

Effect of plating time for electroless nickel coating on rebar surface: An option for application in concrete structure

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Abstract

The ternary Ni–P–Fe alloy coating was developed by an electroless process using a citrate bath. During the steel sample dip in bath, Fe will first get dissolved from the rebar surface and would subsequently get introduced in the bath as Fe^{2+} . This, in turn, would activate the surface and Ni, P and Fe are co-deposited on the activated rebar surface. The first deposition layer would act as catalyst for subsequent metal deposition. The coating was characterised using SEM, EDS and XRD techniques. The bath pH was found to play a strong role on process kinetics as well as composition of the coating but not on coating structure. The weight percentage of Ni, P and Fe in the coating was found to have a relationship with the bath pH. The Tafel and salt spray test were conducted to find out corrosion resistance performance of the coatings. Electrochemical behavior of the coated rebars in simulated concrete environment was influenced by the pH of the concrete pore solution and the ‘P’ content in the coating. Corrosion potential and the corrosion rate of the coating increased with increase in ‘P’ content in the coating and pH of the pore solution, whereas the resistance against chloride attack of the coating increased with increase in ‘P’ content. The marginal drop in the bond strength of the coated rebar with the concrete structure may be due to the higher ‘P’ content which is expected to provide improved surface smoothness.

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1. Introduction

Thermo-mechanically treated (TMT) reinforcing bars are widely used in concrete structures such as bridges, dams, flyovers, parking garages, building structures and for general-purpose reinforcement concrete. The corrosion of Reinforcing Concrete (RC) structures demonstrates a very complicated form of deterioration [1–7] depends on many factors like (i) exposure time [1], (ii) critical chloride concentration for pitting [2], (iii) acidity [3], (iv) temperature [4], (v) concrete resistivity [5], (vi) chloride de-passivity [6] and (vii) Florida [7]. In concrete, the alkaline pore solution passivates the metal surface so that it does not rust/corrode [8]. Due to the carbonation reaction, the pH of the concrete environment decreases [9] and the steel comes from the passive to the active state. However, the widespread deterioration of concrete structures, most significantly among the coastline structures is encountered due to the corrosion of the embedded

steel, in spite of the alkalinity of the concrete. The influence of the Cl^- ions in depassivating the steel surface even at high pH levels can be seen as a function of the net balance between two competing processes: stabilization (and repair) of the film by OH^- ions and disruption of the film by Cl^- ions [8].

For this reason, many studies have been performed to find out the best method of preventing corrosion in reinforcing bars [10–14].

Ni has a good corrosion resistance against chloride and will be the good choice for coating on rebar surface. Although, nickel is expensive, the cost of the coating on rebar surface will be cost competitive since it needs only a very thin coating (10–15 μm). Ni coating on rebars surface by electro deposition technique is unsuitable due to the presence of ribs at regular interval. Nickel coating by electroless process on uneven surface like rebars will be worthy. Electroless nickel (EN) coatings are finding increased use in a variety of applications including the chemical, food, and automotive industries [15]. This technique gives uniform coating with excellent chemical and mechanical properties [16]. The coating obtain by electroless process has good corrosion and wear

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Table 1
The basic composition of TMT material

C	Si	Mn	P	Fe
0.12	0.35	0.64	0.03	98.86

resistance properties [17,18]. The coating using this technique can be applied on different substrates (conductive and non-conductive) and is distributed homogeneously regardless of the substrate geometry [19]. Electroless nickel (EN) is produced by the reduction of nickel ions in the presence of sodium hypophosphite (NaH_2PO_2), producing an alloy of nickel and phosphorus [20]. The Ni and P contents in the alloy coating are governed by the composition, temperature and the pH of the plating bath used [21]. Flis and Duquette [22] evaluated Ni–P alloys in near neutral and alkaline solutions and found both beneficial and detrimental effects depending upon the amount of ‘P’ content in the coating. It is generally accepted that a microcrystalline and amorphous or a co-existence of these two phases can be obtained depending on the phosphorus content [20,23–26]. Amorphous films have better corrosion resistance than their crystalline counterparts [27]. The Ni–P coating lacks in its ability to passivate in highly alkaline environment regardless of the structure [28]. The objective of the present work is to establish the effect of treatment time for electroless Ni alloy coating on rebar surfaces from citrate bath and its applicability in concrete structure.

