A comparative study on the microstructure, hardness and corrosion resistance of epoxy coated and plain rebars

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Abstract

Corrosion of steel rebars and susceptibility of reinforcement steel to chloride ion attacks are the two major problems for the construction industries and thereby a huge amount of money is spent to repair it. Epoxy coating on the steel rebars can be one cost-effective solution to alleviate the detrimental effects of corrosion in concrete structures. In the present research, plain and epoxy coated rebar (ECR) samples were chosen to study the correlation between microstructure, hardness and corrosion performance. The microstructures of the investigated thermomechanically treated (TMT) rebars primarily reveal tempered martensitic rings at the outer surface followed by a narrow bainitic transition zone in between along with a ferrite-pearlite microstructure at the inner core. The corrosion resistance of plain and epoxy-coated rebars in naturally aerated 3.5% NaCl and 1% HCl solutions were studied using gravimetric test, open circuit potential (OCP) test, and linear polarization monitoring techniques. It has been witnessed that the corrosion current (i_corr) has been shifted towards lower values and polarization resistance (R_p) values are higher for ECR samples which is a clear indication of higher corrosion resistance of the ECRs than the plain rebars. Energy dispersive spectroscopy (EDS) analysis reveals the presence of iron hydroxides and iron oxides. However, x-Ray diffraction (XRD) analysis indicates the existence of various types of oxides, hydroxides, and oxy-hydroxides like iron chloride hydroxide [Fe_2(OH)_3Cl], goethite (α-FeO(OH)), lepidocrocite (γ-FeO(OH)), magnetite (Fe_3O_4) and bernalite [Fe(OH)_3(H_2O)_0.23] in the epoxy coated rebar samples whereas, plain rebars indicate the presence of goethite (α-FeO(OH)), maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4), hydrogoethite (Fe_2O_3,H_2O), lepidocrocite (γ-FeO(OH)) and iron oxide (Fe_21.34O_32). All the experimental results confirm that ECR samples are more corrosion resistant under both acidic and saline environments.

1. Introduction

Thermomechanically treated (TMT) rebars are generally used as a reinforcement in concrete materials especially in the construction sectors because concrete has good compressive strengths but suffers from inferior tensile strengths [1–5]. TMT rebars primarily consist of tempered martensite at the outer periphery which acts as a load-bearing constituent and soft ferrite-pearlite microstructure at the inner core that causes ductility, cold formability, and bendability of the rebar. Hot rolling followed by water quenching results in the formation of martensite at the outer surface, bainite in between the transition zone, and austenite at the core. It is well established that the residual thermal gradient across the rebar section allows heat to flow towards the surface of the rebar from the hot austenitic core, which is associated with the formation of tempered martensite. During cooling, the hot austenite in the core of the rebar transforms into a ferrite-pearlite type of microstructure [2].

Reinforcing steel bars in the concrete are generally passivating in nature due to the presence of thermodynamically stable compounds of iron such as iron oxides and oxyhydroxides in the highly alkaline (pH between 13 and 13.8) environment. The incorporation of reinforcing steel into the alkaline concrete results
Several tests were performed to compare the plain and epoxy coated (each having 12 mm diameter) steel rebars based on microstructure, hardness, composition, and corrosion behaviour. Examination of epoxy-coated samples was aimed at finding the defects (holiday defects) in the epoxy coating. For microstructural characterization, surfaces (cross-section) of all the samples were prepared by using some standard metallographic sample preparation techniques such as grinding (belt and paper) followed by cloth polishing (coarse and fine) and etching with 2% nital solution. An inverted type optical microscope (Carl Zeiss Axiovert 40 Mat) was used to observe the microstructural constituents. For hardness evaluation, a Vickers Microhardness Tester (Leica- VMHT) was utilised under 300 gf load and 20 s dwelling time. The hardness value was measured as in the spontaneous formation of a thin oxide film (the passive film), which is protective [6–9]. However, chloride ion penetration through the concrete from external sources (for example seawater) can promote active corrosion which can further damage the structure severely at a later stage, thereby reducing safety. Rapid deterioration of reinforced concrete from chloride ions-induced corrosion is well known, especially in the case of those structures which are placed in aggressive marine and industrial environments [1, 2, 6–10]. Plenty of research has been carried out to date to develop a large number of corrosion reduction techniques to reduce this problem [6]. The accelerated corrosion of concrete reinforcements in chloride-laden environments has been well acknowledged over the past few decades and adequate research has been directed toward this area to abate the problem [1, 10].

Epoxy coating of the steels, which was first proposed in the 1970s, has been widely used as a method to improve corrosion resistance [9–12]. Although many researchers have confirmed superior corrosion resistance properties of the epoxy coating rebar, several studies have reported negligible or no improvement in corrosion properties [7, 8, 13–17]. Epoxy coating on metal surfaces is normally used to provide a physical and electrochemical barrier. The physical barrier offers protection against the water and chloride ions and also prevents the initiation of the corrosion process [17, 18]. It has been reported earlier that macrocell corrosion can be reduced by increasing the electrical resistance at the cathode through the electrochemical barrier because of the high coating resistance [9]. In the case of concrete, the contamination and penetration by chloride ions result in corrosion attack into the coating which further leads to widening of the affected areas followed by debonding of the coating from the rebar. It has been also reported that defects, that are present in the coating act as weak points where localized corrosion can occur at an accelerated rate, which in turn leads to the reduction in cross-sectional area. Some recent studies have shown that a small concentration of defects can be tolerated [4, 18]. Numerous literatures are available on the evaluation and quantification of the benefits of ECRs, but a wide area on reinforcement corrosion by chloride ions is yet to be understood properly [12, 15, 16, 19].

