Corrosion behaviour of microstructurally modified elastic rail clip steel under crevice and aggressive salt fog exposure

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Research Article

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Abstract

In the present work, existing Indian elastic rail clip steel (tempered martensite) is microstructurally modified to bainite using austempering route. Crevice corrosion of elastic rail clip (ERC) is of major concern as metal dissolution can cause the loosening of the rail clip assembly (such as rail clip–insert and rail clip–liner) and lack of performance. Furthermore, the surface of rail clip exposed to the atmosphere could also be affected by the corrosive environment. The present work concentrates on the findings of crevice corrosion and wet–dry salt fog exposure of the austempered ERC steels in 3.5 wt.% NaCl solution for 30 days and compared with the as–received (existing) ERC steel which consists of tempered martensitic structure. The severity of corrosion has been investigated by studying the surface dissolution and the rust formed on the exposed surfaces of the ERC steels after the crevice and salt fog tests. Scanning electron microscopy (SEM) and optical profilometry have been used for the analysis of surface dissolution behaviour. Moreover, the rust formed on the exposed surfaces characterized using SEM shows the presence of various rust phases, such as $\alpha$–FeOOH, $\beta$–FeOOH, $\gamma$–FeOOH, $\alpha$–$\text{Fe}_2\text{O}_3$, etc. Furthermore, Raman spectroscopy has been used for the confirmation and quantification of these rust phases. The higher protective ability index (PAI) calculated from the quantitative assessment of different rust measured from Raman spectroscopy shows the better corrosion resistance of the austempered ERC steels.

1 Introduction

For current requirement of heavy load carriers, there is a need to develop high strength of railway components. Alloying and modifying the microstructure could improve the mechanical strength [1–6] of these components. The formation of the bainitic structure using austempering route can enhance the strength of the various rail components such as elastic rail clips (ERC), rails, wheels, axles, etc. The austempering process has been widely used for medium and high carbon steels along with a high amount of Si [7–10]. Varshney et al. [11–12] have developed various morphologies of bainitic structure by varying the austempering temperatures (300°C, 350°C and 400°C) and holding durations using 0.61C–1.71Si (wt.%) steel. They have reported 1300 MPa–2000 MPa tensile strength, 1000 MPa–1300 MPa yield strength and 12%–27% total elongation of the developed bainitic steels. In addition, Luo et al. [13] have austempered 0.66C–1.71Si (wt.%) steel at 250°C for 12 h and 24 h of holding for the development of lower bainitic structure. They have reported ~2000 MPa of tensile strength and ~15% of total elongation. Furthermore, Wang et al. [14] have used low C–medium Si steel (0.22C–1.0Si, wt.%) for the development of bainitic structure. They have used various austempering temperatures between 250°C–400°C with 2 h of holding. They have reported ~1200–1400 MPa tensile strength and 12%–18% elongation of developed bainitic steels. However, Katiyar et al. [15] have used 0.70C–0.24Si (wt.%) rail steel for the development of pearlitic, bainitic, tempered martensitic and spheroidized microstructures and studied their mechanical behaviour. They have reported higher hardness for the bainitic steel compared to the other developed steels.
Corrosion behaviour of the railway components, such as ERCs, rails, wheels, axles, etc., is a crucial parameter in addition to strength. In addition, the higher mechanical properties of the bainitic steels have led to the growing interest in their corrosion properties. Moon et al. [2] have used 0.71%C–1.15%Mn–0.35%Si steel (in wt. %) for the development of bainitic morphology. They have studied the comparative corrosion behaviour of the developed bainitic steels and the conventional C–Mn pearlitic rail steel using salt–fog test in 3.5 wt.% NaCl solution, and reported higher corrosion resistance of the bainitic steels over the conventional C–Mn pearlitic rail steel. In addition, untransformed austenite and presence of martensite along with the bainitic structure significantly affect the corrosion behaviour of the developed bainitic steels.

Wang et al. [16] have used ultra–low C steels (0.023C and 0.088C) and studied their corrosion behaviour in comparison with the 09CuPCrNi weathering steel using 0.5 mol/L NaCl solution. They have reported high corrosion resistance of the ultra–low C bainitic (ULCB) steel due to low C content, large number of low angle boundaries, homogeneous microstructure and formation of compact protective rust layer. They have observed Fe$_3$–$x$O$_4$ nanocrystalline rust particles in the inner rust layer with the Cu and Cr enriched interface layer between the rust layer and ULCB substrate. These Fe$_3$–$x$O$_4$ nanocrystalline rust particles enhance the formation of a compact, dense and adhesive protective rust layer. In addition, Singh et al. [17] have used 0.86C–1.4Si steel for the development of nano–bainitic structure with varied austempering temperatures and analysed the corrosion behaviour in 3.5 wt.% NaCl solution. They have observed a decrease in corrosion current density, and hence the reduction in corrosion rate, as well as shift of corrosion potential towards the noble side with the decrease in austempering temperature. At lower austempering temperature, high charge transfer resistance of steel has been obtained. They have reported that at lower austempering temperature, a combination of high strength with the high corrosion resistance of the bainitic steel has been obtained.

Present authors [18] have developed a bainitic structure of the existing ERC steel using an austempering route with the variation of isothermal holding durations such as 15 min, 30 min and 60 min, and reported ~1500 MPa tensile strength with ~9% elongation. They have performed austempering at 300°C for the development of lower bainitic structure. Furthermore, Neetu et al. [18] have studied the electrochemical corrosion behaviour of the developed bainitic ERC steels in 3.5 wt.% NaCl solution and observed that the austempered steels exhibit excellent corrosion resistance than the existing ERC steel. Mechanical strength and corrosion resistance are exclusively controlled by microstructural modification of the ERC steels. The comparative study of mechanical properties and corrosion rates of the developed bainitic ERC steel with the existing (conventional) ERC steel [18] shows that bainitic steel could be a promising candidate for ERC applications.

