rate of the Ni-P alloys in 10 wt % HCl was determined.
SantigopalSamant et.al (2016) [23]	1.AmorphousNi-P 2. APIX70steel 3. Hydrogen	1. Transmission Electron Microscopy (TEM) 2.X-ray Photo-electron Spectroscopy (XPS) 3.Potentiodynamic polarization test 4.Salt fog exposure test 5. ElectrochemicalH-permeation test 6.SEM,XRD,EDS	1.Excellent resistance to H-pemeantaion as well as corrosion in chloride environment has been attributed to the amorphous structure of the Ni-P coatings 2.The Ni-P coated steel shows lower corrosion rate than the crystalline Ni-coating. 3.Ni-P coated steel shows no red rust formation even after 3216 h of salt-fog exposure test
Rajendra Kumar Duchaniyaet al. (2011)[28]	1.aluminum substrate 2.Nickel sulphate 3.sodium hypophosphite 4.complexing agents lactic acid propionic acid, Buffering agent NaOH and stabilizers Pb	1.Knoop hardness test 2.weight loss method for corrosion evaluation 3.scanning electron microscopy	Here it was observed to have a uniform film of nickel phosphorous on aluminium substrate.Phosphorous, present in the form ofspherical globules, increased corrosionresistance.Micro hardness was noted to be increasing as the volume of bath increased.
Xiao-jia Liu et. Al. (2019)[29]	1.AZ91D magnesium alloy (25×15×10 mm) 2.Sodium stannate 3. sodium hypophosphite	1. electrochemical impedance spectroscopy (EIS) 2. X-ray diffraction (XRD) analysis	It was observed that the stannate conversion film and the Ni–P gradient coating were all significantly improved the corrosionresistance of AZ91D alloy substrate. The corrosionresistance of Ni–P gradient coating was better than stannate conversion film and was gradually enhanced with increasing P content.
Guangy-ing Sheng, (2016)[33]	1. aluminum alloy 6061 sheet (50mm×50mm×1mm) 2.nickel sulfate 3.sodium hypophosphite	1.Energy dispersive X-ray spectroscop-y (EDS) 2.scanning electron microscope (SEM) 3.Vickers hardness (HV)	With the increase of electroless plating time, the thickness of the coating increased and porosity gets decreased, when the coating thickness is 25μm, and the porosity is 0, the corrosion resistance of the sampleis better, the roughness of the coating decreased, which is due to theinstability of thebath. Here it was experimented that The medium phosphorus (about 8% P) containing coatings is observed to form passive layer of Ni2O3 embedded with Ni5P2 which remains unchanged even after exposing in SPS(+1 M Cl−)solution. ThisIndicates stable passive film in the concrete pore solution which resists the corrosion significantly. The deposited coatings exhibit very
	1. mild steel substrate 2. Ni-P 3. sodium succinate(used as		

	buffer)	1.SEM and EDX analysis 2.EIS and direct current (DC) polarization resistance techniques 3.XRD analysis	fine grain and are microcrystalline in nature with compact and porous free film. This makes the coating highly impervious to diffusion of moisture, chloride and oxygenthrough it. Experiment showed that heattreatment of MEPEN coating makes it vulnerable to pitting and general corrosion.
Singh et. Al (2005)[44]			It was observed in annealing treatment, that coatings deposited on the substrate with the phosphate layer had a high density and a remarkably improved corrosion resistance.
Beilei Ma et al. (2018) [40]	1.AZ31B Mg alloy (10×15 ×3 mm3) 2. Ni-P	1.SEM and EDS analysis 2.electrochemical tests	The highest corrosion resistance was obtained at 50 min deposition with 120.12 Ω, whichrepresents over 50% increase of the coating depositedat 20 min.
Ojo Sunday Isaac Fayomi, (2020) [34]	1.mild steel plate (40 mm × 40 mm× 2 mm) 2.ZnSO4·7H2O 3.NiSO4·6H2O 4.NaH2PO2·H2O	1.scanning electron microscopy (SEM) 2.Energy dispersive spectroscopy (EDS) 3.optical microscopy	

TABLE-4
Electroless Ni-P plating using number of nanoparticles has been reviewed and listed as-

Reference	Type of composite	Characterization techniques	Major findings
Farzaneh et. al. (2010) [47]	1.Silicon carbide (SiC) nanoparticle 2.Nickel – phosphorous (Ni-p) 3.Mild steel specimen (30x50x 6mm)	1. Potentiodynamic polarization and electrochemical impedance spectroscopy(EIS) 2.X-RAY diffraction and scanning electron microscopy(SEM)	1.Presence of SiC nanoparticles in the Ni-P coating enhanced the corrosion resistance of the coating 2.Higher SiC content negatively affected the corrosion behavior of the coatings. 3.Heating treatment also improving the corrosion resistance of the Ni-P-SiC coating, SiC concentration higher than 2g/l negatively affected the corrosion resistance of the coating.

D. Ahmadkhaniha et. al. (2018) [6]	Ni-P SiC low carbon steel and brass panels with area of 25 cm2	1.Scanning electron microscopy (SEM,JEOL 7001F) 2.Surface profilometer (Surtronic 3+) test 3.XRD 4.Differential Scanning Calorimetry (DSC, Netzsch 404C) 4.Vickers indentation (NanoTest Vantage)	1.Ceramic particles and their size affected the coatings morphology, nano particles reduced thesize of nodularity of NiP coatings, while sub-micron particles decreased the nodularity. 2.Heat-treatment had moreinfluence on increasing the microhardness of the coatings than addition of the ceramic particles. Nevertheless, the particles had an extensive hardening effect in combination with heat-treatment.
S.R. Allahkaram et. Al. (2010)[48]			3.Nanometer SiC particles deposited in less vol.% but higher density than submicron ones resulted in comparable microhardness value. 4.Addition of ceramic particles did not have any significant effect on electrochemical behavior of the coatings. By heat-treatment the protective ability of the coatings was reduced due to the formation of microcracks.
	1. X70 steel substrate 2. sodium hypophosphite 3. nano-sized SiC particles acetic acid	scanning electron microscopy (SEM), energydispersive spectroscopy (EDS), X-ray diffraction (XRD)	It was found here that In the CO2 saturated media containing acetic acid, Ni–P/nano-SiC and Ni–P coated X70 steel specimens showed less corrosion current densities than uncoated X70 steel and the Ni–P/nano-SiC coated specimen showed higher corrosion resistance than that of Ni–P coated specimen dueto the reduction of effective metallic area available for corrosive media.
Allahkaram et. Al.(2012)[43]	1. API-5L X65 carbon steel 2. Sodium hypophosphite 3. SiO2 (fumed type oxide by Degussa)	1. SEM, (CAMSCAN MV2300) 2. Philip's Xpert pro type X-ray diffractometer 3. EIS measurements(Solartron Model SI 1255 HF Frequency Response Analyzer (FRA)) 4. EDX analysis	It was observed that surface of Ni–P coating is very smooth, but the surfaces of the composite coatings are coarser. There are many nodular protrusions over the surfaces. It was seen that both types of coating have amorphous structures. It should be mentioned that micro-hardness of Ni-P coating was 608.3 HV150 but in case of nano coating it was found to be increasing upto7 gr/lconcentration of SiO2nano particles and found to be decreasing when concentration is increased further**.** Higher corrosion resistance was obtained for Ni-P/nano-SiO2 over Ni-P coating.
A. Sadeghzadeh-Attar et.al (2016) [19]			1. The hardness and tribological properties of coatings are improved in the presence of SiO2 nanoparticles and hard crystalline precipitates of Ni and Ni3P, which prevent grain growth and mobility of matrix dislocations.
	1.Ni-P electroless 2.SiO2 nano powder 3. low carbon steel alloy 4. St37 steel substrate	1. Scanning electron microscopy (SEM) 2.Energy dispersive X-ray spectrometer (EDS) 3. micro-hardness test	2.A very good correlation between the surface morphology, chemical composition, microhardness, and tribological behavior of coatings was found in this investigation

