Corrosion behavior and electrochemical corrosion of a high manganese steel in simulated marine splash zone

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Abstract
The corrosion behavior of a high manganese steel in simulated marine splash zone environment was studied by dry-wet cyclic corrosion experiment and electrochemical experiment. Corrosion kinetics, composition, surface morphology, cross-section morphology, element distribution, valence state, polarization curve and electrochemical impedance spectroscopy were analyzed with the aim of characterizing the characteristics of corrosion product films. The results show that in chloride-containing environment, in the initial corrosion products, Mn oxides with porous structure lead to higher corrosion rate. As corrosion extends, the formation of alloy element oxides in corrosion products changes the corrosion properties of rust layers at different stages. Mo oxides form a stable passivation film, which reduces the influence of chloride ion on corrosion. Ni oxides in the inner rust layer facilitate the transformation of goethite, and Cr oxides in the outer rust layer increase the densification of the rust layer. The stability and compactness of Fe3O4, α-FeOOH and FeCr2O4 in the later corrosion products inhibit the corrosion action of manganese iron oxides and slow down the corrosion rate. With the corrosion durations, the corrosion current density of the sample with the corrosion product film first increases and then decreases, and the corrosion potential first moves negative and then shifts in a positive direction subsequently, indicating that the protective effect of the corrosion product film is gradually significant.

1. Introduction

With the development of marine products and marine resources, marine engineering steel market space continues to expand, which inspires enthusiasm for exploring new materials that can be applied to marine platforms. A large number of high-priced alloy elements such as nickel, molybdenum and chromium are added to low carbon and low manganese marine high strength steel, which increases its casting cost [1–4]. Therefoer, the newly developed high strength and toughness marine engineering steel replaces Ni and Mo with cheap alloying element manganese [5, 6]. It is well known that the marine spatter area has a harsh corrosion environment. The marine steel serving in this area is subjected to adequate sunshine and storm stress, and alternating dry-wet erosion of seawater with high dissolved oxygen [7–9], resulting in serious corrosion. To solve the thorny corrosion problem, many scholars have done a corrosion study in this area. Considering that environmental protection and resource conservation are usually conducted using a laboratory simulation of a dry-wet cyclic environment [10]. Research by M.D Chen et al [11] shows that the diffusion of chloride and sulfide anions on the rust layer, the cation-selective permeability of the rust layer leads to the anion concentration gradient of the whole rust layer, and limits the back diffusion of anions from the rust/steel interface, resulting in cracks in the rust layer parallel to the rust/steel interface. Zhang et al [12] studied on simulated seawater corrosion of medium manganese steel, which found that manganese compounds are detected in the corrosion products only appeared in splash zone environment, the manganese and molybdenum...
elements are obviously enriched, and the protective ability of corrosion products is reduced by manganese compounds. Fajardo et al. [13] show that the concentration and corrosion rate of manganese oxide in the corrosion products of high manganese steel will increase with the increase of manganese content, lower iron oxide and higher Mn content will reduce its corrosion resistance. In addition, the study shows that the high content of Ni in the rust layer will increase its selective permeability to anions [14]. Cu enriches the inner layer of corrosion products and increases the density, which is similar to that of chromium [15, 16]. Insoluble Mo oxide can reduce cation permeability [17]. Alloy elements such as Ni, Cu, Mo and Cr have synergistic effects on the corrosion behavior of steel [18]. Alloying elements play different roles in different corrosion stages of steel. Ni and Cu elements are enriched in the corrosion products at the initial and later stages of corrosion, while other elements Mo and Cr are gradually enriched only at the interface between matrix and products at the later stage of corrosion [19]. However, the effect and mechanism of alloying element Mn, Ni, Cr, Cu, Mo on corrosion behavior of high manganese steel in marine spatter area have not been systematically elucidated. In this work, the corrosion behaviour of tested steels was studied by an alternative wet/dry cyclic corrosion and electrochemical testing. The influence of the corrosion products of the sample steel in the splash area on the corrosion process is discussed by corrosion dynamics curve, corrosion phase state, rust layer surface appearance and section appearance, element distribution, valence state, polarization test and EIS antifitting analysis. This provides valuable data for studying the corrosion behavior and mechanism of high manganese steel and developing steel with corresponding anticorrosion properties.

### 2. Experiments

#### 2.1. Material preparation

The High manganese steel sample composition is shown in table 1. Corrosion test samples were machined by electric spark wire cutting machine tool (DK7735, Shibeite CNC machine tool factory, Taizhou, China) into two styles of size: 60 mm $\times$ 40 mm $\times$ 4 mm, 15 mm $\times$ 10 mm $\times$ 4 mm, a hole (3 mm) were drilled into all samples for the convenience of hanging experimental samples. The former was used to calculate the corrosion rate by weight loss test, and the latter was used for corrosion products detection and electrochemical test. Samples used for electrochemical testing were welded by copper wire on one of the surfaces, and the rest of the samples were encapsulated with epoxy resin, showing only one surface with an area of 1cm$^2$. Before the experiment, all the samples were polished to 2000# SiC sandpaper, and then with polishing agent (2.5 $\mu$m) for mirror polishing, and the samples were cleaned with acetone, ethanol, deionized water under ultrasonic vibration.

