Electroless Nickel Coating Kinetics on TMT Rebar Surface and Coating Characterisation

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The corrosion resistance Ni–P–Fe alloy coating was obtained on rebar surface by an electroless process using glycolic acid as a complexing agent. During dipping of the iron scale free rebar in electroless solution, Fe first dissolves and the surface is activated. Subsequently, Ni, P and Fe are co-deposited by an autocatalytic process. The coating was characterised using SEM, EDS and XRD techniques. The weight percentage of Ni, P and Fe in the coating showed a relationship with the coating time. The Tafel and salt spray tests were conducted to find out corrosion resistance performance of coated samples. Electrochemical behavior of the coated rebar in simulated concrete environment is influenced by the pH of the concrete pore solution and the P content in the coating. Corrosion potential and the corrosion rate of the coatings increased with the increase in P content in the coating and pH of the pore solution whereas the resistance against chloride attack increased with increase in P content in the coating. Coated rebars showed reduction in bond strength in the range of 8 to 14 % compared to the bare rebars. The maximum (~14 %) drop in bond strength was observed for longer coating time. This can be attributed to the smoother coating surface. The coating obtained under longer coating time showed higher amount of P which contributed to maximum surface smoothness. However, this bond strength was much above the necessary strength requirement according to Indian standard specification.

KEY WORDS: steel reinforced concrete; alkaline corrosion.

1. Introduction

Reinforcing bars are widely used in concrete structures such as bridges, dams, flyovers, parking garages, building structures and for general-purpose reinforced concrete. The corrosion of Reinforced Concrete (RC) structures demonstrates very complicated forms of deterioration^{1–8)} but the main reason for the decrease in the durability of RC structures is due to the corrosion of the reinforcing bar. 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 with time⁹⁾ and the steel converts from the passive to the active state. Coastline structures are deteriorated drastically due to the corrosion of the embedded steel, in spite of the alkaline nature of the concrete environment. The influence of the chloride 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 hydroxyl ions and disruption of the film by chloride ions.⁸⁾ For this reason, many studies have been carried out to find out the best method of preventing the corrosion in reinforcing bar.^{10–22)}

Ni has an excellent corrosion resistance property against chloride and hence, is one of the ideal metals for coating on rebar surface. Ni coating on rebar surface by electro-deposition technique is unsuitable due to non-uniform surface

geometry. On the rebar surface ribs are exist at regular interval. Hence, Ni coating by electroless process will be one of the viable processes. Electroless nickel (EN) coating has been found to be suitable for variety of applications including the chemical, food, and automotive industries.²³⁾ This process gives uniform coating with excellent chemical, mechanical and wears resistance properties.^{24–27)} EN coating can be applied on different substrates (conductive and non-conductive) and is deposited homogeneously regardless of the substrate geometry.²⁸⁾ Once the first layer of nickel is deposited, it acts as a catalytic agent for the plating process. As a result, a linear relationship between the coating and deposition time has been observed.²⁹⁾ EN coating is produced by the autocatalytic reduction of nickel in the presence of sodium hypophosphite (NaH_2PO_2), producing an alloy of nickel and phosphorus.³⁰⁾ The Ni and P contents in the alloy coating are governed by the composition, temperature and the pH of the plating solution.³¹⁾ Flis and Duquette³²⁾ evaluated Ni–P alloys in near neutral and alkaline solutions and found both beneficial and detrimental effects depending upon the amount of P 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 P content.^{30,33–36)} Also it has been claimed that the coating is totally amorphous in nature.^{25,37)} Amorphous film has greater corrosion resistance than crystalline film.³⁸⁾ Limited research work has been done to find out the feasi-

bility of EN coating on rebar surface for application in concrete structure.^{39,40)} Main drawback associated with this process is that coating kinetics is very slow and hence, longer coating time is needed to achieve the desired coating thickness.³⁹⁾

The objective of the present work is to achieve the desired coating using a glycolic acid bath under shorter than earlier coating time.³⁹⁾ Also, coating characterisation for application in concrete structure.

2. Experimental Procedure

The TMT (thermo mechanical treatment) rebar used for the experimental study was 10 mm in diameter. The basic composition of TMT material in weight percent is given in **Table 1**.

The composition of the steel was analysed using optical emission spectrometer according to ASTM E 415-99a standard.⁴¹⁾ The rebar was first subjected to acid pickling to remove iron scale. The scale free rebar was then coated in EN coating solution for different time. The process condition for EN coating is given in **Table 2**.

The microstructure of the EN coated layer was characterised 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 coating was determined using X-ray diffraction (XRD, Philips Analytical X-ray B. V. Machine). Tafel test was conducted for coated and un-coated rebars in simulated concrete pore solutions contaminated with 3.5% chloride under various pH (7, 11 and 13.6) conditions to find out corrosion rate and E_{corr} using the Gamry DC105 system. The composition of the concrete pore solution was formulated according to the composition described by Christensen *et al.*⁴²⁾ consisted of 0.32 mol/L KOH, 0.17 mol/L NaOH and 0.07 mol/L $\text{Ca}(\text{OH})_2$ in distilled water and initial pH was 13.6. The pH of simulated concrete pore solution dropped

Table 1. Basic composition of TMT material in wt%.