It is well established that the water-cement (w/c) ratio of mortar has a significant influence on the corrosion rates of steel rebars. It has been already reported that the corrosion rate of steel rebars increases with an increasing w/c ratio [20]. Nguyen et al has reported that nano Fe3O4 particles can effectively improve the corrosion resistance of the rebar when the concentration of chloride was 0.3 wt% in the cement mortar [21]. However, it cannot be overruled that the application of suitable coatings on rebars can significantly improve corrosion resistance. Tang et al has investigated the passive current density (EIS) for uncoated, pure, double, and mixed enamel-coated steel rebars in 3.5% NaCl solution [22–24]. They have opined that double enamel coatings exhibit the lowest passive current density and thereby achieving the highest corrosion resistance than the other three rebars [22–24]. A similar study by Yan et al has reported that the use of enamel coatings can also enhance the bond strength between the steel and the mortar [23–25]. Tang et al has also reported that epoxy coatings are more corrosion resistant than enamel coatings [26]. It has been reported earlier that Ni-P-W and Ni-P-Cu coated rebars can effectively prevent sulphate attacks [23, 24]. Recently Sharma et al has reported that modified ECRs with nano clay can effectively resist corrosion initiation by delaying the breakdown of the passive layer on the rebar [27]. They have also shown that modified ECRs when microcapsulated with tung oil, can act as a self-healing agent during coating cracking due to corrosion by forming an impenetrable passive layer on the rebar which agrees well with Chen et al [27, 28].

The main objective of the present research is to understand the corrosion behaviour of plain and epoxy coated TMT rebars under marine (3.5% NaCl) and acidic (1% HCl) environments [29–31]. This paper primarily discusses the corrosion rates and various characterisation techniques of the corrosion products in two different aqueous solutions with the required exploration of microstructural constituents and mechanical properties of two TMT rebars which are scanty in literatures. Finally, comparisons have been made for a clear understanding of the variation of performance of the plain and epoxy coated rebars in different corrosive environments. It is expected that the current research will provide greater detail regarding the effect of microstructure on the corrosion behaviour of the ECR and plain rebar samples.

2. Experimental procedure

Several tests were performed to compare the plain and epoxy coated (each having 12 mm diameter) steel rebars based on microstructure, hardness, composition, and corrosion behaviour. Examination of epoxy-coated samples was aimed at finding the defects (holiday defects) in the epoxy coating. For microstructural characterization, surfaces (cross-section) of all the samples were prepared by using some standard metallographic sample preparation techniques such as grinding (belt and paper) followed by cloth polishing (coarse and fine) and etching with 2% nital solution. An inverted type optical microscope (Carl Zeiss Axiovert 40 Mat) was used to observe the microstructural constituents. For hardness evaluation, a Vickers Microhardness Tester (Leica- VMHT) was utilised under 300 gf load and 20 s dwelling time. The hardness value was measured as
Table 1. Chemical composition (wt%) of the rebars used in the study:

| Types of rebar | C   | Mn   | Si   | Cr  | Al  | B   | S   | P   | N   |
|----------------|-----|------|------|-----|-----|-----|-----|-----|-----|
| Plain          | 0.30| 0.23 | 0.16 | —   | —   | 0.040 | 0.035 | —   | —   |
| Epoxy coated   | 0.22| 0.53 | 0.20 | 0.02| 0.0012 | 0.0003 | 0.045 | 0.019 | 0.0068 |

a function of the distance from the centre at an interval of 0.5 mm and the hardness profile was recorded instead of surface hardness because hardness tends to increase from the centre to the periphery in the case of rebar samples.

To study the corrosion-resistant behaviour of the two rebars, both the specimens were submerged in (a) 3.5% NaCl solution (marine) and (b) 1% HCl solution (acidic) for 15 days [29–31]. The solution was prepared from (a) 3.5:1 wt / wt a mixture of sodium chloride (NaCl) with distilled and deionized water and (b) 1:1 wt / wt a mixture of HCl with distilled and deionized water respectively. Before the immersion of steel samples, all solutions were kept in a closed container. Unagitated solutions were then exposed to the laboratory air at the ambient temperature. After removal from the solution, all the samples were then air-dried, inspected visually, and scrubbed lightly with a brush to collect the corrosion product for further investigation. Then the variation of weight has been recorded carefully and used for further calculation of the corrosion rate in mm/year at room temperature. Electrochemical measurements at open circuit potential (OCP) of all the specimens were carried out, using saturated calomel electrode (SCE) equipped with Origalys Potentiostat, combined with Origamaster 5 module apparatus. The counter electrode was placed to one side of the rebar specimen consisting of a graphite cylinder. For each sample, relative electrochemical stability was being ensured by the open circuit potential ($E_{oc}$) measurement via SCE using a high-input impedance DC voltmeter before the electrochemical tests. Linear polarization tests were performed at a scan rate of 1 mV s$^{-1}$ with a range of ±1500 mV. To evaluate the extent of degradation of the plain and coated rebar sample as well as to understand the corrosion product morphology, SEM (HITACHI, S-3400N) operated at 15 kV in secondary electron imaging mode was utilised. The respective chemical analysis was conducted using the Energy Dispersive Spectroscopy (EDS) and for that purpose, the surface was sputtered using a gold ion beam (HITACHI E-1010 ion sputter) to avoid the charging and to get high-quality images, which is similar to earlier observations [1, 2].

Corroded samples were further characterised by using a Bruker-advance D8’ XRD machine integrated with a copper target under an operating voltage of 40 kV and a current of 30 mA [2, 32]. Collection of XRD data was done over a range of 2$\theta$ values from 20–90$^\circ$ with a step of 0.01$^\circ$ s$^{-1}$. Different phases were identified after matching the experimental data with JCPDS files using Xpert High score Plus software and then these obtained values were being plotted using Origin lab software.