#### 2.2. Wet-dry cyclic corrosion experiment

The corrosion effect of sample steel in marine splash zone was simulated by dry-wet cyclic corrosion experiment (The experimental equipment for simulating the corrosion environment of the marine splash zone is patented as ZL 2020 2 1357994.3). The samples were subjected to 24, 72, 168, 288, 432 and 600 h of cyclic corrosion in 3.5% NaCl solution with the pH value of 7 at 25$^{\circ}$C in immersion period, at 27$^{\circ}$C in dry period. Each dry-wet cycle consists of an immersion period (10 min) and a dry period (50 min). In order to reduce the experimental error, all experiments were designed three parallel experiments. For samples for corrosion kinetics calculations, weighing before the experiment, and then at room temperature, the rust layer was removed by a chemical cleaning solution mixed with 37% (vol) % hydrochloric acid (HCl, GR), deionized water and hexamethylenetetramine ($C_6H_{12}N_4$, AR, $\geq99.0\%$) at 100:100:1. After the corrosion products were removed, the samples were cleaned with ethanol, dried and then weighed again after one day.

#### 2.3. Electrochemical measurements

Electrochemical workstation (AUTOLAB PGSTAT302N2) was used to test the corrosion film on the surface of the sample after dry-wet cyclic corrosion at different stages. A three-electrode system was adopted with platinum as auxiliary electrode (CE), KCl-saturated calomel electrode as reference electrode (RE), the samples with rust layer of 1cm$^2$ area after dry wet alternate corrosion for 24, 72, 168, 288, 432 and 600 h were used as working electrodes, and the electrolyte is 3.5% sodium chloride corrosion solution. The corrosion behavior of the samples were detected by open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curve [20, 21]. The process is as follows: the sample steel was put into electrolyte

| Alloy | Mn | C | Cr | Cu | Ni | Mo | Si | Fe |
|-------|----|---|----|----|----|----|----|----|
| Content | 20.95 | 3.03 | 2.73 | 0.51 | 0.08 | 0.04 | 0.31 | Balance |
solution for 1 h open circuit potential detection, when the open circuit potential reaches a stable value, give 
system 10 mV sine wave AC signal, testing the ac impedance value of the sample at a frequency range of 
100 kHz ∼ 10 mHz at this potential. When measuring the polarization curve, the scanning interval is about 
the open circuit potential ± 0.5 V of the sample and the scanning rate of the system is 0.5 m V / s . All the 
measurements of samples were carried out at room temperature (25 ± 1 °C).

2.4. Characterization of corrosion products
The corrosion products of the test steel after different corrosion durations were detected by X-ray diffractometer 
(XRD, D8 ADVANCE, Bruker, Germany) equipped with CuKa radiation (λ = 0.154 nm), the scanning step is 
0.028, and the scanning angle is 10°–70°. The surface morphology of rust layer was observed by field emission high resolution scanning electron microscopy (SEM, SIGMA HD, Carl Zeiss, Jena, Germany). The corrosion samples were cast with epoxy resin, the cross-section morphology of corrosion rust layer was observed by SEM, and the chemical elements in the cross-section of rust layer were detected and analyzed by energy dispersive X-ray spectrometer (EDS, JSM-6390A, Joint-stock Company, Beijing, China). X-ray photoelectron spectroscopy (XPS, K-AIPHA, Thermo Scientific, Oxford, Britain) was used to identify the valence states of 
elements in the corrosion products.

3. Results and discussion

3.1. Corrosion kinetics and corrosion product
The corrosion kinetics curve was characterized by determining the value of the average corrosion rate. The 
corrosion rate was determined by measuring the mass loss of the Sample steel before and after corrosion test. 
The average annual corrosion rate (CR, mm/y) is calculated according to the following equation (1):

$$CR\left[\frac{\text{mm}}{\text{Year}}\right] = \frac{\text{mass loss [g]} \times 8760 [\text{h/year}]}{\text{corrosion time [h]} \times \text{metal density} \left[\frac{\text{g}}{\text{cm}^3}\right] \times \text{exposed area [cm}^2]\right] \times \frac{10[\text{mm}]}{1[\text{cm}]}$$

simplifying:

$$CR\left[\frac{\text{mm}}{\text{Year}}\right] = \frac{\Delta m \times 87600}{t \rho S}$$

Where ∆m is the mass loss (g), t is the corrosion time (h), ρ is the density of tested steel (7.90 g cm⁻³), and S is 
exposed area of the specimen (cm²).

Corrosion kinetics curves of the specimens are shown in figure 1. In the initial stage of corrosion, due to the 
rust layer is very thin, the ions in the corrosion solution diffuse directly to the surface of the matrix, and a strong 
electrochemical reaction occurs with the alloying element in the matrix, which promotes the corrosion process, 
so the corrosion rate is high. After 168 h corrosion, the corrosion rate reached a peak. At the later stage of 
corrosion, as the rust layer grows thicker, the alloying element and their compounds in the matrix are enriched 
in the rust layer, which increases the compactness of the rust layer, inhibits the direct reaction between the

![Figure 1. Corrosion kinetics curve of high manganese steel in wet-dry cyclic environment.](image-url)
corrosion medium and the matrix steel, and slows down the corrosion process. So the corrosion rate is very low and stable after 432 h corrosion.