C	Si	Mn	P	Cu	Al	Fe
0.12	0.35	0.64	0.03	0.035	0.042	~98.79

Table 2. Process conditions for electroless nickel coating.

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ g/L	NaH_2PO_2 g/L	Glycolic acid ml/L	pH	Temperature °C	Treatment time (minutes)
50	25	30	6.85	85-90	10-30

(a)

(b)

Fig. 1. Effect of plating time on (a) bath pH and (b) metal deposition rate.

down with time due to carbonation reaction. The scan rate and immersion time for Tafel test were 1 mV/s and 600 s respectively. To evaluate the resistance of the coatings against chloride attack, salt spray test was conducted in accordance with ASTM B117 standard.⁴³⁾ The bond strength of the rebar surface with concrete structure was evaluated as per Indian standards (IS) 1786 (1985).⁴⁴⁾ All the coated and un-coated rebars were cast in square concrete blocks. Quick setting cement (Convextra GP2) was used for casting and the curing time was varied from 48 to 60 h to achieve crushing strength in the range of 200–300 kg/cm² of the concrete structure according to the IS. After curing of all blocks, relationship between load *versus* slip was measured using 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

During dipping of the scale free rebar in EN solution, Fe first dissolves and the surface is activated. Subsequently, Ni, P and Fe are co-deposited on the activated rebar surface. This first deposit acts as a catalytic agent for subsequent deposition of metal and non-metal. The EN process proceeds by a single anodic and four cathodic reactions.³⁸⁾

Anodic reaction:

Cathodic reactions:

The H^+ ions are being generated and consumed by an anodic and two possible cathodic reactions (ii and iv) respectively. Elemental Ni, P and Fe are deposited on the rebar surfaces by cathodic reactions i, ii and iii. The predominant cathodic reactions are Ni^{2+} and H^+ ions reduction. It is evident from all anodic and cathodic reactions that electroless deposition process is advanced by a cumulative generation of H^+ ions, resulting in drop of pH in the coating solution as shown in **Fig. 1(a)**.

The EN deposition kinetics is controlled by the concentration of hydrogen ions in the coating solution. The anodic reaction rate is decreased with coating time. As a result, the cathodic reaction rate is also decreased. However, the hydrogen evolution rate is still in the higher range due to

higher concentration of H^+ ions, as a consequent deposition rate of metal and non-metal is decreased drastically with elapse of coating time as shown in Fig. 1(b).

3.2. Characterisation of EN Coated Layer

Figures 2 and 3 show the cross sectional SEM micrographs of the coated layer and elemental depth profiles of Ni, P and Fe of these coated layers for different coating time of 10, 20 and 30 min respectively. Increased in coating thickness is found to be marginal with increase in plating time as evident from SEM micrograph in Fig. 2. Approximate coating thickness after different treatment time is given in Table 3. The point P8 in Fig. 2 indicates the steel substrate.

The quantitative elemental depth profile by EDS indicates Ni, P and Fe content is changed through the coating thickness as shown in Fig. 3. The points P1 and P7, shown in Fig. 3 represent the outer coating layer and substrate-coating interface respectively of all the coatings.

The P percentage increased from substrate-coating interface to the outer coating layer, whereas Fe percentage decreased from substrate-coating interface to the outer coating layer. On the other hand, Ni content increased from outer surface to a certain depth in the coating and further decreased towards substrate coating interface. The comparative concentration of Ni^{2+} , Fe^{2+} and H^+ ions with coating time in the solution plays an important role (on coating composition and kinetics) for such elemental depth profile of all the coatings. It is also evident from elemental depth profile that the P content at the outer layer of the coating increased with coating time whereas Fe and Ni content at the outer layer decreased with coating time. The P deposition rate increased with drop of pH in the solution. The X-ray diffraction (XRD) result confirms that the structure of the coating is amorphous (as shown in Fig. 4) in nature irrespective of coating time or P content in the coating.

Fig. 2. SEM micrograph of coated layer for different coating time of (a) 10, (b) 20 and (c) 30 min.

Fig. 3. Elemental depth profile by EDS of (a) Ni, (b) P and (c) Fe of different coated layers.

3.3. Electrochemical Behaviour of the Coating in Simulated Concrete Pore Solution

The electrochemical behaviour of all the coated and uncoated rebars in simulated concrete pore solution under various pH conditions is shown in Fig. 5.