3. Results and discussion

3.1. Alloy design

The detailed chemical composition of both types of TMT rebar used in the present study has been listed in table 1. The present compositions contain lower amounts of carbon since increasing the carbon content leads to the formation of harmful carbides in the as-rolled steels [2]. Except for carbon, other major alloying elements present in the samples are manganese and silicon. It is well accepted that manganese improves the hardenability as well as the tensile strength of steel [2, 3]. Silicon, which acts as a deoxidiser, tends to improve the strength and other properties of the steel [2, 33]. It can be observed from table 1 that the ECR sample contains 3 ppm of boron which is mainly used to achieve improved hardenability [2, 34]. However, it cannot be overruled that nitrogen acts as a ‘poison’, in concerns of hardenability offered by the addition of boron [2, 35]. It is well established that boron steel has aluminium (Al), zirconium (Zr), or titanium (Ti) in sufficient amounts which gets combined with nitrogen and leaves behind the boron in free form, which has been reported to be very essential for increasing the hardenability [2, 36]. Since in the present research none of those alloying elements is present in adequate amounts, there is a possibility that all the boron can effectively combine with the nitrogen which further results in the formation of boron nitride (BN) and boron oxide (B$_2$O$_3$) due to its reactivity. Due to this behaviour, boron, although present in the epoxy coated TMT rebar still does not contribute to improving the hardenability.

The carbon equivalent value (CEV) has been calculated from equation (1) as proposed by the International Institute of Welding (IIW). The measured values of the carbon equivalent are 0.338 for plain rebar and 0.328 for ECR samples. Obviously, a higher carbon equivalent value leads to higher corrosion of the samples [37–40].

$$\text{CEV} = C + \frac{\text{Mn}}{6} + \left(\frac{\text{Cr} + \text{Mo} + \text{V}}{5}\right) + \left(\frac{\text{Cu} + \text{Ni}}{15}\right)$$  \hspace{1cm} (1)

(Where, all the values are in wt%)
3.2. Evolution of microstructure

Figure 1(a) reveals the top view of the cross-section of the TMT rebar sample where three distinguishable zones, the outer rim (A), intermediate (B), and the core (C) region have been shown. In figure 1, tempered martensite was observed over the dark peripheral ring (edge), followed by a narrow bainitic transition zone in between along with a ferrite-pearlite microstructure present at the inner core with a greyish appearance [2, 3, 41, 42]. Figures 1(b) and (c) represent the top view of the plain rebar and epoxy coated rebar samples, respectively.

The optical microstructures of the core, intermediate, and outer rim regions of plain rebars are shown in figures 2(a)–(c) respectively. It can be seen from figure 2(a) that the core primarily consists of polygonal and non-polygonal shape ferrites, which appear white in contrast as indicated by arrows, and lower amounts of pearlite which is concentrated at the triple points and appears comparatively dark in contrast. This is in agreement with the equilibrium microstructure that is expected for low carbon steel at a very slow cooling rate [2, 3]. Figure 2(b) reveals the microstructure of the narrow transition zone which primarily consists of bainite formed via intermediate cooling. It is well known that water quenching of hot-rolled bars allows the diffusionless transformation of martensite due to higher cooling rates. It is necessary to mention here that the rim observed in the plain rebar samples is thinner in the order of ≈1 mm. Residual heat flow across the rebar section during cooling causes tempering of the initially formed rim of martensite leading to the formation of tempered martensite as shown in figure 2(c) [3–5, 43, 44].

Figures 3(a)–(c) reveal the optical microstructures of the core, intermediate and outer rim regions respectively, of the ECR samples. It can be observed from figure 3(a) that the ECR samples core primarily consists of acicular ferrite as the main constituent along with a very little amount of pearlite. Acicular Ferrite (AF) is formed when the equilibrium cooling rates are not achieved, and it shows a dislocation density higher than that of the polygonal ferrite in the case of the plain rebar (figure 2(a) vis-à-vis figure 3(a)) owing to its needle-shaped constituents as denoted by arrows [2]. It cannot be overruled that the presence of boron and low carbon leads to the formation of acicular ferrite [45–47]. Figure 3(b) shows the microstructure of the narrow transition zone which is bainite similar to the plain rebar samples. In figure 3(c), the rim with 1.4 mm thickness
primarily reveals the existence of tempered martensite in the case of ECR samples. In figure 3(c), the microstructure is composed of very fine grains and the micrograph has lower contrast than the core of the intermediate regions (figures 3(a) and (b)), indicating the existence of higher strains. This implies that although the outer region underwent faster cooling, the lower hardenability of the alloy prevented the formation of martensite up to some extent. In this context, it needs to mention here that although the microstructural constituents of the intermediate region are almost similar (figure 2(b) vis-à-vis figure 3(b)) to the core region (figure 2(a) vis-à-vis figure 3(a)) for both the plain and ECR samples but, are finer in case of ECR samples due to the higher cooling rates. However, in the case of the intermediate region in figure 3(b) comparatively lower contrast has been noticed than the outer rim in figure 3(c). Perhaps this can be explained as during the coating of the rebar sample with epoxy resin, a temperature as high as ≈200 °C has been reached, which further causes tempering of the outer rim and therefore releases the internal strains present within the material in the form of dislocations and hence also lowers the etching contrast.