Khuram Shahzad et. Al (2021)[1]			
Iman R. Maf et.al (2011) [3]	1.Nickel phosphorus(NiP) 2.Titanium(Ti) 3. High strength low alloy (HSLA) steel 4. NaCl solution 5. electrochemical cell 6. electric furnace	1. XRD (X-ray diffraction) technique 2. FESEM (field emission scanning electron microscope) 3. EDX (energy dispersive spectroscopy) 4. AFM (atomic force microscope) 5. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PP) methods	1. A substantial improvement in the mechanical response of the Ni-P matrix was noticed with an increasing amount of TNPs, which reached to its ultimate values (hardness 675 Hv, modulus of elasticity 18.26 GPa, and stiffness 9.02 kN/m) at NiP-0.5TNPs coatings composition. 2. A tremendous increase in the corrosion inhibition efficiency of the Ni-P coatings with an increasing amount of TNPs, reaching ~96.4% at a composition of NiP-0.5TNPs.
Changjin Li et.al (2002) [14]	1.Ni–P/PTFE(poly tetrafluoroethylene) 2. Three types of surfactants: sodium dodecyl sulfate (SDS), poly-vinylpyrrolidone (PVP) and cetyltrimethyl ammonium bromide(CTAB)(anionic, non-ionic and cationic respectively) 3. Low carbon steel disks with a diameter of 20 mm and thickness of 5 mm	1.Scanning electron microscopy (SEM) 2.Image analysis technique 3.Energy-dispersive X-ray spectroscopy (EDS) 4.Polarization tests 3.Electrochemical impedance spectroscopy (EIS)	1. PVP and CTAB had the highest deposition rate respectively. The deposition rate for the SDS system was very low 2. The corrosion properties of the Ni–P/PTFE systems were improved significantly by the addition of CTAB and PVP surfactants. At an optimum concentration value of CTAB (0.3 g/l), the corrosion resistance increased almost sixteen times compared with the Ni–P specimen
S. Afroukhteh et.al (2012) [15]	1.Ni–P 2.Micron sized alumina powder(Al2O3) 3.Polymer surfactant(WF211) 4.Steel substrates	1. sol–gel method 2.Acoustic attenuation scattering technique (APS100)	1.The specific surface area increases from 3.3 to 132.13 m2 /g as grinding time increases, indicating a significant decrease of the ground product size from 500 nm to 12 nm. 2. The incorporation of alumina nanoparticles can enhance the micro-hardness and wear resistance of electroless Ni–P–Al2O3 nanocomposite coatings, but affect the corrosion resistance. 1. Even at high co-deposition densities, the particles are still well dispersed in the coatings but the agglomeration occurred. 2. The addition of alumina concentration affects the coating rate deposition inversely. 3.Based on EIS and polarization results, the addition of small amounts of alumina nano-sized (3 g/l) to Ni–P electroless coating bath did not improve polarization resistance

Ojo Sunday Isaac Fayomi et.al (2020) [16]	1. Ni–P 2. Nano Al2O3 powder 3. Low carbon steel 4. Polymeric (non-ionic) surfactants	1. DC polarization tests 2.SEM 3. Energy dispersive X-ray spectroscopy (EDS) 4.X-ray diffraction(XRD) 5.potentiodyna-mic polarization and electrochemical impedance spectroscopy (EIS) technique 5.Polarization tests	compared to that of Ni–P coating, however, the addition of higher concentration of alumina improved the corrosion resistance significantly
Dhani Ram Dhakal et.al (2020) [17]			1. The polarization potential of all the fabricated coatings of Ni–P–Zn matrix increase as the time of deposition increases. 2. The highest corrosion resistance was obtained at 50 min deposition with 120.12 Ω, which represents over 50% increase of the coating deposited at 20 min.
Joël Alexis et.al (2012) [18]	1. Hydrated crystal of ZnSO4·7H2O 2. NiSO4·6H2O 3. NaH2PO2·H2O 4. Mild steel 5. Ni–P–Zn	1.Potentiodynamic polarization technique 2.SEM and EDS spectroscopy	1. The average crystallite size of Ni and Ni3P phase is found to bedecreased in Ni-P-nSN(H) compared to Ni-P(H). 2. Besides, the Raman bands at 1350 cm-1 and 1580 cm-1 corresponding to D and G bands suggest not only Ni and P atoms deposited but alsoCarbon from the organic compounds deposited during the autocatalytic plating process.
A. Sadeghzadeh-Attar et.al (2016) [19]	1. Nickel-Phosphorous (Ni-P) 2. Si3N4 nanoparticles 3. Low carbon steel 4. Sodium Dodecyl Sulfate (SDS) surfactate	1. Rietveld technique 2. SEM Analyasis	1. The roughness of the deposits increases with the incorporation of talc particles in the bath due to an important morphological change 2. The values of the hardness and Young's modulus decrease slightly with the increase in talc content 3. . The hardness increases with the insertion of talc when the deposit is heat-treated at 420 C or with a heat treatment at 600 C. 4. 420 degree C treatment causes an important improvement in the adhesion level of the coating
Dhani Ram Dhakal et.al (2019) [20]	1. Nickel phosphorus composite(NiP) 2. Micro particles of talc 3. Low-alloy steel substrates (36NiCrMo16)	1. Scanning Electron Microscopy (SEM). 2. X-ray diffraction analysis 3. Nanohardness tests 4. Nanoindentation tests 5. Adhesion tests 6. Microscratch test and Microtensile test	1. The hardness and tribological properties of coatings are improved in the presence of SiO2 nanoparticles and hard crystalline precipitates of Ni and Ni3P, which prevent grain growth and mobility of matrix dislocations. 2.A very good correlation between the surface morphology, chemical composition, microhardness, and tribological behavior of coatings was found in this investigation.