The free corrosion potentials of all three coated and uncoated rebars depend on the pH of the pore solution. The free corrosion potential of all three coated rebars is more noble to that of the uncoated rebar in neutral (pH=7) or mildly (pH=11) alkaline pore solution containing 3.5% chloride whereas the free corrosion potential of the coated rebar for the coating obtained under coating time of 20 and 30 min are less active to that of uncoated rebar in highly alkaline (pH=13.6) pore solution containing 3.5% chloride. It is evident that the free corrosion potential of the coating shifted towards more active direction with increase in P content in the coating, irrespective of pH in the pore solution. The corrosion rate or more precisely the dissolution rate of all the coated rebars depends strongly on pH of the pore solution and the P content. The dissolution rate of all three coated rebars is slower than the uncoated rebar in neutral (pH=7) or mildly alkaline (pH=11) pore solution. The coating which was obtained under longer coating time shows slowest dissolution rate. On the other hand, the coating obtained under longer coating time dissolves faster in highly alkaline (pH=13.6) pore solution. The dissolution

Table 3. Approximate coating thickness after different treatment time.

Treatment time (minutes)	Thickness of the coating (μm)
10	3
20	4.5
30	5.5

Fig. 4. X-ray diffraction peaks of coated rebar surfaces for different plating times of (a) 10, (b) 20 and (c) 30 min.

Fig. 5. Polarization curves of un-coated and different coated rebars in simulated pore solution contaminated with 3.5% chloride with pH (a) 7, (b) 11 and (c) 13.6.

Table 4. E_{corr} and corrosion rate of un-coated and different coated rebars (coating time: 10, 20 and 30 min) in concrete pore solution contaminated with 3.5% chloride under varying pH conditions.

Material history	Environment	E_{corr} (V)	Corrosion rate (mm/y)
Coated 10 mins	3.5 % Cl and pH=7	-0.361	0.00538
Coated 20 mins	same	-0.388	0.00226
Coated 30 mins	same	-0.417	0.00109
Un-coated	same	-0.568	0.03439
Coated 10 mins	3.5 % Cl and pH=11	-0.415	0.00625
Coated 20 mins	same	-0.432	0.00284
Coated 30 mins	same	-0.441	0.00160
Un-coated	same	-0.468	0.00716
Coated 10 mins	3.5 % Cl and pH=13.6	-0.459	0.00874
Coated 20 mins	same	-0.486	0.01158
Coated 30 mins	same	-0.506	0.01935
Un-coated	same	-0.435	0.00208

Fig. 6. Weight loss of different coated and un-coated rebars in aggressive chloride environment.

rate of the coating obtained under 30 min of coating time is even faster than un-coated rebar in highly alkaline (pH=13.6) pore solution. The free corrosion potential and the corrosion rate of all three coated and un-coated rebars in simulated concrete pore solution under varied pH condition is shown in Table 4.

3.4. Accelerated Corrosion Test in Aggressive Chloride Environment

Figure 6 shows the dissolution rate of un-coated and three coated (coating time: 10, 20 and 30 min) rebars in aggressive chloride environment. It is evident that all the coatings have much more resistance (Ω) power against chloride attack than un-coated 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 all three coated as well

Fig. 7. Comparative bond strength of un-coated and different coated rebars with concrete structure.

Table 5. Roughness of the uncoated and different EN coated rebar surfaces.

Surface Condition	Uncoated	10 minutes EN coated	20 minutes EN coated	30 minutes EN coated
Roughness (μm)	1.95	1.214	0.873	0.578

as un-coated rebars surface with concrete structure is shown in Fig. 7.

The vertical label in Fig. 3 shows the percentile increment in bond strength with ribbed bar in concrete structure compared to the bar without any rib of same diameter in same structure.

All the coated rebars showed drop in bond strength in the range of 8 to 14%. The maximum ($\sim 14\%$) drop in bond strength was observed for longer coating time. This can be attributed to the smoother coating surface. The coating obtained under longer coating time showed higher amount of P which contributed to maximum surface smoothness (see Table 5). The EN coating with higher amount of P is expected to be providing better amorphous structure compared to the coating with lower amount of P.

However, this bond strength was much above the necessary strength requirement as per Indian standard specification.

4. Conclusions

(1) The corrosion resistant of Ni-P-Fe amorphous alloy coating was obtained on rebar surface using glycolic acid as a complexing agent. The solution pH was found to play a strong role on process kinetics and composition but not on the coating structure. Desired coating under shorter

coating time is possible under pH ~ 7 of the plating solution.

(2) The electrochemical behaviour of all the coated rebars in simulated concrete environment was found to dependent on pH of the concrete pore solution and the P content in all the coatings. The corrosion potential as well as corrosion rate of the coated rebar increased with increase in P content in the coating and pH of the pore solution.

(3) The resistance to chloride attack of the coated rebar increased with increase in P content in the coating, as observed in salt spray tests.

(4) All the coated rebars showed reduction in bond strength in the range of 8 to 14% compared to the bare rebars. The maximum ($\sim 14\%$) drop in bond strength was observed for longer coating time. This can be attributed to the smoother coating surface. The coating obtained under longer coating time showed higher amount of P which contributed to maximum surface smoothness. The EN coating with higher amount of P is expected to be providing better amorphous structure compared to the coating with lower amount of P. However, this bond strength was much above the necessary strength requirement as per Indian standard specification.

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