3.3. Hardness profile

Figure 4 represents the hardness profiles of the plain and ECR sample surfaces (along the cross-sectional diameter) from the centre to the outer surfaces at varying distances. It has been observed from figure 4 that the peripheral hardness is maximum due to the presence of tempered martensite which reduces gradually as the centre approaches, exhibiting the classical U-shaped profile for both the rebar samples which is similar to the earlier observations [2, 5, 48, 49]. The hardness of the outer rim is around 300 HV for ECR samples which indicates the presence of tempered martensite phase [2, 48]. Since the carbon concentration of the ECR sample is very low (≈0.22 wt%), therefore, in this case, the hardness is expected to be low because the hardness of martensite mainly depends on the carbon concentration [2, 50]. It is noticeable that the hardness value in the case of transition zones is ≈220 HV for both the samples due to the presence of lower bainite whereas, at the core or in the ferrite-pearlite region it is below 200 HV in the case of the plain sample and slightly higher for the ECR sample. This may be attributed to the fact that in the case of plain samples the formation of polygonal ferrite with
very low dislocation density at a relatively lower cooling rate tends to lower the hardness value whereas, for the ECR sample, the existence of acicular ferrite as the main microstructural constituent along with the very little amount of pearlite in the core region results in significant improvement in the hardness values [2, 47]. Epoxy coating significantly causes the microstructural changes that increase the hardness values for the ECR sample as evident in figure 4 and also in agreement with the earlier studies [51].

Figure 3. Optical micrographs of (a) core, (b) intermediate, and (c) outer region in epoxy coated rebar.

Figure 4. Hardness profile of plain and epoxy coated rebars.
3.4. Study on corrosion behaviour

3.4.1. Gravimetric test

Table 2 summarises the values of corrosion rates of the experimental rebars in 1% HCl and 3.5% NaCl solutions.

It can be noticed from Table 2 that in 3.5% NaCl solution, corrosion occurred for both plain (plain-NaCl) and ECR (epoxy-NaCl) were almost the same and very less. Therefore, it can be said that both the samples are corrosion resistant in 3.5% NaCl solution. However, among plain rebar and ECR, ECR shows a lower rate of corrosion compared to the plain rebar in 3.5% NaCl; thereby giving a higher corrosion resistance to the ECR samples. Furthermore, both plain (plain-HCl) and ECR (epoxy-HCl) show a higher corrosion rate in 1% HCl solution compared to 3.5% NaCl solution. This can be attributed to the fact that acid solution produces a more corrosive environment than NaCl solution (neutral nature) due to its acidic nature and pH lowering properties along with the presence of water and air \[39, 52\]. Besides, ECR (epoxy-HCl) sample shows a lower corrosion rate compared to the plain (plain-HCl) rebar sample in 1% HCl solution; thereby exhibiting a higher corrosion resistance of ECR samples compared to the plain rebar sample in 1% HCl solution.

3.4.2. Open circuit potential

Figure 5 represents the plots of potential variation with exposure time for both the experimental samples. It can be noticed from figure 5 that the open circuit potential (OCP) (denoted as E_{oc}) values for both specimens were in the range of −480 to −530 mV SCE in NaCl solution, while the values with saturated calomel electrode (SCE) ranged in between −570 to −590 mV SCE in case of HCl solution. It is imperative to mention that potential values experienced a rapid fluctuation for the first few seconds of the exposure for all samples and then it reaches a constant value. E_{oc} values in figure 5 indicate that the corrosion rates of both types of rebar are higher in HCl solution than in NaCl, which agrees with the results of the immersion test as shown in table 2. It can also be noted from figure 5 that in HCl solution, after reaching a constant value of potential, the ECR sample has less corrosion rate than the plain rebar sample which is mainly attributed to the presence of the epoxy coating. It has been reported earlier that the presence of a hydrophilic group in the epoxy coatings allows the absorption of moisture after a certain duration \[53\]. As a result of increased water absorption by the coating with time, corrosion resistance of the ECR in HCl solution decreases with time. The presence of the sharp hump for ECR in 1% HCl solution might be due to the generation of the defects which can be due to the presence of chloride ions at the surface before the application of coating. Chloride ions play a major role in deteriorating the stability of the
rebar. These can migrate through the defected areas of coating and thereby destabilizing the stable oxide phases of the metal and enhancing the corrosion rates. However, for the ECR sample in 3.5% NaCl solution no such behaviour is observed which might be due to less water absorption. It’s also true that the presence of water and moisture at the interface can help to start the corrosion. However, contaminations of the surface with salts of chlorides are also important for the progress of the corrosion which is evident for the ECR sample in 1% HCl solution due to the presence of the defects.

Table 3 represents the potential readings by following the ASTM C876 standard test method for half-cell potentials of plain reinforcing steel in concrete. It is well known that anodic and cathodic reactions on the metal surface produce mixed potentials which are generally denoted as $E_{oc}$ and this potential value has been used by the scientific community as a crude indicator of the corrosion probability of embedded rebars [1, 8]. According to ASTM C876–09 standards, if the open circuit potential (OCP) value of reinforcements exceeds more negative than $−270 \text{ mV SCE}$, then the probability of corrosion occurrence possibility will be greater than 90% [1, 54]. Thus, it can be assumed that a metal having lower values of OCP in a solution dissolve faster or corrodes faster than the one having comparatively higher values of OCP. As a consequence, corrosion rates of the rebars in 1% HCl solution exhibit a higher rate due to their higher negative OCP values lying in the range of ($−570 \text{ to } −590 \text{ mV}$) compared to that of rebars in 3.5% NaCl solution whose OCP values lying in the range of ($−480 \text{ to } −520 \text{ mV}$) SCE; thereby exhibiting a higher corrosion resistance.

Table 3. Corrosion interpretations (ASTM C876) [55].

| Half-cell potential reading (V) | Probability of corrosion |
|--------------------------------|--------------------------|
| CSE$^a$ | SCE$^b$ | |
| $>−0.200$ | $>−0.125$ | Greater than 90% probability of no corrosion |
| $−0.200 \text{ to } −0.350$ | $−0.125 \text{ to } −0.275$ | An increasing probability of corrosion |
| $<−0.350$ | $<−0.275$ | Greater than 90% probability of corrosion |

$^a$ Copper- copper sulphate electrode, $^b$ saturated calomel electrode.