2. Experimental procedure

The TMT rebars used for the experimental study were 10 mm in diameter. The basic composition of TMT material in weight percent is shown in Table 1.

The steel substrate in the form of plates was prepared from rebar for electrochemical study. The metal specimen was first subjected to acid pickling to remove all surface oxides. The cleaned specimens were then treated in EN bath for different times. The starting chemical composition (before rebar dip in the solution) of the EN bath is shown in Table 2. The Fe will first be dissolved from the rebar surface and subsequently introduced in the bath as Fe^{2+} . The microstructure of the EN coated layer was examined by scanning electron microscopy (SEM, JEOL JXA 6400). An Energy Dispersive Spectroscopy (KEVEX Super dry detector) was used to determine the elemental distribution through the depth of the coated layer. The structure of the coated layer was also determined using X-ray diffraction (XRD, Philips Analytical X-ray B.V. Machine). The electrochemical behavior of the coatings in simulated concrete pore solution with different pH was carried out for bare and coated rebars using the Gamry DC105 system. The surface area considered for electrochemical test was 100 mm². The com-

Table 2
The process conditions

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ g/L	NaH_2PO_2 /L	Glycine g/L	Sodium citrate g/L	pH	Temperature °C	Treatment time(min)
30	25	20	20	4.55	90	30–90

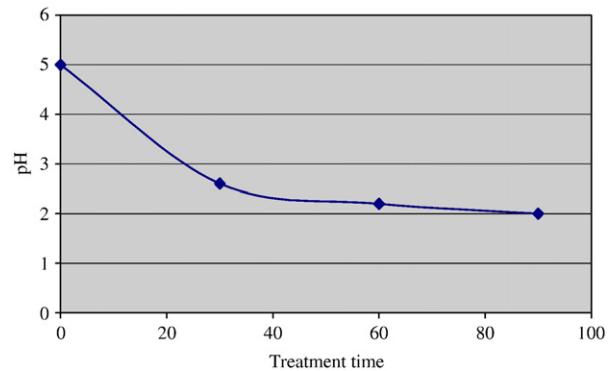


Fig. 1. Effect of treatment time on bath pH.

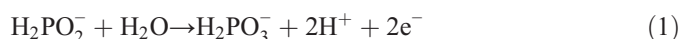
position of the concrete pore solution was formulated according to the composition described by Christensen et al. [29] consisted of 0.32 mol/L KOH, 0.17 mol/L NaOH and 0.07 $\text{Ca}(\text{OH})_2$ in distilled water. The scan rate and immersion time for these tests were 2 mV/S and 300 s respectively. To evaluate the resistance against chloride attack of the coatings, accelerated corrosion test was conducted in aggressive salty environment in accordance with ASTM B117 [29]. The coated as well as bare samples were exposed in a close chamber containing concentrated fumes of 5% chloride solution. The surface roughness of the bare and EN coated steel surfaces were measured using hand-held roughness tested TR200. The bond strength of the rebar surface with concrete structure was evaluated as per IS: 1786 (1985) [30]. Both the coated and fresh rebars were cast in a square concrete block. Quick setting cement (Convextra GP2) was used for casting and the curing time was varied from 48 to 60 h to achieve a crushing strength of 200–300 k/cm² of concrete structure according to the IS specification. After curing of the block, load versus slip were monitored with the help of a tensile testing machine (100 KN FUT make tensile testing machine) fitted with an appropriate precision slip measuring device as per IS: 1786 (1985).