Even though several studies have been performed on the corrosion behaviour of the bainitic steel, it could be highly interesting to evaluate its behavior under extreme corrosion conditions, like crevice and wet–dry salt fog exposure. Moreover, crevice corrosion of elastic rail clip is of major concern as metal dissolution can cause the loosening of the assembly (such as rail clip–insert and rail clip–liner) and affect the performance adversely. A small gap can form crevices between these connected components and affect
their corrosion behaviour due to the entrapment of the acidic solution. Furthermore, the surface of rail clip exposed to the atmosphere could also be affected by the alternate wetting and drying leading to an aggressive corrosion during rainy as well as winter season with high degree of fog or dew formation. In light of this, the current study examines the crevice and wet–dry salt fog corrosion behaviour of the austempered and existing (tempered martensitic) ERC steels and their dissolution mechanism using 3.5 wt.% NaCl solution for 30 days. The present work also focuses on the analysis of various formed rust phases on the crevice and salt fog corrosion tested ERC steels and correlation to its corrosion performance.

2 Experimental Procedures

2.1 Materials preparation

Existing elastic rail clip (ERC) steel (a cross-section of 22 mm diameter) was used in the present study and its chemical composition was analysed using optical emission spectroscopy (OES) (Spectro Maxx) (Table 1).

The ERC steel was received in the final clip form from the Indian railways. Discs with 3 mm thickness were cut from the as–received (AR) ERC steel using wire–cut electrical discharge machining (EDM). Firstly, ERC steel was heated to 950°C with 8 min of holding for complete austenite formation as per the rule of one inch per hour of steel specimen thickness [2]. After the complete austenitization, immediate quenching of the ERC specimens was performed for austempering at 300°C with various holding durations of 15 min, 30 min and 60 min in 80% KNO₃ + 20% NaNO₃ salt bath furnace, followed by quenching at room temperature in water. Therefore, four types of the ERC specimens such as (i) AR (as–received) ERC and austempered ERCs (ii) 15 min, (iii) 30 min and (iv) 60 min were considered in the present study. Here, 15 min, 30 min and 60 min are the isothermal holdings during austempering of the ERC specimens for the development of bainitic structure.

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Al</th>
<th>Ni</th>
<th>S</th>
<th>P</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>1.45</td>
<td>0.86</td>
<td>0.18</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2.2 Microstructural characterization

X–ray diffraction (XRD) analysis of all the ERC specimens was carried out in a Bruker D8 Focus X–ray diffraction using Mo–target (wavelength = 0.71 Å) with 10° to 60° 2θ angle at 30 mA, 40 kV and scanning rate of 0.5° per min. All the ERC specimens were ground with the help of SiC paper up to 2000 grit size, followed by cloth polishing using alumina suspension from 3 to 1 µm sequentially and subjected to XRD analysis.
For the microstructural observation, all the ERC specimens were ground up to 2000 grit size SiC papers followed by cloth polishing. The etching of all the steel specimens was done with 2% Nital solution (2% HNO$_3$ in ethanol) before the microscopic examination. The microscopic examinations of all the specimens were performed using field emission scanning electron microscope (FE–SEM) (Nova Nano FE–SEM 450).

### 2.3 Crevice corrosion testing

Crevice corrosion tests of the ERC steels were carried out in a 3.5 wt.% NaCl solution at room temperature using a crevice setup as per the ASTM G78–15 [19]. Specimens with 22 mm diameter with 3 mm thickness of the ERC steels were prepared in a similar way as prepared for the microstructural examination up to cloth polishing followed by ultrasonic cleaning with ethanol. Minimum three samples for each condition were prepared for the crevice test. The weight of all the ERC specimens was measured using a digital weighing machine (Mettler Toledo XS 205) before the crevice corrosion test for further weight loss analysis. All the specimens fitted with the crevice setups were immersed in separate glass beakers filled with 250 ml of 3.5 wt.% NaCl solution. Figures 1a and b show a setup for the crevice test of the ERC specimens immersed in 3.5 wt.% NaCl solution and ERC specimen after 30 days of crevice test, respectively.

### 2.4 Salt fog test

Salt fog exposure test of all the four types of the ERC specimens was performed by 3 h wetting in a 3.5 wt% NaCl solution and 9 h drying simultaneously for 30 days. Three specimens for each ERC steel were prepared for the salt fog test. All the ERC specimens were prepared similarly to those prepared for the microstructural examination up to cloth polishing followed by ultrasonic cleaning with ethanol. The weight of all the ERC specimens was measured before the salt fog test for further weight loss analysis. Except for the working surface (cross-section of 22 mm dia.), all other surfaces were covered with a standard lacquer (non-corrosive) which is insoluble in 3.5 wt.% NaCl. All the four types of ERC specimens were placed carefully in the salt fog chamber. Here, alternate wet (fog of 3.5 wt% NaCl) and dry cycles were considered for 30 days. Figures 2a and b show the setup for salt fog test and ERC specimen after 30 days of salt fog test, respectively.

### 2.5 Rust phases and corroded surface characterization

After 30 days of the crevice and salt fog test, all the specimens were taken out and dried at room temperature. Rust from each of the ERC specimens was collected carefully. The obtained rust was subjected to scanning electron microscopy (SEM) and Raman spectroscopy for the identification and quantification of various phases present. A Princeton instrument, STR Raman spectroscopy with TE–PMT detector and Nd:YAG laser at 532 nm, was used for the Raman spectra analysis. Further, the integrated intensities of the Raman spectroscopy peaks corresponding to various phases were used for the calculation of the protective ability index (PAI). The PAI (α/γ*), which signifies the protectiveness of the rust, was calculated using the following equation [20].
After the removal of rust from all the ERC specimens after crevice as well as salt fog tests, Clark’s solution (ASTM G1–03) was used for the cleaning off exposed surfaces, followed by ultrasonic cleaning using ethanol. Further weight of all the ERC specimens was measured for the weight loss analysis and weight loss was calculated by subtracting it from the initial weight of the corresponding ERC specimen. Furthermore, weight loss was used for the calculation of the corrosion rate of the ERC specimens as per the following equation (ASTM G31–72) (Ref 40):

\[
PAI \left( \frac{\alpha}{\gamma} \right) = \frac{\text{Fraction}(\alpha - \text{FeOOH})}{\text{Fraction}(\gamma - \text{FeOOH}) + (\beta - \text{FeOOH}) + \text{Fe}_3\text{O}_4} \quad [1]
\]

Here, \( \Delta W \): weight loss (g/cm\(^2\)), \( \rho \): density of steel specimen (g/cm\(^3\)) and \( t \): exposure time (s).