The XRD diffraction patterns of corrosion products after different corrosion durations are shown in figure 2. The results show that the main corrosion products of tested steel in dry and wet alternating corrosion are lepidocrocite (γ-FeOOH), goethite (α-FeOOH), Chromite (FeCr₂O₄), iron oxide (FeO/Fe₂O₃/Fe₃O₄), manganese oxide (MnO/MnO₂/Mn₂O₃), and a small amount of iron and manganese oxide (Fe,Mn)ₓOᵧ and Nickel-Molybdenum oxide (NiMoO₄). γ-FeOOH is a semiconductor with strong electrochemical activity [22–24], it is easy to be reduced to some intermediate substance in corrosive medium and then oxidized again, which promotes the corrosion process. Due to γ-FeOOH special anion selectivity [25, 26], Cl⁻ can promote γ-FeOOH formation. Therefore, the diffraction peaks of corrosion products obviously show more γ-FeOOH. The corrosion products after 24 h and 72 h corrosion appear as the strong diffraction peaks of Fe, which is because the rust layer is thin at the initial stage of corrosion and is easy to be penetrated by X-rays. At the initial stage of corrosion, the iron and manganese oxides in the rust layer mainly exist in the form of Fe₂O₃ and MnO, and the stability is not strong. Especially manganese oxides have special porous structure and strong adsorption, which greatly promote the corrosion process. The corrosion kinetics curve also shows that the corrosion rate shows an upward trend before 168 h corrosion, at the later stage of corrosion, the corrosion rate tends to be stable. XRD diffraction pattern shows that a small amount of (Fe,Mn)ₓOᵧ appears in the corrosion products after 432 h corrosion, Its strong ion adsorption will not only reduce the density of the rust layer, but also promote the adsorption of anions in the corrosion solution, damage to the protection of the rust layer. The Fe₃O₄ and α-FeOOH of the rust layer in the later stage of corrosion increased. α-FeOOH are highly stable insulators with little activity, Fe₃O₄ is an electric conductor, which has good compactness and strong stability, and mainly exists in the inner rust layer, it can be attached to the surface of the matrix to enhance the protection of the rust layer.
FeCr$_2$O$_4$ belongs to spinel oxide film, which improves the compactness of rust layer and promotes the formation of protective rust layer. Their mutual inhibition makes the later corrosion process slow, the corrosion rate decreases and tends to be stable.

### 3.2. Surface and cross-section morphology of corrosion products

The surface morphology of corrosion products formed after different corrosion durations is shown in figure 3. During the initial corrosion stage, the corrosion products are less, the thinner corrosion products are loose and dispersed on the surface of the matrix, forming a lot of pores, which makes the corrosion solution easy to contact with the bare matrix. In the late stage of corrosion, with the growth and accumulation of corrosion products and the evolution of composition, the corrosion products also become thick and dense. The previous pore channels are also filled by new corrosion products. The steel matrix of the sample is separated from the corrosion solution by the rust layer, which effectively inhibits the corrosion process and reduces the corrosion rate. After 72 h of corrosion, the corrosion product is lamellar or flake bone rod, there are a large number of holes between the layers, very loose stacking distribution. As the corrosion time prolonged, after 288 h of corrosion, the lamellar corrosion products grew further, showing a large number of flocs, the surface of the flocs has numerous divergent needle flakes, forming deep holes between the flocs, it reflects that the primary rust layer grows thicker but still loose and not dense. After 600 h of corrosion, the flocculent corrosion products produce numerous spherical or cotton globules, and the holes and pores between the globules are also relatively shallow, indicating that the rust layer is already very thick and the surface is more uniform and smooth, more dense than the previous periods. Combined with XRD results, at the early and middle stages of corrosion, the main corrosion products are needle-like or snowflake-like $\gamma$-FeOOH. The needle-like $\gamma$-FeOOH can evolve into bulbous with the prolongation of corrosion $\alpha$-FeOOH, so it is observed that the divergent needle-like substance aggregates into floc, and then grows into bulbous substance. The later stage of corrosion, due to the increase of Fe$_3$O$_4$ and $\alpha$-FeOOH with better stability and compactness, the compactness of corrosion products is improved, which effectively hinders the diffusion of O$_2$ and anions in the corrosion solution to the matrix [29], inhibits the corrosion reaction process and reduces the corrosion rate.

The cross section morphologies of the corrosion products after different corrosion durations are shown in figure 4. The red contour and the blue dimension mark are the inner and outer contour of the rust layer and the average thickness of the rust layer each corrosion stages, respectively. The average thickness of the rust layer during the initial corrosion stage is only 5.5 $\mu$m. In this state, most of the matrix is exposed to the corrosion solution, and the direct contact with oxygen and ions in the corrosion medium accelerates the corrosion reaction [30]. As the corrosion time increases, the thickness of the rust layer increases [31]. After 72 h corrosion, many cracks and holes can be seen in the section of the rust layer, due to the cationic selective permeability of the rust layer, the anions are blocked at the anion-yang interface, and the high concentration of anions diffuses from the interface to the surface of the outer rust layer, causes the anion-yang interface to appear the big crack. After 168 h corrosion, the concave convex degree of the matrix side is the most obvious, indicating that the corrosion loss of the matrix is the most serious. After 432 h corrosion, the section of the rust layer has been more uniform.
and thick, and the inner and outer sides of the rust layer also show different forms; the outer rust layer is still loose, porous, and has the trend of outward growth, but the inner rust layer near the matrix is dense, and the section of the matrix is more uniform. It shows that the rust layer has certain protective ability. After 600 h corrosion, it can be observed from the cross-section morphology of the corrosion products that the inner and outer rust layers are all very dense. The outer rust layer is thin, and the thick and dense inner rust layer becomes a diaphragm, which prevents the corrosion medium from spreading to the matrix and plays a protective role to the matrix.