Amir Kordijazi (2019) [21]	1.Ni-P electroless 2.SiO2 nano powder 3. low carbon steel alloy 4. St37 steel substrate	1. Scanning electron microscopy (SEM) 2.Energy dispersive X-ray spectrometer (EDS) 3. micro-hardness test	1. The phase and thermal oxidation behavior of Ni-P and Ni-P-TaC system studied via temperature dependent (TD) Raman measurement show that the coating systems are stable in ambient environment up to 500ºC. 2. The electrochemical corrosion test suggests good corrosion resistance properties of the heat treated Ni-P-TaC composite coating over as-plated Ni-P coating.
Mara Cristina Lopes de Oliveira et.al (2017) [22]	1. electroless Ni-P 2. TaCnano particles 3. Cu-plates	1. Vickers microhardness test 2. electrochemical impedance spectroscopy (EIS) 3. potentio-dynamic polarization tests 4.SEM,XRD	1. It was observed that a lower pH level leads to a higher value of phosphorous in coating composition, which results in the formation of an amorphous structure and it is beneficial for anti-corrosion properties 2. Potentiodynamic polarization experiments demonstrate that the coating has the highest resistance against corrosion with corrosion rate of 0.011 mm/year
SantigopalSamant et.al (2016) [23]	1. Electroless Ni-P 2.Zn(zinc) nano powder 3. Low carbon steel (St 37)	1. Energy dispersive analysis of X-rays (EDAX) 2.SEM	1. The highest tungsten content produced a smooth and nodular morphology 2. The corrosion behavior was little affected by tungsten incorporation in the as-plated state whereas the surface stability and corrosion resistance increased for higher tungsten contents in the film after annealing at 400°C
T.R. Tamilarasan et.al (2017) [24]	1. Ni-P electroless alloys 2. Tungsten(W) 3. SAE 1020 carbon steel	1.Nanoindentation test 2.Confocal laser scanning microscopy (CLSM) 3.SEM,EDS Analysis 4. X-ray diffraction (XRD) 5. Annealing treatment 6. Electrochemical measurements	1.Excellent resistance to H-pemeantaion as well as corrosion in chloride environment has been attributed to the amorphous structure of the Ni-P coatings 2.The Ni-P coated steel shows lower corrosion rate than the crystalline Ni-coating. 3.Ni-P coated steel shows no red rust formation even after 3216 h of salt-fog exposure test
D. Liu et.al (2009) [25]	1.AmorphousNi-P 2. APIX70steel 3. Hydrogen	1. Transmission Electron Microscopy (TEM) 2.X-ray Photo-electron Spectroscopy (XPS) 3.Potentiodynamic polarization test 4.Salt fog exposure test 5. ElectrochemicalH-permeation test 6.SEM,XRD,EDS	1. The addition of rGO particles had considerably improved the corrosion and erosion resistance and the best results were achieved at anoptimum concentration of 50 mg/L of rGO in the bath. 2. The microhardness of the coatings increased in the presence of rGO particles up to a maximum of 761 HV.

Promphet et.al (2017) [13]	1.Electroless Ni-P 2.rGO(graphene) 3. AISI 1018 low carbon steel substrates	1. X-ray diffraction and microhardness analysis 2. potentio-dynamic polarization 3.electrochemical impedance spectroscopy (EIS) 4. Erosion-corrosion test	1.The corrosion resistance of the composite coatings was found to increase with the increase in CTAB concentration up to a certain optimum of 20 mg/L, beyond which a decreasing trend of corrosion resistance was observed 2.Compared with Ni–P coating, all the Ni–P–Al2O3 composite
K. Abidali et.al (2021) [11]	1. Electroless Ni–P–Al2O3 2. Mild steel 3.cetyltrimethyle ammonium bromide (CTAB)	1.Salt spray test 2. SEM	1. The incorporation of RGO into NiP-TiO2 sol with well-dispersion and completed coverage on the steel exhibited a significant improvement of both corrosion resistance and electrical conductivity compared to a bare steel. 2. NiP-TiO2 sol-RGO coated steel surface showed a hydrophobic property leading to automatically self-protection from surface wettability
Eman M. Fayyad et.al. (2019) [9]	1.Nickel phosphorus – titanium dioxide sol – reduced graphene oxide (NiP-TiO2 sol-RGO) 2. GO solution 3. 1, 3-propanediol	1. Transmission Electron Microscopy(TEM) 2. Scanning Electron Microscopy(SEM)-EDX 3. Contact angle measurement 4. Electrochemical testing 5.Four-point probe conductivity measurement	1.Coating low carbon steel with Ni-P increases the microhardness from (200 HV) to (470 HV) after heat Treatment 2. Incorporation of both CNT particles in Ni-P coating layers increased microhardness (Ni-P-0.1 CNT) to 460 HV and 560 HV after heat treatment. 3. After heat treatment the weight lost was almost zero through wear test. 4. No flaws were observed in the coating layers after heat treatment
Mukhop Adhyay et.al (2021) [8]	1.Ni-P-CNT 2.Low alloy steel	1. Annealing process 2. TH-717 Vickers hardness tester 3. surface roughness Test (HER210 Model) 4.SEM,EDS 5. wear test	1. The incorporation of lower concentrations of TiNi nanoparticles significantly improved the microhardness and the corrosion resistance of the as-plated and annealed NiP coatings 2. NiP-TiNi NCCs demonstrated antibacterial properties since it decreased the cell viability of E. coli from 70% in the case of TiNi–free coating to 19% in the case of NiP-TiNi NCC with a concentration of 0.8 g L-1 TiNi
	Ni-P TiNi API X100 carbon steel	. Nova NanoSEM 450-SEM,EDX 2. TEM(Talos F200X high resolution transmission electron microscope) 3. Vickers and nanoindentation microhardness testers. Electrochemical impedance spectroscopy (EIS) and potentiodynamic	1. Ni-P-W and Ni-P-Cu coated rebars exhibited negligible change in the nodular morphology and indicating a high-corrosion resistance. 2. Ni-P-W and Ni-P-Cu coatings successfully prevented the rebar from attack of sulphates

	Ni-P Ni-P-W Ni-P-Cu Fe-600 grade steel rebar	1.Electrochemical tests-PDP and EIS 2.EDS and SEM 3.XRD technique 4.Field Emission Scanning Electron Microscope (FESEM) (Sigma-300, ZEISS)	

Experimental Observation

Corrosion

It has been found that coating having medium phosphorus content (about 8%) coating is more impervious and safeguarding in comparison to coating having high phosphorus content (>16%) done on mild steel (MS) substrate. The heat treatment of coatings deposited on mild steel (MS) substrateis found to have adverse effect on their corrosion resistance. Passive films of Ni2O3 and Ni5P2 is formed in the microcrystalline nature of electroless coating of medium phosphorus electroless nickel (MEPEN) observed in X-ray diffraction study [44]. Annealing the coating can also Improvecorrosion resistance. Corrosion resistance of Ni-P coating is enhanced to 21% when annealed at 400°C in air and gradually increased to 31% when annealed at 600°C in comparison to bare steel.Increment of corrosion resistance at 400°C annealed coating was credited to the formation of crystalline Ni and Ni3P phases[60]. Using proper type of surfactants may lead to uniform distribution of nano-particles and properties might be enhanced. It is found that by incorporating PTFE particles into Ni-P matrix corrosion resistance of low carbon steel is enhanced. Defects in the coatings are also reduced when proper type and concentration of surfactants created uniform distribution of PTFE particles in the Ni–P matrix [35]. A sample of Ck45 steel was coated with nickel–phosphorus alloy from a bath which contained reducing agent sodium hypophosphite and different complexing agents (sodium citrate, sodium acetate and lacticacid). For the different coated samples obtained with different complexing agent was tested for anti-corrosion properties of in 3.5% NaCl solution by the weight loss and potentiodynamic polarization techniques. The best result is obtained when the complexing agent was sodium citrate in which the smooth surface and spherical nodular structure of coating showed higher microhardness and anti-corrosion resistance[58]. The sono-deposition of nanocomposite was done on mild steel from a bath containing ultrasonically dispersed diamond nanoparticles (DNP) which resulted in increment of corrosion resistance significantly [50]. The corrosion resistance of Duplex Ni–P–ZrO2/Ni–P coating deposited onto stainless steel substrates was evaluated. The novel duplex coating had both excellent mechanical property and good corrosion resistance due to different corrosion mechanism compare to Ni–P coating[61]. The corrosion resistance enhancement was done by incorporating nano-sized TiC particles into electroless Ni–Pcoating and different types of surfactant(cationic, anionic, and polymeric) were added to the plating bath to increase TiC content in the coating. Addition of surfactant promoted the corrosion resistance of the Ni–P/0.1TiCcoated steel especially in presence of polymeric surfactant[49]. composite coatings of Ni-P-nano-Al2O3 on the mild steel wereprepared by adding Al2O3 nanoparticles into the traditional electroless Ni-P bath. Both cationic and anionic surfactants were used to stop the agglomeration of the incorporated nano-Al2O3 particles. The results showed that compare to the pure Ni-P coating on the mild steel, the coating formed with 6 g/L nano-Al2O3 performed the highest resistance. Under the optimal conditions, the adding of anionic surfactant (SDBS) improved the anti-corrosion performance of the samples further, while the addition of cationic surfactant led to worse corrosion resistance[62]. To enhance the corrosion resistance of Fe-600 grade rebars electroless nickel Ni-P, Ni-P-W and Ni-P-Cu coating was successfully deposited and were subjected to electrochemical tests which revealed that electroless Ni-P-W and Ni-P-Cu coated rebars had a nobler Ecorr and a similar Icorr compare to the bare rebar. Ni-P-W and Ni-P-Cu coated rebars exhibited negligible change in the nodular morphology and indicated a high-corrosion resistance. Overall, Ni-P-W and Ni-P-Cu coatings successfully prevented the rebar from sulphateattack[8]. Properties of duplex coatings were evaluated and compared with single layer coating and it was found that microhardness, wear resistance and corrosion resistance of the duplex coating is higher than Ni–P and Ni–B coatings of similar thickness. Among the two types of duplex coatings studied, hardness and wear resistance ishigher for coatings having Ni–B coating as the outer layer whereas better corrosion resistance is offered by coatings having Ni–P coating as the outer layer[63].