In addition, the surface characterization of the exposed surfaces of all the ERC specimens was performed using scanning electron microscopy (SEM) and optical profilometry (Bruker GT–KO). It is worth mentioning that the exposed surfaces of all the ERC specimens were properly cleaned using Clark’s solution before the surface analysis.

3 Results And Discussion

3.1 Microstructural analysis

3.1.1 X–Ray diffraction (XRD) analysis

XRD patterns of all the four types of ERC specimens (as–received (AR), 15 min, 30 min and 60 min) are shown in Fig. 3 revealing mainly two phases such as austenite (\( \gamma \)) and ferrite (\( \alpha \)). The austenite peaks in Fig. 3 show the presence of RA (retained austenite) in the ERC specimens. RA fraction of all the ERC specimens was calculated using the integrated intensity method [21]. The fractions of RA in the AR–ERC and austempered ERC specimens lie in the range of 0.22–0.26 (Table 2). The RA fraction is highest (~0.26) for the austempered ERC specimen with 15 min of isothermal holding. It starts decreasing with the increase of isothermal holding up to 30 min and stabilizes beyond that. Figure 3 is adopted from work done by the current authors only [18].
Table 2
Fractions of various phases/microconstituents present in all the four types of ERC specimens (AR, 15 min, 30 min and 60 min). (Here, RA: retained austenite, XRD: X-ray diffraction, TM: tempered martensite and B: bainites) [18]

<table>
<thead>
<tr>
<th>ERC Specimen</th>
<th>RA (XRD)</th>
<th>TM</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>0.232 ± 0.006</td>
<td>0.763 ± 0.023</td>
<td>―</td>
</tr>
<tr>
<td>15 min</td>
<td>0.258 ± 0.005</td>
<td>―</td>
<td>0.742 ± 0.029</td>
</tr>
<tr>
<td>30 min</td>
<td>0.219 ± 0.006</td>
<td>―</td>
<td>0.784 ± 0.026</td>
</tr>
<tr>
<td>60 min</td>
<td>0.222 ± 0.004</td>
<td>―</td>
<td>0.781 ± 0.034</td>
</tr>
</tbody>
</table>

3.1.2 SEM characterization

Figures 4a–d show the SEM micrographs of AR, 15 min, 30 min and 60 min ERC specimens, respectively. AR–ERC specimen shows the tempered martensitic structure (Fig. 4a). Here, interconnected carbides can be clearly seen in the ferrite matrix of the tempered martensitic structure of the AR–ERC specimen. Neetu et al. [18] (current authors) have studied the microstructural characterization of all the four types of ERC specimens using transmission electron microscopy (TEM). They have reported the presence of RA with the tempered martensitic structure of the AR–ERC specimen, and this has been also confirmed by the XRD analysis (Fig. 3).

SEM micrographs of the austempered ERC specimens show the lower bainitic structure (Fig. 4b–d). Here, austempering at 300°C was considered for the development of the bainitic structure of the existing rail clip specimens. As the austempering temperature is near the martensite start temperature which is 264°C, the developed structure after austempering shows lower bainitic morphology of the ERC specimens (Fig. 4b–d). In the present work, the bainite fraction of the ERC specimens increases with the increase of isothermal holding from 15 min (~ 0.74) to 30 min (~ 0.78) which becomes stable beyond 30 min (~ 0.78) of isothermal holding (Table 2). Figure 4b–d clearly shows the presence of some amount of RA and prior austenite grain boundaries (PAG) beside the bainitic structure in the austempered ERC specimen. The presence of RA in the austempered ERC specimens has also been confirmed by the XRD analysis (Fig. 3). Neetu et al. [18] have also reported the presence of RA in the currently used austempered ERC specimens using transmission electron microscopy (TEM). They have observed film type of RA between the bainitic ferrite laths of the austempered ERC specimens. Bhadeshia et al. [22] have reported the presence of RA along with the bainitic structure in the case of high Si steel due to the incomplete transformation of bainite during the austempering process. The present steel contains high silicon too.

3.2 Crevice corrosion test

3.2.1 Weight loss measurement

The average weight loss (g/cm²) and average corrosion rate (mm/y) of the AR and the austempered ERC specimens obtained after 30 days of crevice test in 3.5 wt.% NaCl solution are given in Table 3. The
average values of the weight loss and corrosion rates are obtained from three different specimens of the AR and austempered ERC steels. Weight loss of the AR–ERC specimen is higher compared to the austempered ERC specimens. Corrosion rate (mm/y) was calculated with the help of weight loss using Eq. 2. It can be seen from Table 3 that the corrosion rates of the austempered ERC specimens are lower compared to the AR–ERC specimen. For the austempered ERC specimens, corrosion rate has been observed to decrease with the increase of isothermal holding till 30 min. It could be due to the increase of bainite fraction and decrease of RA fraction with the increase of isothermal holding duration of the austempered ERC specimens. Beyond 30 min of isothermal holding, the corrosion rate of the ERC specimen has been observed to be stable. It would be interesting to mention that the bainite and RA fractions also stabilise beyond 30 min of isothermal holding at 300°C austempering.