Table 4. Corrosion parameters obtained from linear polarisation tests.

| Sample Identification | $E_{corr}$ (mV) | $R_p$ (ohm.cm$^2$) | $i_{corr}$ (μA cm$^{-2}$) | $\beta_a$ (mV/dec) | $\beta_c$ (mV/dec) | Corrosion rate (mm/y) |
|----------------------|-----------------|-------------------|--------------------------|----------------|----------------|---------------------|
| Plain-HCl            | $−682.8$        | $32.56$           | $484.9$                  | $133.6$        | $−79.5$       | $5.6194$            |
| Plain-NaCl           | $−964.1$        | $37.81$           | $578.6$                  | $165.2$        | $−115.5$      | $6.7053$            |
| Epoxy-HCl            | $−611.6$        | $2140$            | $18.0966$                | $204.6$        | $−491.2$      | $0.2097$            |
| Epoxy-NaCl           | $−534.7$        | $1300$            | $271.0814$               | $356.9$        | $−638.2$      | $3.1415$            |

Figure 6. Tafel plot for all samples.
3.4.3 Linear polarisation

Figure 6 shows the Tafel plot for both the experimental samples. It can be seen from figure 6 that the polarization curve for plain rebar in HCl solution shows a bulge at the start of the anodic domain due to the formation of corrosion products.

Table 5. Corrosion current density versus condition of the rebar [37].

| Corrosion current ($I_{corr}$) | Conditions of rebar       |
|-------------------------------|---------------------------|
| <0.1 $\mu$A cm$^{-2}$         | Passive condition         |
| 0.1-0.5 $\mu$A cm$^{-2}$      | Low-to-moderate corrosion |
| 0.5-1.0 $\mu$A cm$^{-2}$      | Moderate-to-high corrosion|
| >1.0 $\mu$A cm$^{-2}$         | High corrosion rate       |

3.4.3. Linear polarisation

Figure 6 shows the Tafel plot for both the experimental samples. It can be seen from figure 6 that the polarization curve for plain rebar in HCl solution shows a bulge at the start of the anodic domain due to the formation of corrosion products.
passive film on the surface, which is expected in the case of steel samples [39]. Although, it cannot be also dominated that the passive region is minute and the metal quickly undergoes trans passivation, no other rebar exhibits passivity. It has been observed from figure 6 that the polarization resistance of the ECR sample is higher than plain rebars in both solutions. Table 4 summarises the values of various corrosion parameters which were obtained from linear polarisation tests. It is noticeable from figure 6 and table 4 that the corrosion current (\( i_{\text{corr}} \)) has been shifted towards lower values in the case of the ECR sample, indicating a higher corrosion resistance. It has been reported earlier that the linear polarization technique quantifies the charge transfer resistance of a metal, which implies that the corrosion resistance will improve with increasing the polarization resistance (\( R_p \)) [56]. From table 4, it can be observed that the \( R_p \) values for ECR samples ranged from 1300 ohm.cm\(^2\) in NaCl solution whereas, it is more than 2000 ohm.cm\(^2\) in the case of HCl solution which depicts a higher corrosion resistance tendency of ECR samples. However, in the case of plain rebars, this value ranges between 30-40 ohm.cm\(^2\) in both the solutions, which is much lower than the ECR samples and thereby indicates low corrosion resistance as evident from table 4. It is also well established that for concrete materials which contain substantial moisture, an average sustained corrosion rate higher than \((0.1-0.2) \mu \text{A cm}^{-2}\) has been considered as the main criterion for active corrosion [19, 57].

Table 5 summarises the severity of corrosion of rebars with the corrosion current density. The measured values of the corrosion current from the polarisation resistance data were between 0.01 mA cm\(^{-2}\) to 0.6 mA cm\(^{-2}\) for the tested specimens, which depicts the corrosion current densities, as well as corrosion rates, are higher as evident from table 5. It is well-known that high corrosion potential and low corrosion current density determine better corrosion resistance [58]. It is evident from table 4 that the ECR samples show high corrosion potential values and low corrosion current values in both 1% HCl and 3.5% NaCl solution compared to that of plain rebars; thereby exhibiting a higher corrosion resistance of the ECR samples which is likely due to the presence of the epoxy coating on the surface that acts as a barrier to the entry of the corrosive ions into the sample surface. It is well evident in table 4 that the ECR samples have lower values of the corrosion rate compared to that of plain rebars; thereby resulting in higher corrosion resistance of the former.

Figure 8. SEM micrograph showing (a) corrosion products on the surface of S2, (b) EDS spectra of region 1, (c) EDS spectra of region 2, and (d) EDS spectra of region 3 for plain rebar in 3.5% NaCl solution.
3.4.4. Corrosion micrographs and EDS analysis of corrosion products

Figures 7–10 display the SEM micrographs and corresponding EDS spectra of the corroded sample surfaces. These micrographs mainly reveal a deterioration in the smoothness of the rebar sample surfaces, indicating the chloride ion penetration into the surface of the material and thereby leading to the formation of corrosion products. The EDS analysis at different regions reveals the chemical compositions of the corrosion products present in the samples. In this connection, it is imperative to mention that all these rebar samples were made of ferrous materials, and the corrosion products are expected to be in the form of rust i.e., oxides and hydroxides of iron \[Fe_{2}, 55\]. These rust corrosion products in the form of oxides appear as an adherent film which can be seen under suitable SEM magnification. It is well known that iron corrosion in the atmosphere proceeds by hydrated oxides formation \[40, 52, 59\]. The half-cell reactions can be expressed by the following Equations

\[
\begin{align*}
(1/2)O_2 + H_2O + 2e^- &= 2(OH)^- \quad \text{(Cathodic Reaction)} \\
Fe &= Fe^{2+} + 2e^- \quad \text{(Anodic Reaction)} \\
Fe^{2+} + 2(OH)^- &= Fe(OH)_2 \\
2Fe(OH)_2 + H_2O + (1/2)O_2 &= 2Fe(OH)_3
\end{align*}
\]

It has been reported earlier that a stable film on iron surface forms via \(2(OH)^-\) under an alkaline environment which tends to protect the surface of rebar \[2, 60–63\]. It is also known that oxygen availability and solution pH are the two main factors on which this film stability depends \[2, 64\]. Earlier studies have also suggested that the chloride solution leads to the destruction of the passive film and the localization of corrosion \[65\].