Hardness

It showed from results of many researches that the Ni-P and Ni-B electroless coating on substrate as deposited hardness of electroless Ni-P and Ni-B coatings are equivalent to many hardened alloy steels. It was also seen that the heat treated to hardness of EN can be comparable to those of electrodeposited chromium. The maximum value of hardness can be achieved in 10 h at 260°C or 1 h at about 400°C. It was observed that as increasing phosphorus or boron content the ability to maintain the hardness of EN deposits under elevated temperature also increased but it was decreased rapidly when temperature exceeds 385°C. To achieve good wear resistance at elevated temperature Ni-B coatings show better results, therefore Ni-B widely used in such conditions. Yan et al. deposited electroless Ni-P on substrate at 8% phosphorus content and varying the ratio of lactic acid to acetic acid in the electroless bath, the result shows a high hardness value of 910 HV0.1 and high wear resistance[52]. As increasing the concentration of TiNi up to 0.4 g L^{-1} the microhardness of the EN composite coating significantly enhanced and further improvement takes place after heat treatment, it was observed by Eman M. Fayyad et. al.[9]. It was studied by Abdul Raheem K. Abidali et. al that the microhardness of steel substrate which is coated by low carbon with Ni-P was increases after heat treatment from 200 HV to 470 HV. It was also seen that the microhardness of steel substrate which incorporated with CNT particles in Ni-P coating was increased from 460 HV and 560 HV after heat treatment[11].].Due to excellent thermal and chemical stabilization and higher hardness value of C3N4 nanosheets, it was used with electroless Ni-P for the purpose of coating of API X100 carbon steel substrate. It was seen that the alkaline electroless bath produced a NiP–C3N4 nano coating layer with a microhardness value of 250 HV which was

higher than that produced from the acidic bath. For achieving a better homogeneity of the nanocomposite coating and microhardness a small concentration of pyrrolidone (PVP) was added as a surfactant [12]. The incorporation of titanium nano particles (TNPs) with Ni-P was successfully done on the surfaces of HSLA steel substrate by electroless method of deposition and found that these coating of Ni-P-TNPs gave a significant influence on mechanical properties such as microhardness and nanoindentation to its ultimate values for the NiP-0.5TNPs nanocomposite coating composition[1]. B. H. Chen et. al. used nine different types of surfactants which was employed with the plating process of electroless Ni-P deposits and the effects of these particles on the properties of the resulting coating of electroless Ni-P deposits was examined. It was found that the deposition rate of surfactant bath was increased by 25% as compare to the surfactant-free bath when a small amount of surfactant was added in the bath. Due to presence of surfactant in the bath the reduction was seen in the formation of micro-pitting and due to this corresponding corrosion resistance was also enhanced[2]. The Ni-P-talc composite coatings were developed on the different types of substrates to achieve hard coating with a lubricating effect at 600◦c. Since this process of coating was free from the hexavalent chromium, hence it could be provided a reliable substitute for the electrodeposition of hard chromium coating which used in different industrial applications. Nano-and micro-hardness, micro-tensile and nano-scratch testing were used for found out the local responses to static and dynamic mechanical loading. It was observed that as the amount of talc increases the hardness and stiffness value slightly decreases for untreated coatings. Due to crystallization a higher hardness value and young's modulus may be seen at a 420◦c of heat treatment. Whereas, a 600◦c of heat treatment could lower these values because of overaging. The adherence and cohesion of talc coated surface were also improved at 420◦c heat treatment[18,20]. If SiO2-sol solution used in electroless Ni-P bath for coating of St37 steel substrate than it was seen by structural phase analysis that the amorphous phase changed to crystalline phases. If a comparison is done between the micro-hardness and wear properties of Ni-P and Ni-P-SiO2 composite coating than it shown in different experimental results that both properties such as microhardness and wear resistance of Ni-P enhanced in the presence of SiO2 nanoparticles, also at 400 °C for 1 h of heat-treated coating of nanoparticles help to achieve a maximum microhardness of 970 Hv100, also reduced the coefficient of friction up to 0.25 and minimum wear loss seen up to 4.4 mg[19]. A film of Ni-P-W was incorporated on the substrate of steel substrate by electroless deposition method. The observation was made with different concentration of tungsten in the bath. The XRD results show that after annealing at 400°C Ni and Ni3P crystallites were present in the coating was independent of the concentration of tungsten but the morphology of film was affected by tungsten incorporation. A reduction was observed in the phosphorus content of film with increase in tungsten content. After annealing and scaled with tungsten concentration, hardness of coating was also increase. The surface roughness was decreasing as the surface morphology became more nodular. The lowest friction coefficient was associated with the hardest and smoothest surfaces which was achieved for the coatings with high tungsten concentrations[22]. T.R. Tamilarasan et. al. observed that the microhardness of theNi-P-rGO coatings increased in the presence of rGO particles up to a maximum of 761 HV[24].

WEAR RESISTANCE

Electroless nickel (EN) is one of the most frequently used coating material which is used for different types of substrate coating in the application of wear resistance and to achieve a good hardened surface of substrate. This type of electroless coating is famous for achieving higher hardness value and good wear resistance. Heat treatment is a process which further helps to increase these important characteristics of substrate. It has been seen in different experimental result that heating for 1 hr at 400°C of substrate a optimum hardness is found out which is almost comparable to hard chromium deposited in hardness and wear resistance[54]. A hardness value of 1700 to 2000 HV0.1 can be achieved by heat treatment of substrate around 290°C temperature to keep treatment in long term duration(approximately 30 to 40 weeks) [55]. These low-temperature treatments result in a finer dispersion of nickel boride than do higher temperatures and in the formation of iron borides (such as Fe2B and Fe3C0.2 B0.8) within the coating, when the substrate is ferrous alloy.