### Table 3

<table>
<thead>
<tr>
<th>ERC specimen</th>
<th>Average weight loss (g/cm²)</th>
<th>Corrosion rate (mm/y)</th>
<th>PAI</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>0.061 ± 0.003</td>
<td>0.958 ± 0.031</td>
<td>0.194 ± 0.004</td>
</tr>
<tr>
<td>15 min</td>
<td>0.048 ± 0.002</td>
<td>0.755 ± 0.025</td>
<td>0.213 ± 0.006</td>
</tr>
<tr>
<td>30 min</td>
<td>0.041 ± 0.001</td>
<td>0.648 ± 0.024</td>
<td>0.254 ± 0.003</td>
</tr>
<tr>
<td>60 min</td>
<td>0.042 ± 0.002</td>
<td>0.653 ± 0.022</td>
<td>0.248 ± 0.005</td>
</tr>
</tbody>
</table>

#### 3.2.2 Raman spectroscopy

Figure 5 shows the Raman spectra of the rust formed on the exposed surfaces of all four types of the ERC specimens after 30 days of crevice test in 3.5 wt.% NaCl solution. Raman spectra show various peaks of α–FeOOH, γ–FeOOH, β–FeOOH, α–Fe₂O₃ and Fe₃O₄. The α–FeOOH peak has been observed at 379 cm⁻¹, while the γ–FeOOH peaks have been observed at 251 cm⁻¹, 526 cm⁻¹ and 1303 cm⁻¹ [23–24]. The peaks of α–Fe₂O₃ and Fe₃O₄ can also be identified at 214 cm⁻¹ and 644 cm⁻¹, respectively, [23–24]. β–FeOOH is also present at 309 cm⁻¹ peak [23]. All these rust phases have been observed on the corroded surfaces of all the four types of ERC specimens. However, their fractions are different. These phase fractions have been calculated with the help of the corresponding peaks of the Raman spectra by following process as mentioned in earlier reports [25–27]. The variation in the rust phase (α–FeOOH, β–FeOOH, γ–FeOOH, α–Fe₂O₃ and Fe₃O₄) fractions could be influenced by the microstructural variation and presence of various fractions of phases/microstructural constituents such as tempered martensite, bainite and RA in the ERC specimens.

The Protective ability index (PAI, α/γ*) for each ERC specimen has been calculated using Eq. 1 and given in Table 3. It can be clearly seen from Table 3 that the AR–ERC specimen consists of the lowest PAI. It has been observed for the austempered ERC specimens that the PAI value increases with the increase in the isothermal holding till 30 min and becomes stable afterward. Moreover, the bainite and RA fractions remain similar after 30 min of isothermal holding, the PAI value also remains similar. It has been reported
in previous studies that the PAI value shows an inverse relation with the corrosion rate [25–27]. Here, the PAI values also corroborate well with the corrosion rate data obtained from the weight loss measurement (Table 3) of the ERC specimens after 30 days of crevice tests. Hence, it can be concluded from both the PAI and corrosion rate data after the crevice test that the austempered ERC specimens show higher corrosion resistance than the AR–ERC specimen.

### 3.2.3 Rust morphologies after crevice test

Figure 6a shows the SEM micrograph of the austempered ERC specimen (30 min) after the crevice test in 3.5 wt.% NaCl solution as a representation. The crevice region can be clearly distinguished from the non-crevice regions as the crevice region shows the dissolution on the ERC steel surface. Various rust morphologies have been observed on the corroded surfaces of ERC specimens after the crevice test. Earlier Raman spectroscopy (Fig. 5) shows that the corroded surfaces of all the ERC specimens contain similar types of rust phases such as \( \alpha \)-FeOOH, \( \gamma \)-FeOOH, \( \beta \)-FeOOH and \( \alpha \)-Fe\(_2\)O\(_3\).

Furthermore, the rust phase analysis of all the four types of ERC specimens has been performed using SEM microscopy. Figures 6b, c, d and e show the various rust morphologies on the crevice surface of the austempered ERC specimen with 30 min of isothermal holding. Other ERC specimens also contain similar rust morphologies. \( \alpha \)-FeOOH has been observed as a needle or whisker–like morphology as shown in Fig. 6b, while the \( \gamma \)-FeOOH can be seen as flower petals–like morphology in the corrosion products (Fig. 6c). Alcantara et al. [23] have reported similar types of whiskers and flower petals–like morphologies corresponding to \( \alpha \)-FeOOH and \( \gamma \)-FeOOH, respectively, of the rust formed on the surface of the carbon steel exposed in the marine environment. Several other researchers have also reported similar morphologies for \( \alpha \)-FeOOH and \( \gamma \)-FeOOH in the rust phases [28–30].

Furthermore, Fig. 6d shows the plate–type crystals which reveal the presence of \( \beta \)-FeOOH in the rust products. Fuente et al. [24] have observed a similar morphology in the rust products of 0.13 C–0.09 Si steel exposed in the marine environment and reported it as \( \beta \)-FeOOH. Katiyar et al. [27] and Panda et al. [31] have also reported the presence of \( \beta \)-FeOOH in the rust products of the steel when chloride ions are present in the corrosive media. Figure 6e shows the morphology of \( \alpha \)-Fe\(_2\)O\(_3\). Sayed et al. [32] and Zhu et al. [33] have also observed similar spherical morphology of Fe\(_2\)O\(_3\) in the shape and phase evaluation of different iron oxides.

Fuente et al. [24] have found that \( \gamma \)-FeOOH is preferentially present on the outermost surface of the corrosion products while \( \alpha \)-FeOOH and \( \beta \)-FeOOH are present on the innermost surface near the base metal. Dhaiveegan et al. [29] have shown that the presence of \( \alpha \)-FeOOH in the inner rust layer increases the stability of the rust products which provides the compact and dense protective rust layer. Therefore, the presence of a high amount of \( \alpha \)-FeOOH corresponding to the high PAI represents the formation of protective rust layer in the austempered ERC specimens. Furthermore, Sun et al. [30] have studied the corrosion behaviour of the weathering steel with the variation of Si content (0.12%, 0.34% and 0.48%) and reported that the presence of high Si could also increase the stability of the rust layer as high Si increases the tendency of transformation of \( \gamma \)-FeOOH and \( \beta \)-FeOOH in the stable rust phases.
3.2.4 Surface morphology obtained via SEM and optical profilometer after crevice test