3. Results and discussion

3.1. Kinetics of electroless nickel coating process

The Fe will first be dissolved from the rebar surface and subsequently introduced in the bath as Fe^{2+} . This in turn would activate the surface and Ni, P and Fe are deposited on the activated rebar surface. This first deposition acts as a catalyst for the subsequent depositions. The EN process proceeds by a single anodic and four simultaneous cathodic reactions [31].

Anodic reaction:



Cathodic reactions:



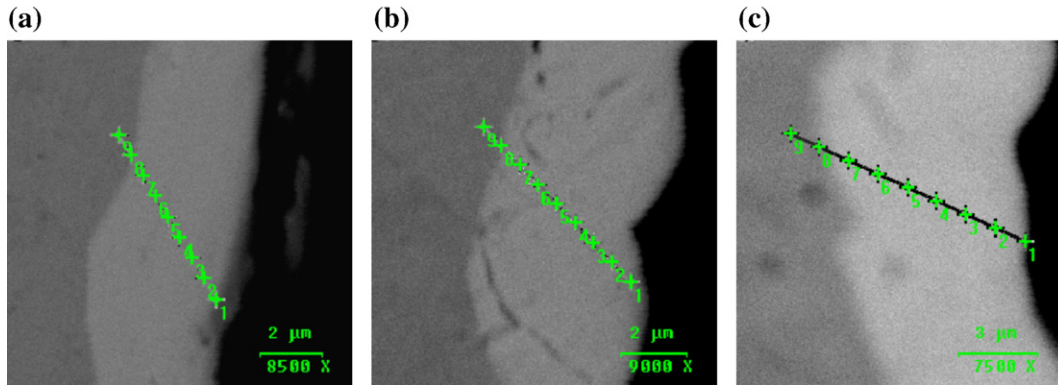


Fig. 2. SEM micrograph of electroless nickel coated layer after treatment times of (a) 30 min, (b) 60 min and (c) 90 min.

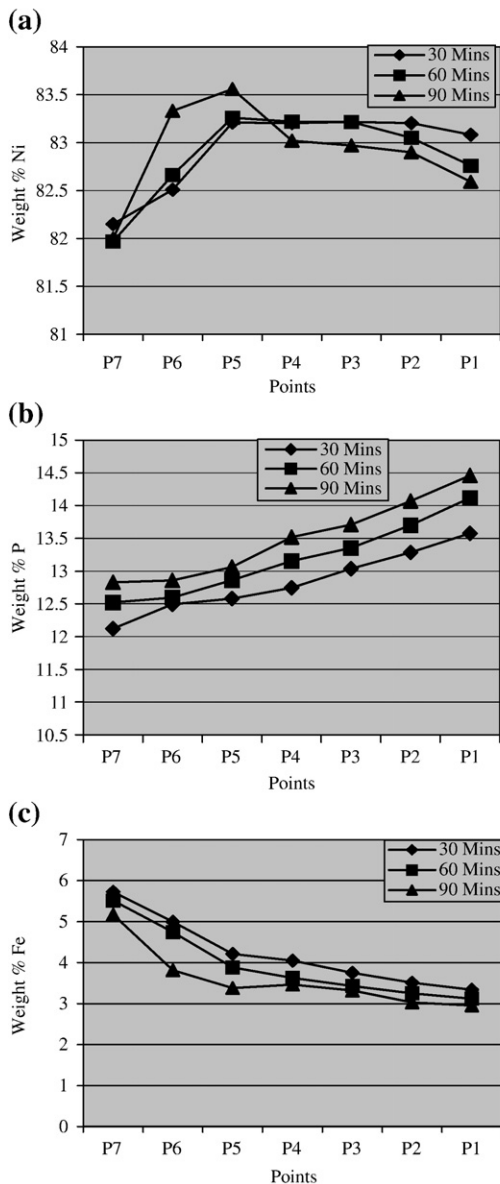


Fig. 3. Elemental depth profile of coated layer using EDS technique for (a) Ni, (b) P and (c) Fe.