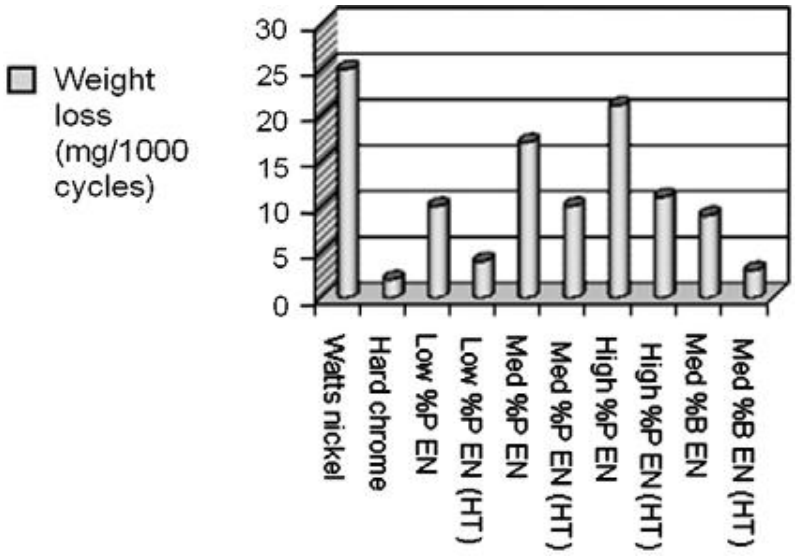

Fig. 4 Taber wear resistance of various kinds of coating.

The electroless nickel (EN) is widely used latest technology. This method of plating process is used in different engineering field to increase the life period of various engineering materials (metallic or non-metallic) to prevent it from loss of material properties due to attack of various species which is present in our environment, these species cause corrosion as well as wear effect. This type of EN plating can enhance corrosion and wear resistance

which helps in batter performance in various components which are used in different-different engineering fields eg. Liquid or gases following valves, aluminum piston heads, aircraft engine shafts, components of gas turbines and engine mounts in the aircraft industry, and such automotive parts as differential pinion ball shafts, fuel injectors, ball studs, disk brake pistons, transmission thrust washers, knuckle pins, and hose couplings[15]. Sometimes better wear resistance requires for some substrate materials such as mining application materials and materials which are used as material-handlingequipments in such cases EN has been substituted with chromium to achieve better result. Due to its unique properties that it can be easy to coat specific areas, the EN has a very important application in the salvage of worm surfaces. Thus,Sahoo worked in this field of EN and optimized the coating process parameters on L27 Taguchi orthogonal design on the basis of minimum wear. He focused on four parameters which is related to this study such as temperature of bath, annealing temperature, concentration of reducing agent and concentration of nickel source solution. It was found from the result that bath temperature and annealing temperature have been played the most significant roll to control the wear characteristics. Also, the concentration of nickel solution and bath temperature has influence some batter wear resistance properties [53]. By electroless Ni-P coating on the friction surfaces, wear resistance characteristics of self- mated groups of Ni, Cu, and Ni-P coatings has been examined. During friction enhancement by incorporation of electroless Ni-P coating the growth of transfer particles in Cu/Cu and Ni/Ni rubbing systems seen. It has been seen that due to the incorporation of coating materials the particles were gets harder than the original surface. This is the main reason which is responsible for the increment of the growth of transfer particles incorporated with the coating during friction. The tribological properties have been also well enhanced when electroless nickel deposited with hard nano particles such as silicon carbide or boron nitride or solid-lubricant particles (PTFE). As compared to Ni-P coating Ni-P-PTFE coating exhibited less wear resistance[10]. With incremental concentration of CNT upto 0.1 g/L, the coefficient of friction was decreased as a result shear of lubricating film of carbon may be too easy, which was responsible for decreases in direct contact among counterpart and surface of samples. Some additional effect on the behavior of wear of sample is its surface roughness. The larger surface roughness can lead to abrasive interactions among the roughness on surface sample Ni-P-0.4g/L CNT and counterpart to be conquered after the heat treatment, however, the weight lost was almost zero through wear test. Thus, after the heat treatment there were no flaws observed in the coating layers[11]. It was observed that incorporation of Si3N4 nanoparticles in the Ni-P coating matrix helps to improvement in tribological and mechanical properties of surface after the heat treatment. It was shown in the XRD data that due to the strain imposed by Si3N4 nanoparticles during the growth of Ni and Ni3P crystallite grains, the contraction in lattice parameters of the Ni and Ni3P crystals in heat-treated Ni-P-nSN(H) specimen. As compared to Ni-P(H), the average crystallite size of Ni and Ni3P phase was found to be decreased in Ni-P-nSN(H). Because of these some excellent properties, the hardness and the wear resistance properties of Ni-P-nSN(H) are increased. As grain boundary phase was weak so cracks or voids propagation take placed too easily but such cracks were not noticeable in Ni-P-nSN(H). Moreover, it was revealed by Raman measurement that the presence of NiO in the wear debris generated from as-plated and heat-treated specimens. Besides, the Raman bands at 1350 cm-1 and 1580 cm-1 corresponding to D and G bands suggest not only Ni and P atoms deposited but also Carbon from the organic compounds deposited during the autocatalytic plating process[17]. As Ni-P-Zn coating was well-known for its excellent corrosion and wear resistance, it was investigated by Amir Kordijazi and found that the optimal bath is comprised of 10 g/l and 15 g/l of reducing agent and zinc agent, respectively. The pH value is 10.5 and deposition time is 60 min. The optimal solution results in an excellent corrosion resistant layer with corrosion current density of 0.23 µA/cm²[21].Electroless Ni-P-rGO coatings were successfully obtained on low carbon steel substrates by adding various concentrations of rGO particles to the conventional electroless Ni-P bath. There was even dispersion of rGO particles for coatings deposited with 50 mg/L of rGO bath concentration. The increase in the rGO concentration in the bath led to changes in the surface heterogeneity and enlarged nodule sizes in the coating matrix. EDS and XRD results confirm the existence of incorporated rGO particles in the coatings[24].

CHARACTERIZATION OF EL NI-P BASED NANO COMPOSITE COATINGS

EDS/EDXA ANALYSIS

Element quantification is done by EDS analysis to evaluate the quantity of the elements present in the Ni-P coating. The results of this analysisisgiven below in table 5. It is observed that coating contains 9.35 wt% Phosphor which falls in the category of high P coating.It is also worth noting that P content in Nickle-Phosphor-Copper coatings is getting reduced with the increasing concentration of Cu nano-particles observable from the EDS results of table 6.This is mainly because Copper particles are mechanically immersed into the sub-layer through the electroless of the Ni-P-Cu coatings [56].

Table 5. Theamountof different elements (EDS results) in the Nickle-Phosphor coating.

Element	Atomic % of the elements	Weight percent
Nickle	83.51	90.50
Phosphor	16.35	9.35
Iron	0.14	0.15

Table 6. The amount of P (EDS results) in the Ni-P-Cu nano-composite coatings under differentCu concentrations.

(Cu concentration in the electroless bath (gr/lit)	Amount of P (wt%)
1	7.60
3	6.79
5	6.01
7	5.10

In another paper, EDS results indicated thatadding surfactant can lead to increment of phosphorus content of the coatings from 9% to 12 wt%. Coating with higher P content resulted in higher amount of Ni3P compound which might be the reason for improving corrosion performance at the presence of surfactant. When surfactant added, Ni3P in the deposit takes nanostructure form and decreases the porosity of coating[58].