Figure 7 shows the SEM micrographs of the rust layer formed on the exposed surfaces of all the four types of ERC specimens (AR, 15 min, 30 min and 60 min) after 30 days of crevice test in 3.5 wt.% NaCl solution. A cracked rust layer and some pits morphology can be seen on the exposed surface of AR–ERC specimen (Fig. 7a). The rust formed on the austempered ERC specimens is quite homogeneous and the outer rust surface appeared to be cracked, which is interconnected throughout the corroded surface (Figs. 7b, c and d). In comparison with the austempered ERC specimens, wider cracks have been observed for the AR–ERC specimen. On the outer rust layer, formation of pits can be clearly seen for AR–ERC specimen (Fig. 7a) whereas no pit formation has been observed for the austempered ERC specimens. The pits formed for the austempered ERC specimens could be very small which are not visible due to the formation of rust layer on the top most surface. Pits formation of all the four ERC specimens has been discussed further with the help of optical profilometry.

A heavy dissolution of the AR–ERC specimen could be due to the presence of interconnected carbides. Neetu et al. [18] have reported higher C concentration of these interconnected carbides compared to ferrite matrix of the AR–ERC steel using an electron probe micro–analyzer (EPMA). The higher C concentration of these interconnected carbides results in the higher dissolution of ferrite matrix within the tempered martensitic structure of the AR–ERC specimen. Moreover, the austempered ERC specimens contain similar phases/micro–constituents (bainite and RA) resulting in similar types of rust layer formation.

Furthermore, optical profilometry has been used to understand the surface morphology of the ERC specimens after the crevice test. It is worth mentioning that all the ERC specimens have been cleaned properly to remove the rust formed on the exposed surfaces before the optical profilometry analysis. Figures 8a, c, e and g show the 2D optical profilometry images of the exposed surfaces of the AR, 15 min, 30 min and 60 min austempered ERC specimens, respectively, after the crevice test in 3.5 wt.% NaCl solution. Their corresponding 3D images are shown in Fig. 8b, d, f and h, respectively. Pit–type morphology on the exposed surfaces of all four types of ERC specimens can be clearly seen from these images (Fig. 8). The average pit depth has been measured to be $30 \pm 3 \, \mu\text{m}$ for the AR–ERC specimen, whereas the austempered ERC specimens with 15 min, 30 min and 60 min of the isothermal holding show $24 \pm 2 \, \mu\text{m}$, $22 \pm 2 \, \mu\text{m}$ and $22 \pm 1 \, \mu\text{m}$ of average pit depths, respectively (Fig. 8). The AR–ERC specimen shows higher pit depth as compared to the austempered ERC specimens. In addition, interconnected pits have been observed in the AR–ERC specimens. It could be due to the presence of interconnected carbides in the tempered martensitic structure of the AR–ERC specimen where the ferrite phase acts as an anode compared to the cathodic carbide phase. Moreover, it can be clearly seen from Fig. 8a–b that the pits are wider in the AR–ERC specimens as compared to the austempered ERC specimens (Fig. 8c–h). Furthermore, the fine and uniform distribution of carbides (cathode) in the ferrite
matrix (anode) has led to the fine distribution of pits on the exposed surface of the austempered ERC specimens.

Even though all the austempered ERC specimens show a similar pit depth, the morphology of pits varies with the variation of isothermal holding durations. It can be seen from Fig. 8c–d that the pits formed on the austempered ERC specimen with 15 min of isothermal holding are wider than the other austempered specimens. The width of the pits decreases with the increase of isothermal holding from 15 min to 30 min and 60 min. It could be due to the increase of bainite fraction and decrease of RA fraction in the austempered ERC specimens with the increase of isothermal holding durations (Table 2).

The variation in the depth and width of pits of the austempered ERC specimens could be due to the variation of shape, size and distribution of RA and carbides with the bainitic structure. The surface morphology and depth of the pits corroborate well with the corrosion rate of the AR and austempered ERC specimens obtained after the crevice tests (Table 3).

3.2.5 Correlation of the corrosion rate with PAI and pit depth obtained from the crevice test of the ERC specimens

Figure 9 shows the correlation of the corrosion rate of all four types of ERC specimens with PAI and pit depths obtained from 30 days of crevice tests in 3.5 wt.% NaCl solution. It can be seen from Fig. 9 that the corrosion rate of the AR–ERC specimen is higher as compared to the austempered ERC specimens. It has been observed for the austempered ERC specimens that the corrosion rate decreases with the increase in holding duration at 300°C of austempering from 15 min to 30 min which becomes stable with increase of holding duration to 60 min. Obtained PAI values and pit depths of all the ERC specimens after the crevice test are in well correlation with the corresponding corrosion rate. Here, pit depth is directly proportional whereas the PAI value is inversely proportional to the corrosion rate of the corresponding ERC specimen.

3.3 Salt fog test

3.3.1 Weight loss measurement

The average weight loss (g/cm²) and average corrosion rate (mm/y) of the AR and the austempered ERC specimens obtained after 30 days of salt fog test in 3.5 wt.% NaCl solution are given in Table 4. It is worth mentioning that the weight loss of the ERC specimens has been calculated after the complete removal of the rust using Clark's solution as indicated in the experimental section. Minimum 3 specimens of each heat–treated ERC steel were considered for the weight loss and corrosion rates calculation. It has been observed from Table 4 that the weight loss of the AR–ERC specimen is higher than the austempered ERC specimens.
Various parameters of the AR and austempered ERC specimens obtained after 30 days of salt–fog tests in 3.5 wt.% NaCl solution.