### 3.3. Element distribution and valence state of rust layer

Element distribution of corrosion products after corrosion for 24 h and 600 h is shown in figure 5. The alloying element Mn, Ni, Cr, Mo and Cu are enriched in different degrees in the corrosion products. Comparing the element content of corrosion products after 24 h and 600 h, the enrichment of Fe and Mn is the most obvious. The content of Mn and Ni is high in the products at the initial stage of corrosion, and the enrichment of Mn is significantly reduced at the later of corrosion. The enrichment of Cr and Mo at the later of corrosion is significantly higher than that at the initial corrosion stage. The content of Cu in the corrosion products at each stage is low and uniform with the increase of rust layer thickness. Due to the significant enrichment of Mn during the initial corrosion stage, the manganese rich phase is easy to lose electrons as anode in the electrochemical system of corrosion solution, which promotes the dissolution of anode metal element and speeds up the corrosion process [32]. Cu element is uniformly distributed in the rust layer, which enriches the composition of the corrosion products and improves the uniformity of the rust layer. In the later stage of corrosion, the content of Cr in the corrosion products increased significantly, and mainly enriched in the outer rust layer. The existence of Cr element inhibits the corrosion sensitivity of Mn element to the rust layer, and balances the corrosion reaction process [28]. The Cr oxide in the rust layer has a special spinel structure, which increases the compactness of the rust layer and forms a protective layer in the rust layer. The Ni is enriched in the inner rust layer near the matrix, which can change the properties of corrosion products, improve their corrosion potential, and promote the formation of goethite (α-FeOOH) [33–35]. Therefore, the peak of goethite also increases obviously in the XRD diffraction peak of rust layer in the later stage of corrosion. After 600 h, the content of Mo element in the corrosion products is higher, and the Mo oxide can form a stable passive film,
reduce the influence of chloride ion on corrosion, play an inhibition role [36–38], and enhance the protection of rust layer.

The XPS scanning spectrum of the corrosion product after 168 h, 288 h, 432 h corrosion of the sample, as shown in figure 6. The spectra show that the peaks of Fe2p, Mn2p, Cr2p, O1s and C1s are detected by the spectrum of corrosion products after three different corrosion stages. Mo3d peaks were also found in 288 h and 432 h spectra, and Ni2p peaks were detected in 432 h. Spectral peaks of the three corrosion phases indicate that Fe and Mn element play a significant role throughout the corrosion evolution, the main components are determined by the Fe2p and Mn2p peak fitting of the corrosion products after different time corrosion by Xpspeak4.1 software. The XPS patterns of iron and manganese element in the product after different corrosion times are shown in figure 7. After 168 h of corrosion, Fe2p3/2 and Fe2p1/2 of peak corresponding Fe (II) at 707.42 eV, 721.02 eV in Fe2p spectrum, Fe (+2) satellite peaks at 712.71 eV, the deconvolution peaks at 709.42 eV and 716.79 eV demonstrate the presence of Fe (+3) oxides and hydroxides (FeOOH) in the corrosion products, and the peak of Fe2p1/2 is 723.02 eV. After 288 h of corrosion, the peak 709.75 eV and 723.25 eV belongs to the Fe2p3/2 and Fe2p1/2 of the Fe (III), 714.43 eV and 717 eV are satellite peaks Fe2p3/2 in both valence states. After 432 h of corrosion, the Fe2p3/2 at 709.86 eV and the deconvolution peaks at 714.6 eV, 718.21 eV prove the main Fe2O3, FeOOH and Fe3O4 in the corrosion products. The Mn2p spectrum after 168 h corrosion, the Mn2p3/2 peaks at 638.06 eV and 639.63 eV demonstrate the presence of MnO and MnO2 in corrosion products, the peak of Mn2p1/2 at 648.76 eV, 651.33 eV corresponds to the Mn2p1/2 of Mn (+2) and Mn (+4), respectively.

3.4. Electrochemical measurement of corrosion products

Figure 8 showed the potentiodynamic polarization curves of corroded steel exposed for different time. From the results, the cathodic polarization curves of the steel rust layer of the sample are basically similar after different corrosion times, and the anodic polarization curves show different corrosion behaviors. The anodic polarization curves show that the rust layer in each corrosion stage has different degrees of passivation in the range of −0.2 V ~ −0.4 V. At the strong polarization region (the Tafel region), the polarization curve is basically a
According to analysis of the polarization curve, the corrosion current density can be obtained by the intersection of the straight line and the slope of the anode, and then the corrosion rate of the working electrode is judged. The larger the polarization slope of the anode in the active region, the smaller the corrosion current density, the greater the reaction resistance and the smaller the corrosion rate, indicating that the better the corrosion resistance of the protective film formed by the rust layer on the surface of the sample in this corrosion stage. According to the fitting results of Tafel parameters in table 2, the corrosion current density ($i_{corr}$), corrosion potential ($E_{corr}$) and corrosion time were plotted, as shown in figure 8(b). At the initial stage of corrosion, the corrosion potential of rust layer moves along the negative direction of $y$-axis, and the corrosion current density increases gradually, which indicates that the electrochemical activity of corrosion products is very strong at this time. At this stage, the rust layer did not form an effective protective film, and its composition promoted the corrosion process. In the middle and late stage of corrosion, the corrosion current density
decreases gradually with the forward movement of corrosion potential, indicating that the corrosion products in the middle and late stage of corrosion improve the electronegativity of the rust layer, reduce the electrochemical activity and increase the reaction resistance. With the increase of corrosion time, the corrosion products form a relatively dense and thermodynamically stable protective film, which reduces the dissolution of anode metal element and effectively prevents the diffusion of dissolved oxygen and corrosion ions to the matrix on the cathode side \[39, 40\], the corrosion reaction trend and corrosion reaction rate were reduced.