The hydrogen ions are being generated and consumed by one anodic and two cathodic reactions respectively. Elemental nickel, phosphorous and iron deposited on the rebar surfaces by cathodic reactions as mentioned in Eqs. (2), (3) and (4). The predominant cathodic reactions are nickel reduction and hydrogen evolution. Nickel reduced due to higher amount of nickel ions concentration in the solution, where as hydrogen evolved due to its thermodynamic property. It is evident from all anodic and cathodic reactions that electroless metal deposition process advances by net hydrogen ions generation resulting in drop in bath pH as shown in Fig. 1. The EN reaction kinetics was controlled by the bath hydrogen ions concentration. The anodic reaction rate decreased with treatment time due to increase of hydrogen ions concentration according to La Satellier principle. As a result, the over all cathodic reactions rate also decreased. The hydrogen evolution rate increased due to the increase in hydrogen ion concentration, as a consequent elemental deposition rate expected to decrease drastically with treatment time.

3.2. Characterization of EN coated layer

Figs. 2 and 3 showed the cross sectional SEM micrograph and EDS elemental distribution for different treatment times of

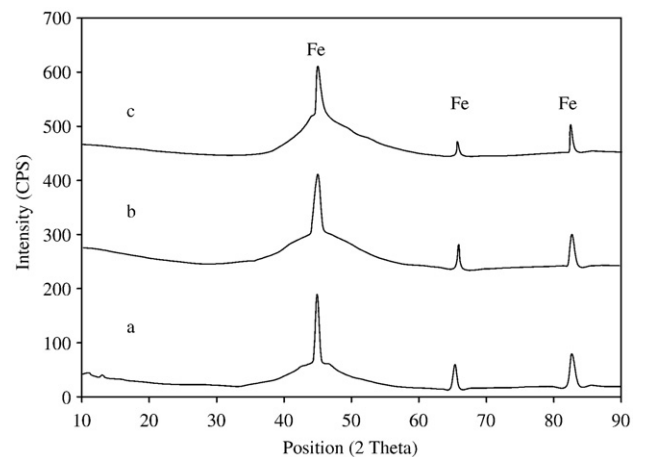


Fig. 4. XRD peaks of the electroless nickel coated surface for treatment times of (a) 30 min, (b) 60 min and (c) 90 min.

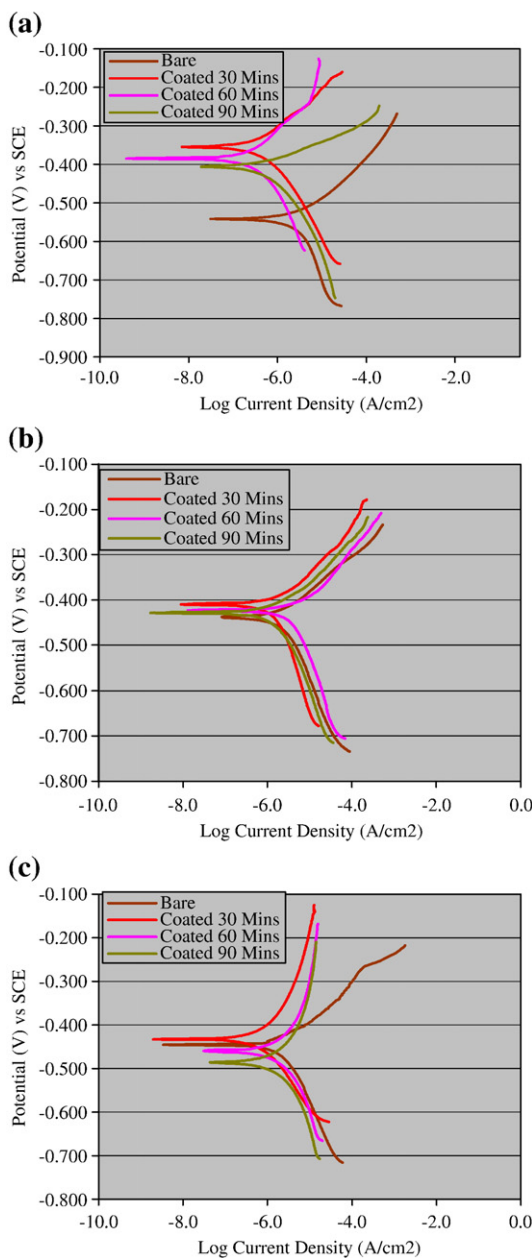
30, 60 and 90 min respectively. Increase in coating thickness was marginal with increase in treatment time as evident from SEM micrographs as shown in Fig. 2.