<table>
<thead>
<tr>
<th>ERC specimen</th>
<th>Average weight loss (g/cm²)</th>
<th>Corrosion rate (mm/y)</th>
<th>Protective ability index (PAI)</th>
<th>Average surface roughness (Rₐ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AR</td>
<td>0.169 ± 0.021</td>
<td>2.602 ± 0.323</td>
<td>0.038 ± 0.008</td>
<td>19.0 ± 1.1</td>
</tr>
<tr>
<td>15 min</td>
<td>0.112 ± 0.010</td>
<td>1.724 ± 0.154</td>
<td>0.079 ± 0.007</td>
<td>16.4 ± 0.5</td>
</tr>
<tr>
<td>30 min</td>
<td>0.072 ± 0.007</td>
<td>1.108 ± 0.107</td>
<td>0.129 ± 0.005</td>
<td>14.5 ± 0.8</td>
</tr>
<tr>
<td>60 min</td>
<td>0.071 ± 0.008</td>
<td>1.093 ± 0.123</td>
<td>0.131 ± 0.007</td>
<td>14.8 ± 0.6</td>
</tr>
</tbody>
</table>

The corrosion rate (mm/y) of the ERC specimen is calculated with the help of the corresponding weight loss using Eq. 3 and given in Table 4. The corrosion rate of the ERC specimens has been observed to decrease with the decrease in weight loss after the salt fog test. The trend in variation of the corrosion rate of all four types of ERC specimens obtained from the salt fog test (Table 4) is exactly similar to the corrosion rate obtained from the crevice test (Table 3). It has been observed that the corrosion rate of the developed bainitic (austempered) ERC specimens is lower than the AR–ERC specimen (Table 4). It is due to the presence of interconnected carbides in the tempered martensitic structure of the AR–ERC specimens and uniform distribution of fine carbides within the bainitic ferrite of the austempered ERC specimens.

### 3.3.2 Raman spectroscopy

Figure 10 shows the Raman spectra of the rust formed on the exposed surface of all four types of ERC specimens after 30 days of salt fog test in 3.5 wt.% NaCl solution. Raman spectra show various peaks of α-FeOOH, γ-FeOOH, β-FeOOH, α-Fe₂O₃ and Fe₃O₄. The α-FeOOH peak has been observed at 397 cm⁻¹ and the γ-FeOOH peak has been observed at 1310 cm⁻¹ [23–24]. The peaks of α-Fe₂O₃ can be identified at 227 cm⁻¹, 292 cm⁻¹ and 608 cm⁻¹ [23–24]. The peak of Fe₃O₄ can also be identified at 662 cm⁻¹. The peaks of β-FeOOH can be clearly seen at 384 cm⁻¹ and 715 cm⁻¹ [23]. Though similar phases are present in the rust formed on the exposed surfaces of all the four types (AR, 15 min, 30 min and 60 min) of ERC specimens, their fractions vary for a particular specimen. Fractions of each rust phase have been calculated with the help of the corresponding peaks of the Raman spectra.

Furthermore, the protective ability index (PAI, α/γ*) values for each ERC specimen have been calculated using Eq. 1 and given in Table 4. The PAI values of all the ERC specimens obtained from the salt fog test are in well correlation with the PAI values obtained from the crevice test (Tables 3 and 4). The AR–ERC specimen consists of the lower PAI than the austempered ERC specimens. PAI values are in inverse relation with the corrosion rate of the ERC specimens after the salt fog test (Table 4). An inverse relation between PAI and corrosion rate has been reported in various studies [21, 26–27, 34–35]. From Table 4, it can be seen that the higher the PAI lower is the corrosion rate of the ERC specimen. Hence, the higher PAI
of the austempered ERC specimens represents their higher corrosion resistance compared to the AR–ERC specimen.

### 3.3.3 Rust morphologies after salt fog test

The exposed surfaces of the ERC specimens consist of various rust morphologies after the salt fog test. It can be seen from the Raman spectra that all the four types of ERC specimens (AR, 15 min, 30 min and 60 min) contain similar rust morphologies such as $\alpha$–FeOOH, $\beta$–FeOOH, $\gamma$–FeOOH, $\alpha$–Fe$_2$O$_3$, etc. Figures 11a, b, c and d show SEM micrographs of $\alpha$–FeOOH, $\gamma$–FeOOH, $\beta$–FeOOH and $\alpha$–Fe$_2$O$_3$, respectively, present in the corroded surface of the austempered ERC specimen (30 min of isothermal holding) after 30 days of salt fog test in 3.5 wt. % NaCl solution. It is worth mentioning that the other ERC specimens (AR, 15 min and 60 min) also show similar rust morphologies. Figure 11a shows the whiskers or needle–like morphologies which represent formation of $\alpha$–FeOOH in the rust phase. Raman et al. [36] have studied the rust phase morphologies formed by various laboratories test on weathering steel. They have reported whiskers like rust morphology corresponding to $\alpha$–FeOOH on the exposed surface of weathering steel after a salt fog test in 3.5 wt. % NaCl solution. Figure 11b shows the formation of flowers petal–like morphologies representing $\gamma$–FeOOH on the exposed surface of ERC specimen. In addition, Thalib et al. [37] have reported similar flower petal–like morphologies of $\gamma$–FeOOH in rust formed on the surface of 0.31C–0.72Mn (in wt. %) steel after 6 months of atmospheric exposure.

Furthermore, Fig. 11c shows the plate/rod–type crystals which reveal the presence of $\beta$–FeOOH in the rust products. Alcantara et al. [23] and Fuente et al. [24] have observed a similar rod–type morphology of the $\beta$–FeOOH in the rust products of steels exposed to the chloride containing environment. Figure 11d shows the spherical morphology of $\alpha$–Fe$_2$O$_3$. Furthermore, various researchers have reported the presence of $\alpha$–FeOOH, $\gamma$–FeOOH and $\beta$–FeOOH in the rust products of the steel when exposed to the chloride containing environment [28–33, 38–39].

### 3.3.4 Surface morphologies obtained via SEM and optical profilometer after the salt fog test

Figure 12 shows the SEM micrographs of the rust layer formed on the surface of ERC specimens after 30 days of salt fog test in 3.5 wt.% NaCl solution. A homogeneous formation of rust can be clearly seen on the exposed surfaces of all the four types of ERC specimens (Fig. 12). In addition, cracks on the outer layer of rust have also been observed for the ERC specimens. Though the outer layer of all the ERC specimens shows compact rust surface, cracks formation for the AR–ERC specimen is much wider compared to the austempered ERC specimens.