Figure 9 shows open circuit potential (OCP) and electrochemical impedance of the rust layer after corrosion for different durations. The corrosion film formed on the surface of the sample after alternate wet and dry corrosion for different durations was tested by open circuit potential for 1 h. The results show that the open circuit potential of the corrosion film on the surface of the sample moves first negative and then gradually positive along the $y$-axis with the extension of alternate wet and dry corrosion time. The Nyquist diagram of the rust layer of each corrosion stage can be seen as incomplete formed capacitive arc in high frequency region, and no other linear or diffusion arc is formed in low frequency region, which indicates that the corrosion process has only electrochemical reaction controlled charge transfer step. Due to the surface of the working electrode is a rough rust layer, which is equivalent to increasing the domain surface in the diffusion process, resulting in uneven electric field in the double layer. Therefore, the Nyquist diagram of the EIS of the sample rust layer shows that these capacitive arcs are not standard complete semicircle, but flattened semicircle. As shown in figure 9(c), in the relationship between frequency and phase angle of the EIS bode diagram, each curve presents a peak at low

Table 2. Polarization parameters of tested steel exposed to wet-dry cyclic environment for different time.

| Parameters | 24 h | 72 h | 168 h | 288 h | 432 h | 600 h |
|------------|------|------|-------|-------|-------|-------|
| $E_{corr}$ (V) | -0.932 | -0.950 | -1.006 | -0.909 | -0.882 | -0.829 |
| $i_{corr}$ (A/cm$^2$) | $9.81 \times 10^{-5}$ | $1.38 \times 10^{-4}$ | $6.18 \times 10^{-4}$ | $4.32 \times 10^{-4}$ | $2.40 \times 10^{-4}$ | $1.81 \times 10^{-4}$ |
The corrosion process of high manganese steel in the splash zone of seawater can be divided into three stages: the initial stage of corrosion, the middle stage of corrosion and the late stage of corrosion. The corrosion process of high manganese steel in the splash zone of seawater can be divided into three stages: the initial stage of corrosion, the middle stage of corrosion and the late stage of corrosion. During the initial stage of corrosion, the steel substrate exposed in the corrosion solution reacts directly with the O₂, H₂O and Cl⁻ ions in the corrosion medium, as shown in figure 11(a). The ionized Fe²⁺ ions are further oxidized to unstable corrosion intermediates such as FeO, Fe₂H₂O₇, 4H₂O and Fe³⁺(OH)₆Cl·2H₂O in high concentrations of dissolved oxygen and chloride ions, and further transformed into γ-FeOOH, α-FeOOH and 

\[ \text{FeOOH} \rightarrow \gamma-\text{FeOOH} \rightarrow \alpha-\text{FeOOH} \]

frequency and a Valley at high frequency. Therefore, it can be determined that there are two time constants for EIS of steel rust layer at each corrosion stage. Capacitive reactance arc is a constant phase angle element, which has the characteristics of porous electrode. In this test frequency range, there are not only the charging and discharging process of surface electric double layer, but also the influence of substrate surface corrosion reaction on current density. The larger the radius of the reactance arc indicates the charge transfer resistance in the corrosion process, the larger the radius of the reactance arc indicates the greater the charge transfer resistance [41–43]. As shown in figure 9(d), the relationship between frequency and impedance mode of the EIS bode diagram shows, with the increase of dry and wet corrosion time, the total impedance modulus at low frequency decreases first and then increases gradually. The results show that the corrosion resistance of the rust layer increases gradually during the corrosion process.

To evaluate the impedance capability of the protective film formed on the sample surface by corrosion products after different corrosion durations, the equivalent circuit (EEC) (figure 10) was used for impedance fitting analysis. The equivalent circuit code is \( R_s \) (\( Q_1 \) (\( R_p \) (\( Q_2 \) Rₜ)))).

Table 3 shows the fitting parameters of electrochemical impedance spectra of rust layer after different corrosion durations. \( Q_1 \) and \( Q_2 \) are the non ideal and parallel double layer capacitors of the corrosion products on the surface of the sample. \( R_s \) is the solution resistance. \( R_p \) is the resistance of charge transfer [44], which indicates the resistance of ion migration under the action of electric field. The larger the value is, the less anions are on the passive film. The surface of the working electrode only limited adsorbed active anions, which reduces the reaction speed of the negative and positive poles of the passive film and slows down the corrosion rate, thus improves the corrosion resistance. \( R_p \) is the resistance value of the corrosion product on the surface of the sample, the larger the value, the more stable the protective film formed by corrosion products on the substrate surface. It can be seen from table 3 that the \( R_p \) value fitted by EIS of the rust layer first decreases and then increases with the extension of corrosion durations, indicating that the corrosion resistance of the corrosion film gradually increases. These are consistent with the results of linear polarization curve and Nyquist diagram.