The quantitative depth profile by EDS has indicated that Ni, P and Fe changed through the coating thickness as shown in Fig. 3. The phosphorous percentage increased from substrate–coating interface to the outer coating layer where as iron percentage decreased from substrate–coating interface to the outer coating layer. On the other hand, the nickel content increased up to certain coating thickness after which it reduced to the outer coating layer. From EDS depth profile it is also evident that the ‘P’ content at the outer surface of the coating

Table 3

E_{corr} and corrosion rate of bare and electroless nickel coated rebar

Material history	Environment	E_{corr} (V)	Corrosion rate (mpy)																															
Bare	3.5% Cl and pH=7	-0.542	1.399																															
Coated 30 min	–	-0.3548	0.253																															
Coated 60 min	–	-0.3843	0.101																															
Coated 90 min	–	-0.4054	Bare	3.5% Cl and pH=11	0.4382	0.271	Coated 30 min	–	-0.4103	0.146	Coated 60 min	–	-0.4236	0.112	Coated 90 min	–	-0.429	0.063	Bare	3.5% Cl and pH=13.6	-0.4057	0.018	Coated 30 min	–	-0.4381	0.331	Coated 60 min	–	-0.4557	0.446	Coated 90 min	–	-0.4863	0.750
Bare	3.5% Cl and pH=11	0.4382	0.271																															
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Coated 60 min	–	-0.4236	0.112																															
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was found to increase with increase in plating time where as Ni and Fe content at the outer surface of the coating was found to decrease with increase in plating time. The pH of the solution drops down with increase in plating time resulted favourable for ‘P’ deposition according to La Satellier principle as mentioned in Eq. (3). The XRD results confirmed that structure of the coating was amorphous in nature irrespective of treatment times or content of ‘P’ in the coatings as shown in Fig. 4.

3.3. Electrochemical behavior of the coatings in simulated concrete pore solution

The electrochemical behaviors of the bare and coated steel substrate in simulated concrete pore solution with different pH are shown in Fig. 5. The free corrosion potential of three coatings and bare steel depends on the alkalinity of the pore solution. The free corrosion potential of all three coatings were more (nobler to steel) than the base steel in neutral (pH=7) or mildly (pH=11) alkaline pore solutions containing 3.5% chloride, where as the free corrosion potential of the coatings formed for treatment time 60 and 90 min were less (active to steel) than base steel in highly (pH=13.6) alkaline pore solution containing 3.5% chloride. It is evident that the free corrosion

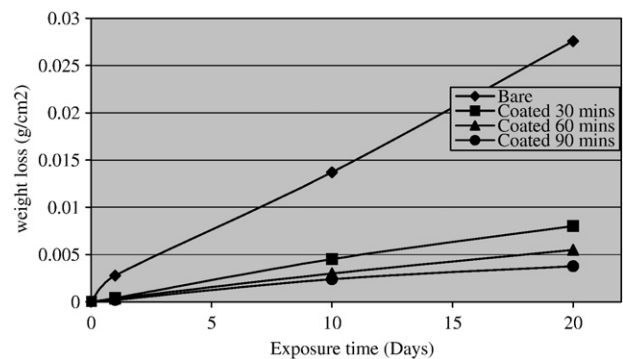


Fig. 5. Tafel test result of bare and electroless nickel coated rebars in simulated pore solution with (a) pH=7, (b) pH=11 and (c) pH=13.6.