Raman spectra (Fig. 10) and SEM micrographs (Fig. 11) of rust formed on the exposed surfaces of ERC specimens clearly show the presence of $\alpha$–FeOOH in the rust layer after the salt fog test. The $\alpha$–FeOOH present on the exposed surface increases the stability of rust layer resulting in the formation of a compact and dense rust surface [29]. The variation in the outer rust layer could be due to the presence of
various phase/microconstituents such as tempered martensite, bainite and RA and their fractions in the ERC specimens.

Furthermore, the surface roughness of the ERC specimens after the salt fog test has been analysed using an optical profilometer. It is worth mentioning that all the ERC specimens were cleaned carefully with the help of Clark's solution before the surface analysis using the optical profilometer. Figures 13a, c, e and g show the optical profilometry images (2D) of the exposed surfaces of the AR, 15 min, 30 min and 60 min austempered ERC specimens, respectively, after the salt fog test in 3.5 wt.% NaCl solution. Their corresponding 3D images are shown in Fig. 13b, d, f and h, respectively.

The average surface roughness ($R_a$) of all the four types of ERC specimens obtained from the optical profilometry is given in Table 4. The average surface roughness has been measured to be $19.0 \pm 1.1 \, \mu m$ for the AR–ERC specimen. The austempered ERC specimens with 15 min, 30 min and 60 min of the isothermal holding show $16.4 \pm 0.5 \, \mu m$, $14.5 \pm 0.8 \, \mu m$ and $14.8 \pm 0.6 \, \mu m$ of average surface roughness, respectively (Fig. 13). The surface roughness of the austempered ERC specimens is lower than the AR–ERC specimen (Fig. 13 and Table 4). Uniform dissolution on the exposed surfaces of all the four types of ERC specimens can be clearly seen from 2D optical profilometry images (Fig. 13). Furthermore, the severity of dissolution is higher for the AR–ERC specimen than the austempered ERC specimens. The presence of interconnected carbides in the tempered martensitic structure has resulted in the higher dissolution and higher surface roughness of the exposed surfaces of the AR–ERC specimen. Here, interconnected carbides act as cathodes due to high C concentration compared to the ferrite matrix resulting in the dissolution of the ferrite within the tempered martensitic structure of the AR–ERC specimen. Furthermore, the fine and uniform distribution of carbides (cathode) in the bainitic ferrite matrix (anode) has led to the lower dissolution on the exposed surface of the austempered ERC specimens compared to the AR–ERC specimen.

It can be clearly seen from Fig. 13 and Table 4 that the average surface roughness of the austempered ERC specimen decreases with the increase of isothermal holding from 15 min to 30 min. However, beyond 30 min of isothermal holding not much change in average surface roughness has been observed for the austempered ERC specimens. It could be due to the presence of a higher fraction of RA beside the bainitic morphology in the austempered ERC specimen with 15 min of isothermal holding. Further, RA fraction decreases in the austempered ERC specimens with the increase of isothermal holding beyond 15 min, resulting in the decrease of average surface roughness, whereas beyond 30 min of isothermal holding, bainite and RA fractions stabilises resulting in less variation of average surface roughness.

Moreover, the difference in the surface roughness of the ERC specimens could be due to the presence of various phases/microconstituents, such as tempered martensite, bainite and RA, and their fractions. In addition, the surface roughness of all the ERC specimens is corroborated well with the corrosion rate obtained from the weight loss after the salt fog test (Table 4). Hence, lower surface roughness indicates the lower dissolution of the austempered ERC specimens resulting in higher corrosion resistance.
3.3.5 Correlation of the corrosion rate, average surface roughness and PAI obtained from the salt fog test

Figure 14 shows the correlation of the corrosion rate with average surface roughness (R\textsubscript{a}) and PAI of all the four types of ERC specimens after 30 days of salt fog test in 3.5 wt.% NaCl solution. It can be clearly seen from Fig. 14 that the corrosion rate is higher in the AR–ERC specimen as compared to the austempered ERC specimens. In addition, the corrosion rate of the austempered ERC specimens decreases with the increase in isothermal holding till 30 min and later becomes stable with a further increase in holding duration. It has been observed from the comparative graph that the average surface roughness and PAI values are in well correlation with the corrosion rate of all the four ERC specimens (Fig. 14). Average surface roughness of the ERC specimens is directly proportional to the corrosion rate. In contrast, the PAI value is in inverse relation to the corresponding corrosion rate. Moreover, the variation in the average surface roughness of the austempered ERC specimens could be due to the variation of shape, size and distribution of RA and cementite present with the bainitic structure.

3.4 Correlation of the corrosion rate obtained from the crevice and salt fog tests with various phases/microconstituents of the ERC specimens

Figure 15 shows the correlation of the corrosion rate with the various phases present in all four types of ERC specimens (AR, 15 min, 30 min and 60 min) after the crevice and salt fog tests in 3.5 wt.% NaCl solution. It can be clearly seen from Fig. 15 that the corrosion rate is higher in the AR–ERC specimen (tempered martensitic structure) for both the crevice and salt fog tests. It could be due to a large cathodic area of interconnected carbides in the tempered martensitic structure of the AR–ERC specimen resulting in the higher dissolution of ferrite matrix. In addition, Neetu et al. [18] have reported that the interconnected carbides of the AR–ERC specimen contain higher C concentration as compared to the bainitic structure leading to the higher dissolution of the ferritic matrix of the AR–ERC specimen as well as the higher corrosion rate than the austempered ERC specimen. The presence of bainite and some amount of RA uniquely affect the corrosion behaviour of the austempered ERC specimen. The corrosion rate of austempered ERC specimens decreases with the increase in isothermal holding till 30 min and becomes stable with a further increase in holding duration. There is not much change in the contents of different phases beyond 15 min of austempering.