### 4. Discussions

The corrosion process of high manganese steel in the splash zone of seawater can be divided into three stages: the initial stage of corrosion, the middle stage of corrosion and the late stage of corrosion. During the initial corrosion stage, the steel substrate exposed in the corrosion solution reacts directly with the O₂, H₂O and Cl⁻ ions in the corrosion medium, as shown in figure 11(a). The ionized Fe²⁺ ions are further oxidized to unstable corrosion intermediates such as FeO, Fe₂H₂O₇, 4H₂O and Fe³⁺(OH)₆Cl·2H₂O in high concentrations of dissolved oxygen and chloride ions, and further transformed into γ-FeOOH, α-FeOOH and 

\[ \text{FeOOH} \rightarrow \gamma-\text{FeOOH} \rightarrow \alpha-\text{FeOOH} \]
At this stage, the energy spectrum shows that the main Fe, Mn and Ni of the alloy elements enriched in the corrosion products. The existing studies show that the electronegativity of Mn is lower than that of Fe and its ability to adsorb electrons is weaker than that of the latter two, so the manganese-rich region is easy to lose electrons and act as anode in electrochemical system in NaCl strong electrolyte solution, which accelerates the dissolution of iron matrix. The enrichment of Ni in the rust layer enriched by high Mn element did not show good corrosion resistance, which may be related to the Ni of divalent to replace the Fe$^{2+}$ formation NiFe$_2$O$_4$ in the Fe$_3$O$_4$. Because the electrochemical and chemical reactions are carried out simultaneously, the high manganese steel at the initial stage of corrosion shows a high corrosion rate.

During the middle stage of corrosion, the corrosion products grow and accumulate and attach to the surface of the steel matrix to form a corrosion film, the corrosion medium is isolated out of the rust layer and slows down the dissolution of the steel matrix, so the corrosion reaction mainly occurs in the rust layer during this process, as shown in figure 11 (b). The rust layer near the corrosion solution is loose, Mn oxides enriched in the outer rust layer have special pore structure and ion adsorption. This lead to the corrosion medium can still diffuse inward. Previous studies have shown that the Fe$_3$O$_4$ is mainly stored in the inner rust layer, and its good stability improves the compactness of the inner rust layer, so the main protective effect in the medium term of corrosion is the inner rust layer. Because of the special cation selective permeability of the rust layer, the anions are blocked at the yin-yang interface of the inner rust layer. A large number of anions agglomerate, which makes the concentration increase and diffuses from the interface of yin - yang to the outer rust layer, resulting in parallel cracks in the inner show layer. The dissolved oxygen in the corrosion medium diffuses inward through

![Figure 11](image_url)
the crack pores, which will continue to oxidize the FeO, Fe₂O₃, FeOOH in the corrosion products and transform them into Fe₃O₄, which further enhances the compactness and stability of the inner rust layer, so the corrosion rate at this stage begins to decrease obviously compared with the previous stage.

During the late stage of corrosion, the rust layer has become thick with the corrosion extension, and the corrosion reaction has become slow and stable compared with the previous two stages, as shown in figure 11(c). At this stage, the enrichment of alloying elements plays a major role in the corrosion of rust layer. Ni, Cr, Mo, Cu were enriched in the rust layer by EDS detection. Ni enrichment in the inner rust layer promotes the evolution of γ-FeOOH to α-FeOOH and increases the stability of the rust layer, it can also increase the self-rotation potential and enhance the electrochemical impedance of the corrosion products, which is in agreement with the EIS results. According to previous studies, the special spinel structure of Cr oxides increases the compactness of corrosion products and greatly mentions the protective ability of rust layer. The Cr of the outer rust layer enriched at the end of corrosion reduces the electrical conductivity of the rust layer, promotes the formation of FeOOH, inhibits the corrosion sensitivity of the Mn element to the rust layer and improves the compactness of the outer rust layer. Therefore, the later stage of corrosion rust layer stratification is not obvious. Many Mo are uniformly enriched in the rust layer, and the Mo oxides can form a stable passivation film to reduce the effect of Cl⁻ on corrosion. Moreover, some studies have shown that the NH₄⁺ generated by the reaction between the N-rich phase in steel and the electrolyte solution increases the pH value of the interface between the rust layer and the corrosion solution, creating a favorable environment for the formation of MoO₄²⁻, which can enhance the bipolar corrosion inhibition of corrosion film and improve the corrosion of rust layer, so the corrosion rate is very low and tends to be stable at the late of corrosion.

5. Conclusion

The corrosion kinetics, corrosion products, surface and cross-sectional morphology, elemental distribution and valence, polarization curves and EIS of the samples at different corrosion stages in dry-wet cyclic environment were analyzed by scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and electrochemical workstation. The conclusions are as follows:

1. The rust layer presents a double-layer structure of loose outer layer and dense inner layer in dry-wet cyclic corrosion environment. With the extension of corrosion time, the corrosion rate increases first and then decreases and tends to be stable. The increase of Fe₃O₄, α-FeOOH and FeCr₂O₄ in the corrosion products improves the stability and compactness of the rust layer, thereby inhibiting the corrosion of manganese iron oxides and slowing down the corrosion rate.

2. The corrosion performance of the rust layer is related to the enrichment of alloying elements. The Mn-rich phase at the initial corrosion stage accelerates the dissolution of anodic metal elements in the electrochemical system. The nickel oxides of the inner rust layer facilitated the transformation of goethite and increased the corrosion potential. Cr and Mo were obviously enriched at the end of corrosion, and the special spinel structure of Cr oxides in the outer rust layer enhanced the compactness of the rust layer. The molybdenum oxides can form a stable passivation film and reduce the effect of chloride ion on corrosion.