It can be seen from figure 7(a) that those three regions were chosen for the EDS analysis of S1. These EDS analyses confirm the presence of iron, oxygen, chlorine, and also the traces of other metals like Au, Mg, Si, and Ca as evident in figures 7(b)–(d). It is also evident from these EDS analyses that the segregated corrosion products of spectrum 1 and 3 (figures 7(b) and (d)) shows higher concentrations of oxygen than spectrum 2 (figure 7(c)) which is an indication of the existence of iron oxides. However, EDS analysis of the corrosion products of spectrum 2 (figure 7(c)) shows relatively higher iron concentrations. Thus, it is evident from

Figure 9. SEM micrograph showing (a) corrosion products on the surface of S3, (b) EDS spectra of region 1, (c) EDS spectra of region 2, and (d) EDS spectra of region 3 for ECR in 1% HCl solution.
figures 7(a)–(d) that among the three regions spectrum 1 and spectrum 3 regions have experienced higher corrosion due to the presence of higher oxygen-containing iron oxides. Whereas in the case of spectrum 2 (figure 7(c)), the lesser content of oxygen signifies inferior corrosion relative to the other two regions. It is also evident from figure 7(a) that for S1, a porous white layer of corrosion product has appeared on the sample surface in spectrums 1 and 3 but no such type of conclusive evidence has been found in spectrum 2. It is also factual that Au appears in the spectrum due to the coating provided before observation. In figure 7(f), the line scan analysis for sample S1 using a linear variation suggests the corrosion behaviour and elemental profile distribution from a higher corrosive area to a lesser corrosive area. The line scan reveals regions with higher corrosion behaviour and having corrosion products with higher peak values while the areas with lower corrosion have low peak values. Since the nature of variation was similar for the other three samples, a similar kind of information is not being mentioned in figure 8, the EDS analysis of S2 with the selected corroded regions of spectrums 2 & 3 (figure 8(c) and (d)) showing a slightly higher amount of oxygen and therefore the evidence of higher corrosion as compared to spectrum 1 (figure 8(b)) which undergoes comparatively less corrosion. Products of the corrosion in spectrum 2 as evident from (figure 8(a) vis-à-vis (c)) have the morphology of cracked layers of dark corrosion products while in spectrum 3 (figure 8(a) vis-à-vis (d)) corrosion products can be classified as white porous ridges or accumulated particles which is in agreement with earlier observations [2, 53].

In the case of the ECR sample, the coating was almost intact except for a few locations. The locations where corrosion cells emerged were defects or leaks in the coating. Figure 9 shows SEM micrographs and corresponding EDS analysis of S3 which reveal carbon and oxygen were most prominently present elements in all three cases (figures 9(b)–(d)). This is mainly attributed to the nature and composition of the coating. It cannot be overruled that negligible traces of chlorine accumulation were detected. Figure 10 shows SEM micrographs and corresponding EDS analysis of S4. Figures 10(a)–(d) mainly reveal two regions where corrosion products undergo segregation (figures 10(b) and (c)) and these two regions were analysed along with the one where the coating was undamaged (figure 10(d)). The corresponding EDS analysis of spectrum 1 (figure 10(b)) shows the maximum amount of oxygen percentage (40.4%) as it has the presence of segregated corrosion product followed by spectrum 2 (figure 10(c)) where, its value reaches 30.3% as it also displays the presence of comparatively less
intense, dispersed and accumulated corrosion product and finally in spectrum 3 (figure 10(d)), the least value of 28.82 indicates relatively lower corrosion compared to other two regions. It is also noticeable from figures 10(b)-(d) that the undamaged regions and less corroded regions have shown higher carbon percentages (figure 10(d)) due to anticipated less oxidation than the higher corroded regions or enriched oxygen zones. It is also true that the corroded regions contain smaller amounts of iron and other elements.

It has been informed earlier that keeping the Fe-O weight percentage lower than 90% may cause the formation of oxides in the form of wustite (FeO) predominantly, with some amount of magnetite (Fe₃O₄) or hematite (Fe₂O₃) [3, 66]. In this connection, Chitty et al reported that the end corrosion product may be iron oxy-hydroxides (Fe(OH)₃), akageneite (β-FeO(OH)), goethite (α-FeO(OH)), lepidocrocite (γ-FeO(OH)) which contain marbling of iron oxides such as maghemite (γ-Fe₂O₃) and/or magnetite (Fe₃O₄) [67]. Table 6 summarises the different ratios of Fe/O at which different expected corrosion products can be obtained for both the samples which agree well with previous studies [3, 66]. It is evident from table 6 that for S1, spectrums 1 and 3 have shown a low Fe/O atomic ratio, which indicates the oxygen-rich environment and high corrosion. On the other hand, spectrum 2 has shown a relatively high Fe/O atomic ratio which suggests low corroded regions. For S2, spectrum 1 has a higher Fe/O atomic ratio than spectrums 2 and 3 which in turn suggests relatively lesser corrosion than the rest two spectrums. It can also be seen from table 6 that for ECR samples (S3), spectrums 1 and 2 display a low Fe/O atomic ratio and hence more corrosion when compared to spectrum 3. Interestingly, spectrum 3 has some defects and leaks which results in a high Fe/O atomic ratio and appears less corrosive. For S4, the correlation between the Fe/O atomic ratio and percentage oxygen variation shows a similar kind of result. Therefore, higher corrosion rates of S1 and S3 were observed compared to that of S2 and S4 which further confirms that the corrosion rates of both types of samples are higher in 1% HCl than in 3.5% NaCl and it indicates a higher corrosive nature of HCl environment as compared to NaCl environment as discussed earlier. It cannot be overruled that in the case of ECR samples, the coating remains unaffected up to a greater extent, which signifies that the solution is not able to reach the base metal as well as also indicates a good adherence between the coating and the bare metal and due to this ECR samples show more corrosion resistance. It has been reported earlier that oxidation of Fe at the anode results in the formation of Fe²⁺ which follows the reduction of the dissolving oxygen as OH⁻ at the cathode. Finally, these two deposits together as hydroxide solid Fe(OH)₂ and electrolytes like NaCl and HCl solutions and thereby enhance this corrosion to a greater extent [52].