Figures 16a, b and c show the corrosion behaviour of all the four types of specimens (AR, 15 min, 30 min and 60 min) obtained from various corrosion techniques such as electrochemical test (Ref 33), crevice test (30 days) and salt fog test (30 days), respectively, in 3.5 wt% NaCl solution. It is worth mentioning that the electrochemical tests (Ref 33) of the four types of ERC specimens (AR, 15 min, 30 min and 60 min) have been performed by the current authors. It can be clearly seen from all three corrosion tests (electrochemical, crevice and salt fog) that the austempered ERC specimens show lower corrosion rate than the AR–ERC specimen. Higher strength [18] as well as the corrosion resistance of the austempered ERC steel makes it a suitable candidate for the rail clip application.

4. Conclusions
Microstructural analysis reveals the of tempered martensitic structure of the as-received (AR) ERC specimen with some amount of retained austenite (RA). Austempering of the AR-ERC specimen results in the development of a lower bainitic structure.

The bainite fraction increases and RA fraction decreases with the increase of isothermal holding till 30 min of the austempered ERC specimens. Beyond 30 min, the amount of bainite formation becomes stable.

The crevice corrosion test exhibits pits-like morphologies in the exposed surfaces of the AR and austempered ERC specimens. The average pit depth, from the optical profilometry analysis, has been measured to be 30 ± 3 µm for the AR-ERC specimen, whereas austempered ERC specimens with 15 min, 30 min and 60 min of the isothermal holding show 24 ± 2 µm, 22 ± 2 µm and 22 ± 1 µm of average pit depths, respectively.

Salt fog tests of ERC specimens result in the uniform dissolution of the exposed surfaces in 3.5 wt.% NaCl solution. The average surface roughness has been measured to be 19.0 ± 1.1 µm for the AR-ERC specimen, whereas austempered ERC specimens with 15 min, 30 min and 60 min of the isothermal holding show 16.4 ± 0.5 µm, 14.5 ± 0.8 µm and 14.8 ± 0.6 µm of average surface roughness, respectively.

SEM and Raman spectroscopy reveal the presence of α-FeOOH, β-FeOOH, γ-FeOOH and α-Fe₂O₃ in the rust formed on the ERC specimens after the crevice and salt fog tests. Calculated PAI values from the rust phase fractions show the higher corrosion resistance of the austempered ERC specimens.

References


Figures

![Figure 1](image-url)

**Figure 1**

(a) Crevice corrosion setup and (b) ERC specimen after 30 days of crevice test in 3.5 wt.% NaCl solution
Figure 2

(a) Salt fog setup and (b) ERC specimen after 30 days of salt fog test in 3.5 wt.% NaCl solution
Figure 3

X-ray diffraction (XRD) patterns of all the four types of ERC specimens (AR, 15 min, 30 min and 60 min) [18]
Figure 4

SEM micrographs of all the four types of ERC specimens; (a) AR, (b) 15 min, (c) 30 min and (d) 60 min. (Here, TM: tempered martensite, B: bainite, RA: retained austenite and PAG: prior austenite grain boundaries)
Figure 5

Raman spectra of the rust formed on the exposed surface of all four types of the ERC specimens (AR, 15 min, 30 min and 60 min) after 30 days of crevice tests in 3.5 wt.% NaCl solution
Figure 6

SEM micrographs of (a) crevice surface and various rust morphologies after the crevice test in 3.5 wt. % NaCl solution; (b) α-FeOOH, (c) γ-FeOOH, (d) β-FeOOH and (e) α-Fe₂O₃ present in the corroded surfaces of the austempered ERC specimens with 30 min of isothermal holding.
Figure 7

SEM micrographs of exposed surface of ERC specimens (a) AR, (b) 15 min, (c) 30 min and (d) 60 min after 30 days of crevice test in 3.5 wt.% NaCl solution
Figure 8

Optical profilometry images of the corroded surfaces of all the four ERC specimens (AR, 15 min, 30 min and 60 min) after 30 days of crevice test in 3.5 wt.% NaCl solution
Figure 9

Correlation of the corrosion rates (CR) with pit depth and PAI obtained from the crevice tests in 3.5 wt.% NaCl solution of all the four types of ERC specimens (AR, 15 min, 30 min and 60 min)
Figure 10

Raman spectra of the rust formed on the exposed surface of all four types of the ERC specimens (AR, 15 min, 30 min and 60 min) after 30 days of salt fog test in 3.5 wt.% NaCl solution
Figure 11

SEM micrographs of various rust morphologies after the salt fog test in 3.5 wt. % NaCl solution; (a) $\alpha$-FeOOH, (b) $\gamma$-FeOOH, (c) $\beta$-FeOOH and (d) $\alpha$-Fe$_2$O$_3$ present in the corroded surfaces of the austempered ERC specimens with 30 min of isothermal holding
Figure 12

SEM micrographs of the exposed surfaces of ERC specimens (a) AR, (b) 15 min, (c) 30 min and (d) 60 min after 30 days of salt fog test
Figure 13

Optical profilometry images of the corroded surfaces of all the four ERC specimens (AR, 15 min, 30 min and 60 min) after 30 days of salt fog test in 3.5 wt.% NaCl solution
Figure 14

Correlation of the corrosion rates (CR) with average surface roughness ($R_a$) and PAI obtained from the salt fog tests in 3.5 wt.% NaCl solution of all the four types of ERC specimens (AR, 15 min, 30 min and 60 min)
Figure 15

Correlation of the corrosion rate obtained from the crevice and salt fog test in 3.5 wt.% NaCl solution with the various phases of all the four types of ERC specimens (AR, 15 min, 30 min and 60 min). (Here CR: Corrosion rate, B: bainite, RA: retained austenite)
Figure 16

Comparative curves of corrosion rate of all the four types of ERC specimens (AR, 15 min, 30 min and 60 min) after (a) electrochemical test [18], (b) crevice test (30 days) and (c) salt fog test (30 days) in 3.5 wt% NaCl solution