3. The Fe₂p and Mn₂p spectra of the corrosion products proved the difference in the valence states of Fe and Mn in the products at different corrosion times. The main components at 168 h and 288 h were Fe (II) and Fe (III) oxides and FeOOH, as well as Mn (+2) and Mn (+4) oxides. In the corrosion products at 432 h, except Fe₃O₄ and FeOH oxides, Mn existed in three valence states at the same time.

4. With the corrosion durations, the corrosion potential of the corrosion film of the sample first moved negatively along the y-axis and then moved positively. The corrosion current density increased first and then decreased. The resistance value (Rp) of the corrosion product film decreased first and then increased gradually, indicating that the protective effect of the corrosion product film is gradually significant.

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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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References

[1] Sohn S H, Hong S, Lee J, Sub C, Kim S K, Lee B I, Kim N J and Lee S 2015 Effects of Mn and Al contents on cryogenic-temperature tensile and charpy impact properties in four austenitic high-Mn steels Acta Mater. 100 39–52
[2] Choi K J, Lee S G, Park Y H, Han I W and Morris J W Jr 2012 High Manganese Austenitic Steel for Cryogenic Applications, in Twenty-Second International Offshore and Polar Engineering Conference (Rhodes, Greece, June 17–22, 2012) (The Twenty-second International Offshore and Polar Engineering Conference) 29–35 (Department of Materials Science and Engineering, University of California at Berkeley, California)
[3] Chang Y, Wang C Y, Zhao K M, Dong H and Yan J W 2016 An introduction to medium-Mn steel: metallurgy, mechanical properties and warm stamping process Mater. Des. 94 424–32
[4] Liu Z Y, Tang S, Chen J, Ye Q B and Wang G D 2015 Latest progress on development and production of steels for offshore platform and their development tendency Angew Technol. 1 1–7
[5] Hu J, Du L X, Liu H, Sun G S, Xie H, Yi H L and Misra R D K 2015 Structure-Mechanical property relationship in a low-C medium-Mn ultra high strength heavy plate steel with austenite-martensite submicro-laminate structure Mater. Sci. Eng. A 647 144–51
[6] Hu J, Du L X, Sun G S, Xie H and Misra R D K 2015 The determining role of reversed austenite in enhancing toughness of a novel ultra-low carbon medium manganese high strength steel Scr. Mater. 104 87–90
[7] Jeffrey R and Melchers R E 2009 Corrosion of V eritical mild steel strips in seawater Corr. Sci. 51 2291–7
[8] Xiang-rong Z, Gui-qiao H and Cai-feng L 1997 Study on the corrosion peak of carbon steel in marine splash zone Chin. J. Oceanol. Limn. 15 378–80
[9] Humble H 1949 Cathodic protection of steel piling in sea water Corrosion 5 292–302
[10] Wang H-D and Du M 2017 Corrosion behavior of a low-carbon steel in simulated marine splash zone Acta Metall. Sin. 30 1–9
[11] Mindong C et al 2018 Influence of rust permeability on corrosion of e960 steel in industrial and non-industrial marine splash zones J. Mater. Eng. Perform. 27 3742–9
[12] Ul-Hamid A, Saricimen H, Quddus A, Mohammed A I and Al-Hems L M 2017 Corrosion study of ss304 and ss316 alloys in atmospheric, underground and seawater splash zone in the arabian gulf, corros Eng. Sci. Techn. 52 p 134–40
[13] Fajardo S, Llorente I, Jiménez J A, Bastidas J M and Bastidas D M 2019 Effect of mn additions on the corrosion behaviour of twip fe-mn-al-si austenitic steel in chloride solution Corros. Sci. 154 246–53
[14] Nishimura T and Kodama T 2003 Clarification of chemical state for alloying elements in iron rust using a binary-phase potential–diagram and physical analyses Corr. Sci. 45 1073–84
[15] Kinmura M, Kihira H, Ohta N, Hashimoto M and Senuma T 2005 Control of Fe(O,OH)6 nano-network structures of rust for high atmospheric-corrosion resistance Corros. Sci. 47 2499–509
[16] Liu Z G, Gao X H, Yu C, Du L X, Li J P and Hao P J 2015 Corrosion behavior of low-alloy pipeline steel with 1% Cr under CO2 condition Acta Metall. Sin. (Engl. Lett.) 28 739–47
[17] Itagaki M, Nozue R, Watanabe K, Katayama H and Noda K 2004 Electrochemical impedance of thin rust film of low-alloy steels Corros. Sci. 46 1361–10
[18] Su G, Gao X, Zhang D, Cui C, Du L, Yu C, Hu J and Liu Z 2017 Offset effect of chromium on the adverse impact of manganese in a low-C medium-Mn steel with reversed austenite in the neutral salt spray condition Corrosion 73 1367–80
[19] Su G, Gao X, Huo M, Xie H, Du L, Xu J and Jiang Z 2020 New insights into the corrosion behaviour of medium manganese steel exposed to a NaCl solution spray Constr. Build. Mater. 261 1–12
[20] Khashayar M B, Pooria N, Mahmoud P and Nika Z 2019 The effect of surface modification on the corrosion protection ability of the passive films of sensitized UNS S31803 duplex stainless steel Corrosion Engineering, Science and Technology 54 174–83