| Sample | Sample name | Spectrum | Fe/O (Atomic ratio) | Fe/O (Weight percentage ratio) |
|--------|-------------|----------|---------------------|-------------------------------|
| S1     | Plain rebar in 1% HCl solution | 1 | 0.0444 | 15.39 |
|        |             | 2 | 0.2536 | 89.51 |
|        |             | 3 | 0.044 | 15.492 |
| S2     | Plain rebar in 3.5% NaCl solution | 1 | 0.6943 | 242 |
|        |             | 2 | 0.62 | 216.4 |
|        |             | 3 | 0.62 | 216.5 |
| S3     | Epoxy coated rebar in 1% HCl solution | 1 | 0.0038 | 2.1 |
|        |             | 2 | 0.0056 | 1.917 |
|        |             | 3 | 0.11467 | 40 |
| S4     | Epoxy coated rebar in 3.5% NaCl solution | 1 | 0.072 | 25.3 |
|        |             | 2 | 0.024 | 8.6 |
|        |             | 3 | 0.0083 | 2.91 |

3.4.5. Correlation between microstructure and corrosion resistance

In connection with the corrosion resistance, it is pertinent to mention that both microstructure and composition play a key role in determining the corrosion resistance of the TMT rebar. In the context of composition, the presence of a higher carbon percentage (0.30 wt%) for plain rebar leads to higher corrosion compared to that of ECR having a lower carbon percentage (0.22 wt%) (table 1) [37-40]. For plain rebar, high carbon martensite generates a higher amount of lattice defects which enhances the corrosion rate of these rebars compared to the ECR samples having low carbon martensite [68]. It has been reported earlier that the acicular ferrite in ECR shows an enhanced corrosion resistance when compared to that of polygonal ferrite in plain rebar [68, 69]. It has also been observed that those steels with finer ferrite-pearlite microstructures exhibit a higher corrosion resistance than coarser ferrite-pearlite microstructures in 3.5% NaCl solution [69, 70]. The microstructural refinement and finer grain play a key role in controlling the corrosion behaviour [69, 71]. They can improve the corrosion resistance significantly by forming stable, compact, and non-porous rust layers on their surfaces which further blocks the penetration of the corrosive ions into the solution [68-72]. In the case of polygonal ferrite, loose, porous microstructures exhibit poor corrosion resistance [69]. Also, the pearlite content
is lower for the ECR (4.1 wt%) as compared to the plain rebar (2.9 wt%) when calculated based on the lever rule. It is well-known that in pearlite, due to its interlamellar microstructure and higher stability of the cementite compared to ferrite, galvanic effect enhances the ferritic corrosion and as a result, ECR with low pearlite content tends to exhibit better corrosion resistance compared to that of plain rebar [68]. Similar results were obtained in the present study as depicted from the OCP and linear polarization corrosion tests. OCP test displays an enhanced corrosion resistance behaviour for ECR in 3.5% NaCl solution with a less negative $E_{oc}$ value compared to that of plain rebar. The linear polarization technique depicts a higher corrosion resistance of ECRs in 3.5% NaCl solution by a higher $R_p$ value and lower corrosion rate and corrosion current values compared to that of plain rebars. Similar behaviour was also observed in the case of ECR samples in 1% HCl solution; thereby concluding that ECR samples are more corrosion resistant compared to plain rebars in both 3.5% NaCl and 1% HCl solutions.
3.4.6. XRD study of corrosion products

Figure 11 shows the x-ray diffraction (XRD) analysis of the corrosion products formed on both the plain rebar and ECR sample surfaces in 3.5% NaCl and 1% HCl solution. For the plain rebar samples, the x-Ray profiles primarily reveal the presence of goethite (α-FeO(OH)) (JCPDS Ref. Code: 00-003-0251), maghemite (γ-Fe₂O₃) (JCPDS Ref. Code: 00-024-0081), magnetite (Fe₃O₄) (JCPDS Ref. Code: 01-076-0958), lepidocrocite (γ-FeO(OH)) (JCPDS Ref. Code: 00-001-0136), hydrogoethite (Fe₂O₃·H₂O) (JCPDS Ref. Code: 00-008-0097), and iron oxide (Fe₂₁·₃₄O₃₂) (JCPDS Ref. Code: 01-080-2186). Figures 11(c) and (f) display the standard XRD profile of the plain rebar sample in 1% HCl and 3.5% NaCl, respectively. A comparison of the standard with the current plain rebar sample in 1% HCl solution, indicates the presence of BCC peak is observed closer to the 45°, whereas goethite, maghemite, and magnetite are observed around 35° and 64°, respectively. Similarly, in the case of 3.5% NaCl solution, goethite is observed at angles closer to 40°, magnetite and maghemite at around 37°, lepidocrocite closer to 53°, and BCC peak is observed at higher angles. Hence it has been observed that the current study agrees well with the standard results reported previously [2, 52]. For the plain rebar samples, the obtained BCC peak has been found from the XRD profiles which are similar to earlier observations [2, 29, 52, 73]. It has been reported earlier that the presence of γ-Fe₂O₃ and Fe₃O₄ type oxides reduces the corrosion rates and protects the steel surface moderately from further dissolutions [2, 74]. Dissolution results in the formation of γ-FeO(OH) which can transform into ferric oxy-hydroxide like α-FeO(OH) or Fe₂O₄ followed by further transformation into Fe₂O₄ to γ-Fe₂O₃ [2, 75]. It has been reported in the earlier studies that the phase transformation of γ-FeO(OH) to α-FeO(OH) caused by the saline environment causes a net lowering of the corrosion rate in the case of carbon steel which is well evident in the present research, as in the case of 3.5% NaCl solution lower corrosion behaviour is observed for both plain and epoxy coated rebar samples [55, 59, 65].