Phase Analysis

Phase analysis of coating is carried out by XRD method in which Structural aspects of EN coatings in as-deposited condition is observed. Binary as well as ternary EN coatings are primarily amorphous in nature because of the fact that they have high P content (P > 8%). Ni-P coatings in as-deposited condition are amorphous in nature which is confirmed in the XRD spectrum as a broad hump (Fig.5(a)) which indicates disorder in arrangement and amorphous characteristics. In nanocomposite Ni-P-W coatings (Fig. 5(b)), a sharp peak super imposed with short ones can be observed where sharp peak is superimposed by short ones and the broad hump is still there. So, alittle improvement in the crystallinity of the nanocomposite coatingcan be therefore concluded on W co-deposition. The XRD results ofelectroless coating of Ni-P-Cu nanocomposite in as-plated condition is shown in Fig. 5(c). The deposits have amorphous characteristics in as-deposited state[12]. It is observed that the Ni and P contents have decreased when PTFE content is increased. In the XRD analyses (Fig. 6), all the coatings observed to have an amorphous structure. It can be observed from the figure that a broad peak at 45° is seen in all the EN deposits indicating the amorphous profile of Ni–P deposits. The XRD patterns also prove the presence of the PTFE particles ingrained into the Ni–P matrix for the CTAB system. The content of PTFE with no added surfactant is very small (less than 5 wt.%) due to which PTFE diffraction peaks is not observed in their XRD patterns[3]. XRD analysis of a coating containing medium concentration of phosphorus exposed in milder SPS environment is done and observed to not have any of phosphate peak in XRD spectra (Fig. 7). In-depth analysis of XRD spectra of corrosion products formed on MEPEN observed to have Ni2O3 and Ni5P2 phases with small peaks of NiCl2 and CaH2 which suggested that the phosphorus present in the coating forms insoluble Ni5P2 compound and blocks the defects present in passive oxide of the metal[1].

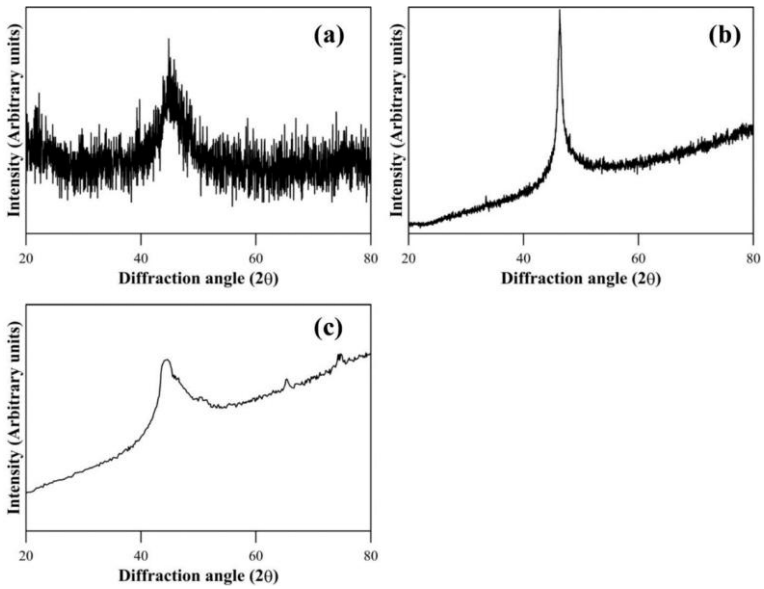

Fig. 5 XRD analysis of as-deposited electroless (a) Ni-P (b) Ni-P-W and (c) Ni-P-Cu coatings.

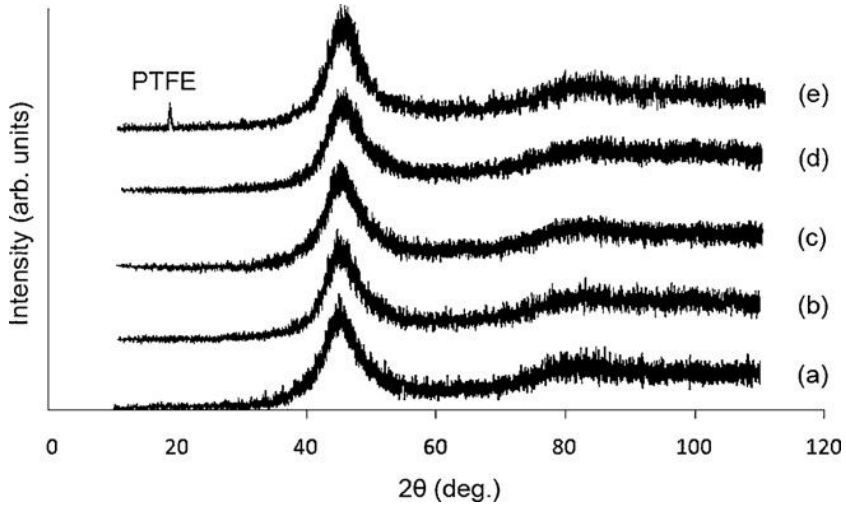

Fig. 6 XRD patterns of EN coatings deposited from the bath with and without additives:(a) Ni–P, (b) Ni–P/PTFE, (c) Ni–P/PTFE + 0.3 g/l SDS, (d) Ni–P/PTFE + 0.2 g/l PVP,(e) Ni–P/PTFE + 0.3 g/l CTAB.

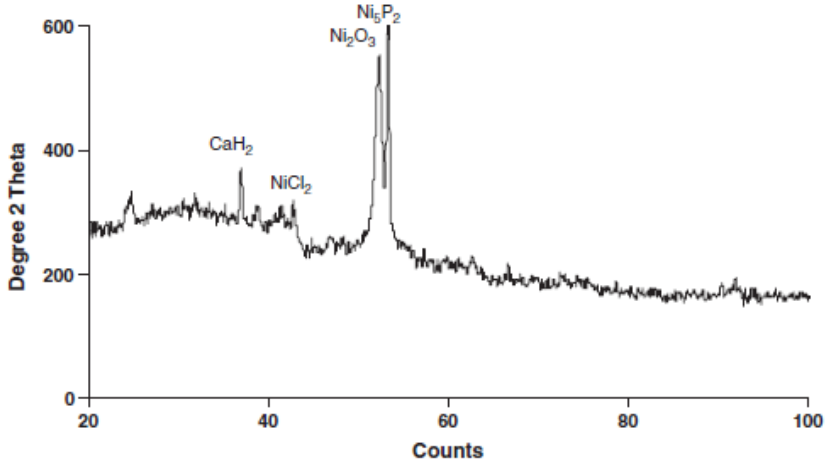

Fig. 7 XRD spectra of corrosion products formed during the exposure of MEPEN coating for 9 months in SPS + 1 M Cl−

Metallographic Analysis

The morphological study of coating is done by scanning electron microscopy (SEM). From SEM analysis, obtained SEM micrographs of EN coatings in as-deposited condition are shown in Fig. 8. The Ni-P coatings shows a dense morphology havingnodulated structures (Fig. 8(a)). The surface has grey appearance without any defects or porosity. These nodules have the average sizeof 5 to 10 μm. Such globular morphology which is commonly observed in EN coatings and has been widely compared with that of a cauliflower. If the coating has compact defect free microstructure it results in improvement of corrosion resistance and provides barrier protection to the substrate. It is found in the SEM analysis of electroless Ni-P-W coatings that nodulated growths are larger for the same and the average size is almost 20 μm (Fig. 8(b)) which is double the size of the nodules observed in Ni-P coatings. Analysing it further shows distinct cellular boundaries in Ni-P-W coatings which can be attributed to the fact that crystallinity of Ni-P-W coatings is higher than Ni-P as observed in XRD results (Fig. 5). But the size of electroless Ni-P-Cu coatings (Fig. 8(c)) is observed to have even lower when compared with Ni-P or Ni-P-W. As a matter of fact the surface morphology of Ni-P-Cu coating is comprised of cluster of nodules and appears to be rough compared to Ni-P and Ni-P-W coatings[12]. In another paper the annealing effect in the coating is observed by SEM analysis shown Fig. 9(a) the SEM image of as-deposited Ni–P coating while Fig. 9(b–d) shows the cross-sectional image of Ni–P coating annealed at 200 ◦C, 400 ◦C and 600 ◦C respectively in air. From the Fig. 9(a–d), the coatings were found to be dense, uniform and without any pores and cracks. The coating thickness was observed to be in the range of 20–25 μm [2].