[21] Khashayar M-B, Nika Z, Pooria N and Mahmoud P 2021 A survey on the passivity of tempered AISI 420 martensitic stainless steel Corros. Sci. 183 109304
[22] Tanaka H, Hatamaka N, Muguruma M, Ishikawa T and Nakayama T 2013 Influence of anions on the formation of artificial steelrust particles prepared from acidic aqueous f(e)ii-solution Corr. Sci. 66 136–41
[23] Singh D, Yadav S and Sahaj J 2008 Role of climatic conditions on corrosion characteristics of structural steels Corr. Sci. 50 93–110
[24] Hao L, Zhang S, Dong J and Ke W 2012 Evolution of corrosion of mcnpusion weathering steel unpolished to wet/dry cyclic tests in a simulated coastal atmosphere Corr. Sci. 58 175–80
[25] Alca ‘ntara J, Chico B, Díaz I, de la Fuente D and Morcillo M 2015 Airborne chloride deposit and its effect on marine atmospheric corrosion of mild steel Corros. Sci. 97 74–88
[26] Han W, Pan C, Wang Z Y and Yu G C 2014 A study on the initial corrosion behavior of carbon steel exposed to outdoor wet-dry cyclic condition Corros. Sci. 88 99–100
[27] Kamimura T, Hara S, Miyuki H, Yamashita M and Uchida H 2006 Composition and protective ability of rust layer formed on weathering steel exposed to various environments Corros. Sci. 48 2799–812
[28] Hao L, Zhang S X, Dong J H and Ke W 2012 A study of the evolution of rust on mo-cu-bearing fire-resistant steel unpolished to simulated atmospheric corrosion Corros. Sci. 54 244–50
[29] Han W, Pan C, Wang Z Y and Yu G C 2015 Initial atmospheric corrosion of carbon steel in industrial environment J. Mater. Eng. Perform. 24 864–74
[30] Guo Q, Liu J H, Yu J M and Li S M 2015 Influence of rust layers on the corrosion behavior of ultra-high strength steel 300 m subjected to wet-dry cyclic environment with chloride and low humidity Acta Metall. Sin. (Engl. Lett.) 28 139–46
[31] Wen C, Tian Y, Wang G, Hu J and Deng P 2016 The influence of nickel on corrosion behavior of low alloy steel in a cyclic wet-dry condition Int. J. Electrochem. Sci. 11 4161–73
[32] Ha H Y, Jang M H and Lee T H 2016 Influences of mn in solid solution on the pitting corrosion behavior of fe-23 wt%cr-based alloys Electrochim. Acta 191 864–75
[33] Dillmann P, Mazaudier F and Heerle S 2004 Advances in understanding atmospheric corrosion of iron. I. Rust characterisation of ancient ferrous artefacts exposed to indoor atmospheric Corrosion, Corr. Sci. 46 1401–29
[34] Nishimura T and Kodama T 2003 Clarification of chemical state for alloying element in iron rust using a binary-phase potential–ph diagram and physical analyses Corr. Sci. 45 1073–84
[35] Zhang Q, Wang J, Wu J, Zheng W, Chen J and Li A 2001 Effect of ion selective property on protective ability of rust layer formed on weathering steel exposed in the marine atmosphere Acta Metall. Sin. 37 193–6
[36] Mesquita T J, Chauveau E, Mantel M, Kinsman N, Roche V and Nogueira R P 2012 Lean duplex stainless steels—the role of molybdenum in pitting corrosion of concrete reinforcement studied with industrial and laboratory castings Mater. Chem. Phys. 132 967–72
[37] Lv J L, Liang T X and Wang C 2016 Surface enriched molybdenum enhancing the corrosion resistance of 316l stainless steel Mater. Lett. 171 38–41
[38] Thee C, Hao L, Dong J, Mu X, Wei X, Li X and Ke W 2014 Atmospheric corrosion monitoring of a weathering steel under an electrolyte film in cyclic wet–dry condition Corr. Sci. 78 130–7
[39] Yadav A P, Nishikata A and Tsuru T 2004 Electrochemical impedance study on galvanized steel corrosion under cyclic wet–dry conditions—influence of time of wetness Corr. Sci. 46 169–81
[40] Nady H, El-Rabiei M M and Samy M 2017 Corrosion behavior and electrochemical properties of carbon steel, commercial pure titanium, copper and copper–aluminum–nickel alloy in 3.5% sodium chloride containing sulfide ions, egypt J. Petrol. 26 79–94
[41] Cheng Z J, Song D, Jiang J Y, Jiang J H, Ma X L, You K and Ma A B 2016 Microstructure characteristic and electrochemical corrosion behavior of surface nano–crystallization modified carbon steel J. Iron. Steel Res. Int. 23 1281–9
[42] Seikh A H, Halla H, Baig M, Sohall M A and Khan 2017 Microstructure characterization and corrosion resistance behavior of new cobalt-free maraging steel produced through esr techniques J. Mater. Eng. Perform. 26 1589–97
[43] Raabe D, Sandløbes S, Millán J, Ponge D, Assadi H, Herbig M and Choi P–P 2013 Segregation engineering enables nanoscale martensite to austenite phase transformation at grain boundaries: a pathway to ductile martensite ActaMater. 61 6132–52
[44] Khashayar M B, Pooria N, Nika Z and Mahmoud P 2021 A detailed electrochemical analysis of sensitized AISI 410 martensitic stainless steel Mater. Res. Express 8 056501