Fig. 6. Weight loss of bare and electroless nickel coated rebar in aggressive chloride environments.

potential moved in active direction with increase in phosphorous content in the coatings, irrespective of the pore solution pH. The corrosion rate or more specifically the dissolution of the coatings or base steel depended on pH of the pore solution and the 'P' content in the coatings. The dissolution rate of the coatings was slower than base steel in neutral or mildly alkaline pore solutions and the coating obtained under longer treatment time dissolved in slowest rate. On the other hand, the coating obtained for longer plating time dissolved in faster out of three coatings in highly alkaline pore solution. The dissolution rate of the coating obtained for 90 min plating time was even faster than base steel in highly alkaline pore solution. The free corrosion potential and the corrosion rate of three coating and bare steel in simulated concrete pore solution with different pH is shown in Table 3.

3.4. Accelerated corrosion test in aggressive chloride environment

Fig. 6 showed the dissolution rate of the bare and three coated (under different treatment time) rebars in aggressive chloride environment. It is evident that the coatings have much more resistance power against chloride attack than bare rebar. It is also evident that the coating obtained under longer plating time showed maximum resistance against chloride attack.

3.5. Pull-out test results

The comparative bond strength of three coated as well as bare rebar surface with concrete is shown in Fig. 7. It is evident from this figure that the EN coated rebars showed marginal drop in the bond strength with the concrete structure. The drop in bond strength was maximum (around 15%) for the coating obtained under longer time. However, it was much above the necessary according to IS specification. The drop in bond strength can be attributed by the high 'P' content in the coated surface for longer treatment time, which was expected to give maximum smoothness as shown in Table 4. The degree of surface smoothness of electroless nickel coated surface depends on particle size and coating thickness [32]. Also, high 'P' containing coating was found to dissolve in faster rate in highly

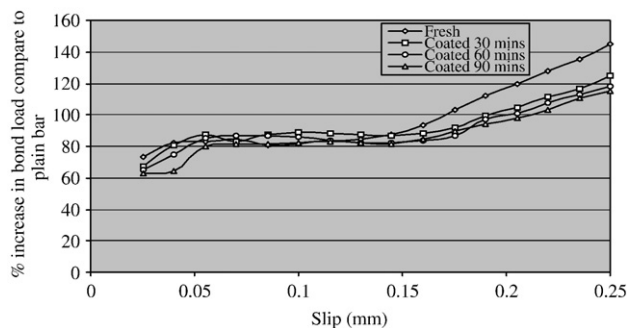


Fig. 7. Comparative bond strength of bare and electroless nickel coated bars with concrete structure.

Table 4
Roughness of the bare and different EN coated rebar surfaces

Surface condition	Bare	30 min EN coated	60 min EN coated	90 min EN coated
Roughness (μm)	1.95	1.015	0.684	0.498

alkaline environment, leading to hydrogen gas evolution which creates a gap in between rebar surface and concrete.

4. Conclusions

1. The bath pH was found to play a strong role in the kinetics and composition of the ternary Ni–P–Fe coatings but not on the coating structure.
2. The pH of the concrete pore solution and 'P' content in the coating were found to influence the electrochemical behavior of the coated rebars. The corrosion potential as well as corrosion rate of the coating increased with increase in pH of the pore solution and 'P' content in the coating.
3. The resistance to chloride attack of the coating was found to increase with increases in 'P' content in the coating as observed this in salt spray test.
4. There was a marginal drop in bond strength which may be due to higher phosphorous content in the coating. This in turn, reduced the surface roughness of the coated rebar. However, this bond strength was found to satisfy IS specification.
5. The electroless nickel coated rebar can be produce through batch process utilizing a coating bath installed next to the production line.

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