In this context, the following equations exhibit the cathodic and anodic reactions:

Cathodic reaction: \( \beta - \text{FeO(OH)} + e^- \rightarrow \text{Fe}_2\text{O}_4 \)  
(6)

Anodic Reaction: \( \text{Fe}_2\text{O}_4 \rightarrow \gamma - \text{Fe}_2\text{O}_3 + e^- \)  
(7)

It can be seen from figure 11 that for the ECR samples, XRD profiles primarily reveal the occurrence of iron chloride hydroxide [Fe₅(OH)₃Cl] (JCPDS Ref. Code: 00-034-0199), goethite (α-FeO(OH)) (JCPDS Ref. Code: 00-029-0713), magnetite (Fe₃O₄) (JCPDS Ref. Code:01-076-0958), lepidocrocite (γ-FeO(OH)) (JCPDS Ref. Code: 01-074-1877), and bernalite [Fe(OH)₃·H₂O] (JCPDS Ref. Code: 01-081-2022) which were also validated in the earlier studies [53, 76]. It is also well known that the reaction between corrosive media and base metal causes substrate anode dissolution in the gap which is t away from the defected areas with a lower oxygen concentration of the coatings. It has been reported earlier that the main corrosion reactions of iron occur at the anodic site under the coating in the saline environment as shown below [76].

\[ \text{Fe}_2\text{H}_2\text{O}_{ad} + \text{Cl}^- \rightarrow \text{FeCl}^-_{ad} + \text{H}_2\text{O} \]  
(8)

\[ \text{FeCl}^-_{ad} + \text{H}_2\text{O} \rightarrow \text{FeOH}^{++} + \text{Cl}^- + e^- \]  
(9)

\[ \text{FeOH}^{++} + \text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O} \]  
(10)

The produced Fe²⁺ cations as shown by equation (9) can be further hydrolysed and oxidized with acidification according to the following reactions as shown by equations 10–12. The above reactions led to the generation of corrosion products as FeCl₂·4H₂O, Fe₂O₃·H₂O, and FeO(OH) which were also validated in the XRD analysis shown in figures 11(c) and (d).

\[ 4\text{Fe}^{2+} + \text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{FeO(OH)} + 8\text{H}^+ \]  
(11)

\[ \text{Fe}^{2+} + 2\text{Cl}^- + 4\text{H}_2\text{O} \rightarrow \text{FeCl}_2\cdot4\text{H}_2\text{O} \]  
(12)

\[ 2\text{Fe}^{2+} + \text{Cl}^- + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2(\text{OH})_3\text{Cl} + 3\text{H}^+ \]  
(13)

As evident from equations 10–12, the increase of H⁺ ions can promote the dissolution of iron. It also cannot be overruled that the charged neutrality of the products formed by Fe²⁺ and H⁺ ions need negatively charged ions, which can further transport more Cl⁻ ions to the corroded site. Finally, both of them can enhance the ferrous chloride concentration in the corrosion products [53, 76].

4. Conclusions

The major conclusions drawn from the present investigation are listed below:

1. Present microstructural study of all the TMT rebars reveals three distinct zones starting from a tempered martensite ring at the periphery followed by a narrow bainitic transition zone along with a ferrite-pearlite mixed microstructure at the core. The microstructure of the core varies as ECR shows acicular ferrite and pearlite, whereas the plain rebar shows polygonal, non-polygonal ferrite, and pearlite.
2. Hardness evolution reveals a classical U-shaped profile with a maximum hardness at the periphery due to the presence of harder phases like tempered martensite, which decreases gradually towards the centre due to the existence of a much softer ferrite-pearlite mixed-phase microstructure. ECR shows higher hardness compared to plain rebar.

3. Gravimetric test, OCP, and linear polarization studies reveal the corrosion behaviour of the ECR and plain rebar. The gravimetric test reveals a lower corrosion rate for ECR compared to plain rebar in both 1% HCl solution and 3.5% NaCl solutions. OCP test further supports this study by exhibiting higher negative OCP values for both types of rebars in 1% HCl solution; thereby confirming higher corrosion behaviour in 1% HCl solution. From linear polarization, higher corrosion potential and lower corrosion current values along with lower corrosion rate reveals enhanced corrosion resistance of ECR compared to plain rebar.

4. EDS and XRD analyses of corrosion products in 3.5% NaCl and 1% HCl solution reveal the presence of goethite (α-FeO(OH)), maghemite (γ-Fe₂O₃), magnetite (Fe₃O₄), lepidocrocite (γ-FeO(OH)), hydrogoethite (Fe₃O₄·H₂O) and iron oxide (Fe₂O₃·O₂) in plain rebar, whereas for ECR the occurrence of iron chloride hydroxide [Fe₂(OH)₃Cl], goethite (α-FeO(OH)), magnetite (Fe₃O₄), lepidocrocite (γ-FeO(OH)) and bernalite [Fe(OH)₃·(H₂O)₀·₂₅] is evidenced.

Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

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