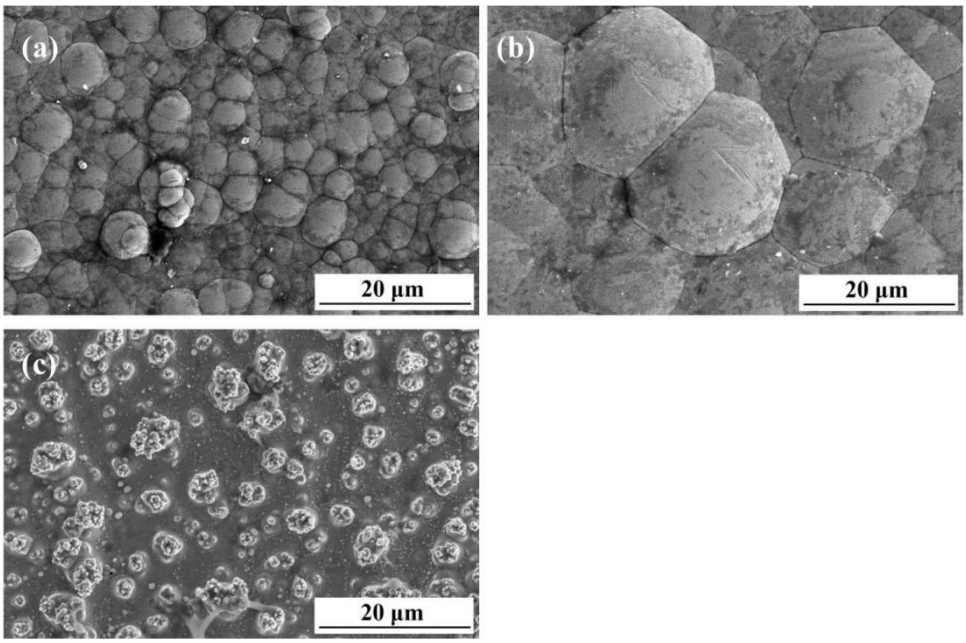

Fig. 8. SEM of as-deposited electroless (a) Ni-P (b) Ni-P-W and (c) Ni-P-Cu coatings.

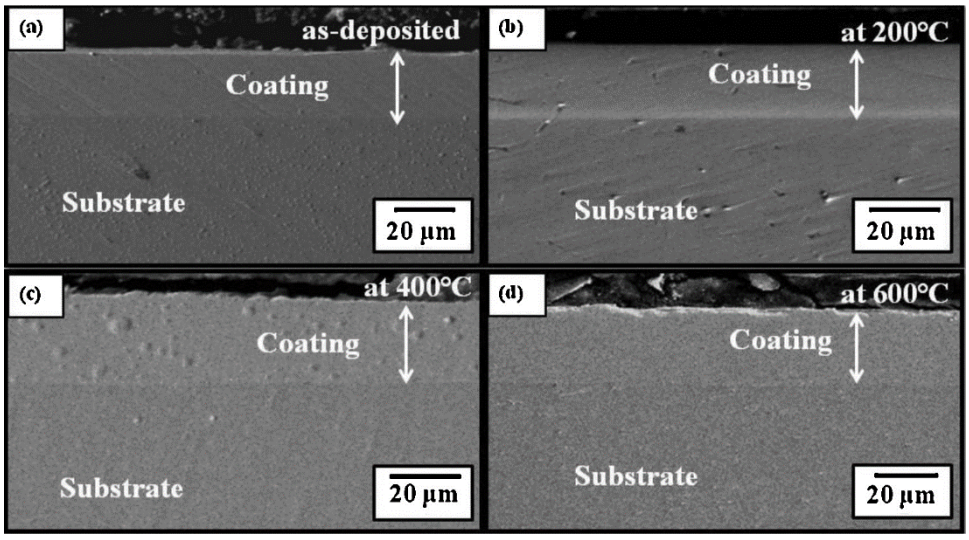

Fig. 9 SEM cross-sectional images of electroless Ni–P coating (a) as-deposited, (b) annealed at200◦C, (c) annealed at 400◦C and (d) annealed at 600◦C. Thickness of all the coatings is in range of 20–25 µm.

Corrosion rate measurements

1. Weight loss technique

Corrosion measurement of metallic surface is done with this technique. The corrosion resistance of the Ni–P coating prepared with different complexing agents in 3.5% NaCl solution was compared with substrates via the weight loss method (Fig. 10). Fig. 10 shown below compares the corrosion rates of carbon steel substrates with Ni–P composite coatings in 3.5% NaCl solution during the 480 h (20 days) corrosion tests. For the substrate it is observed to havelinear increament of weight loss with respect to time. On the contrary, a minimum increase in weight loss for the Ni–P coatings is observed only after 200 h of immersion. It is also noted from the curves below that after 480 h immersion in 3.5% NaCl solution, steel has the highest weight loss of 4.90 mg cm2 while Ni–P obtained using bath A is showing the lowest weight loss of 1.45 mgcm2 in 3.5% NaCl solution [58].

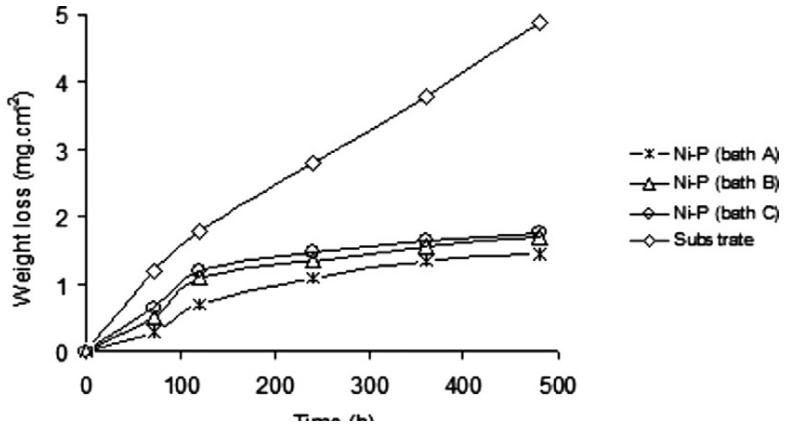

Fig. 10 Comparison of the corrosion rates of Ni–P composite coatings with different complexing agents and substrate in 3.5% NaCl solutions.

2. Electrochemical impedencespectroscopy(EIS) and potentiodynamic polarization (PDP) tests

EIS is a well – known method to evaluate the corrosion performance of coatings in short time. EIS tests in OCP with the voltage of 10 mV having frequency ranges of 10 mHz-100kHz is performed as well aspotentiodynamic polarization tests, with the scanning rate of 0.001 V/s, in the range of -400 mV to +1000 mV with respect to OCP is also performed. The polarization curves obtained in the analysis for the Nickel-Phosphor coating and the Nickle-Phosphor-Copper nanocomposite layers in 1 M HCl solution are shown in figure 11. The corrosion current density, icorr, of the Nickle-Phosphor coating is found to be 7.4594 μA/cm2, although for the nano coatings containing different amounts of reinforcement particles (Cu), the number is greater than the Nickle-Phosphor coating. Actually, it can be observed that icorr increases at higher amount of the Cu particles whichresulting in inferior resistance against corrosion of the nano coatings. By comparing the polarization curves of different coatings, it is found that the presence of coating enhances the corrosion resistance of the plain carbon steel which is due to the fact of disconnection of the plain carbon steel with the corroding environment. As described above, the presence of micron size particles reduces the resistance against corrosion of the nano coatings. Actually, these particles are micro-cracks initiators andmicro-cracks are suitable locations for the advancement of corrosion. Therefore,higher the amount of these particles, higher is the crack locations. Moreover, corrosion resistance is greatly dependent on the amount of P element in the coating. Finally, the lower the amount of P element in the coating, the lower is the resistance against corrosion of the nano coating. It is also observed that with the increase of the constituents' concentration, the content of Phosphor element in the nano coating reduced as well. Consequently, with the increase in the amount of the particles in the coating, the corrosion resistance of the nano coating gets reduced [56]. Theoretically, corrosion current density is related to the polarization resistance (Rp) through
Stern-Geary equation as follows [59]:

$$Rp = \beta/icorr \quad (1)$$

Where β is (βaβc)/(2.303(βa + βc)).

The parameters in the above given equations, such as βa, βc, Ecorr, icorr and Rp, for the Nickel-Phosphor coatings and the nano-composite coatings, has been shown in Table 7. It can be observed in the table that polarization resistance (Rp) is reduced by raising the amount of the Copper nano particles in the Nickle-Phosphor-Copper coatings.

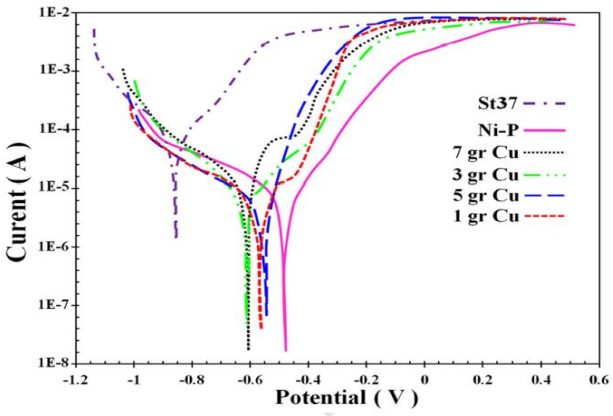

Figure 11. Polarization graphs of the St37 and Nickle-Phosphor coating with different concentrations of the reinforcement particles.

Table 7. Comparison of corrosion current density and potential in the St37, Nickle-Phosphor coating and the nano coatings under different concentrations of Cu.

Sample	E_{corr} (mv)	I_{corr} ($\mu A/cm^2$)	Polarization resistance (Ω)	ba (V/dec)	bc (V/dec)
Ni-P-1 (g/l) Cu	-605.50±0.15	18.637±0.2	6615±4	0.168	0.277
Ni-P-3 (g/l) Cu	-667.12±0.15	26.934±0.2	4849±4	0.204	0.375
Ni-P-5 (g/l) Cu	-577.38±0.15	31.302±0.2	4618±4	0.263	0.066

Normally, the results of electrochemical impedance tests are shown in number of ways. The most common ways for the same is through the Nyquist plot in which real impedance (Z') against virtual impedance (Z'') for every frequency is plotted. Nyquist plot for the virtual impedance (Z'') against the real impedance (Z') has been shown in fig. (12) for each frequency of the applied voltages in the Ni-P coating andNi-P-Cu nano coatings in the solution of 1 M HCl. It can be observed in figure 12 that by raising the amount of the Cu nano particles in the Ni-P-Cunanocomposite coatings, the diameter of the half-circle in the Nyquist plots gets reduced. These half-circles are indicative of the extent of corrosion resistance. Therefore, it can be found from the figure that by increasing the amount of the Cu nano particles in the Ni-P-Cunano-composites, the resistance against corrosion of the Ni-P electroless layers is reduced. Also, corrosion resistance results obtained from the impedance spectroscopyissame as the potentiodynamic polarization results obtained above.

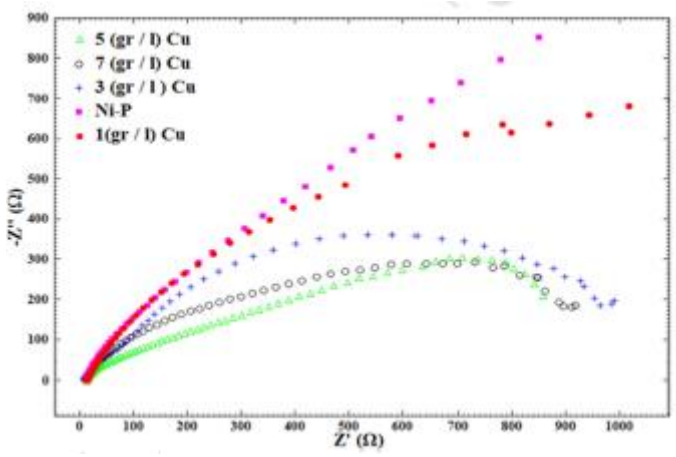

Figure 12. a) Nyquist plots of EIS tests for the Nickle-Phosphor and Nickle-Phosphor-Copper nano coatings under different amounts of Cu.

CONCLUDING REMARKS

This review paperoutlines the results of electroless plating found out after experimentingwith number ofnano particles,elements and alloys in detail.It has been observed that different physical and chemical properties can be advantageously obtained here depending upon the requirements by incorporatingdifferent elements (copper, zinc, Titanium etc.), particles (SiC, TiO2, PTFE, Al2O3 etc.) and suitable surface treatments like heat treatment, laser treatment etc.The properties which make it suitable to be used in various application are its hardness, low friction, wear resistance and corrosion resistance. Electroless coating has ability to coat any substrate (metal or nonmetal) uniformly. In this paper particularly Anticorrosion performance of electroless plating has been discussed.

It is important to note that incorporation of nanoparticles in electroless plating is found to be improving corrosion resistance however higher content of it might reduce the corrosion resistance. The effect of coating deposition time, bath solution temperature, pH of the coating solution of electroless Ni-P coatings has a slight impact on corrosion resistance. Surfactant can also improve corrosion resistance. However, heat treatment upto 300 oCfor electroless Ni-P composite coated substrate has a detrimental effect on corrosion property but annealing at higher temperature improves corrosion resistance. In Ni-P electroless coating, Phosphorus content between 9 to18wt% shows the best results in terms of corrosion resistance.

Electroless deposited ternary/quaternary alloycoatings, composite coatings, duplex coatings, graded coatings and multilayer coatings are some of the promising developments to achieve improved corrosion resistance. Future of electroless plating involves advanced operation technology and controllers for optimum improvement. We should now move forward towards cleaner production technology and more efficient use of raw materials. In the long run, electroless nickel plating will make a substantial contribution to the resources and energy saving andenvironmentalfriendly society.

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