



Atmospheric corrosion resistance of MnCuP weathering steel in simulated environments

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ABSTRACT

In this work, atmospheric corrosion resistance of low cost MnCuP weathering steel in simulated coastal, industrial, and coastal–industrial atmospheric environments was investigated by wet/dry cyclic acceleration corrosion tests. The results indicate that MnCuP weathering steel exhibits high corrosion resistance in the three atmospheres. Besides, the alloying effect of Mn, Cu, and P elements on the anti-corrosion mechanism of MnCuP weathering steel was discussed by techniques of X-ray photoelectron spectroscopy, potential–pH diagram, and electron probe microanalysis.

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1. Introduction

The effects of corrosion on our society are enormous, and it destroys more than three percent of the world's GDP [1]. More than 50% of that amount is caused by atmospheric corrosion [2]. Atmospheric corrosion of steels is an electrochemical interaction resulting between steel and its surrounding atmospheric environment [3]. Atmospheres containing chlorides and/or sulphur dioxide usually lead to much more severe corrosion damage [4,5]. The most effective and economical way in mitigating atmospheric corrosion of steel is alloying the steel with less than 3 mass% amounts of elements such as Cr, Ni, Cu, and P to develop weathering steels [6]. These steels can exhibit relatively 1–7 times higher corrosion resistance than carbon steel does [7,8] in many types of atmospheres with certain environmental properties, due to its ability in forming a compact, adherent rust layer (corrosion product) during extended exposure to natural atmospheric environments [9,10]. Accordingly, painting or galvanizing, which is usually required for protecting carbon steel [11], can be avoided, and therefore leads to a reduction in self-supporting weight and maintenance cost of steel structures [12]. COR-TEN weathering steels, alloyed with Cu, P, Cr, and Ni, have been widely used since they were developed by US Steel Corp. in the 1930s [6,13]. Decades of application and practice have demonstrated that the steels exhibit high corrosion resistance in coastal atmospheres (containing Cl[−]) when a protective rust layer responsible for the high corrosion resistance has been formed after a long

term exposure, and they have been widely employed in the construction of bridges, transmission towers, buildings, guardrails, and lighting poles [14–16]. Yamashita et al. [17] clarified the effect of Cr in enhancing the corrosion resistance of weathering steel and explained its mechanism. Chromium accumulates only in the inner rust layer, leading to the formation of a dense and compact rust layer with improved ability for protecting the steel against the corrosive atmosphere. In addition, Cr³⁺ in the rust layer is coordinated with O^{2−} and positioned in the double chains of vacant sites within the FeO₃(OH)₃ octahedra network in the goethite crystal, leading to improved protective performance. Chen et al. [18] reported that rust layers on weathering steels containing more than 4 mass% Ni is cation-selective. Besides, Fe is substituted by Ni and the inverse spinel oxide, NiFe₂O₄, is formed, which enhances the corrosion resistance of Ni-alloying steel [19].

As the traditional COR-TEN weathering steels contains elements Cr and Ni, and their costs are relatively high. During the 21st century, lower cost and higher performance weathering steels were developed, driven by the need to develop steels that were more resistant to the deteriorating atmosphere, particularly with the rise in SO₂ (acid rain) along with chloride ion in polluted marine atmospheres [8]. For example, MnCu steel is a low cost weathering steel, not alloyed with Cr and Ni [20] that exhibits a high corrosion resistance in coastal atmospheres. However, its corrosion resistance in industrial atmospheres is even worse than that of Q235 carbon steel [21]. Phosphorous is an abundant and low cost element, and it is traditionally believed that higher P content can lead to the development of cold brittleness in the steel, due to its segregation on the grain boundaries, but Liu et al. [22] have found that refinement,

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especially ultra-refinement, of the steel grain size can greatly alleviate this problem. Recently, Dong et al. [23] alloyed MnCu weathering steel with P element aiming at that the steel can show high corrosion resistance not only in coastal atmospheres but also in industrial atmospheres and in coastal–industrial atmospheres that contain Cl^- and SO_2 .

It is well known that the field investigation of atmospheric corrosion provides actual information on corrosion of materials [2,3], and it is the most important method for investigating atmospheric corrosion [6,7]. However, it usually takes about 10–20 years for one evaluation test, which makes it difficult to evaluate new materials designed to resist atmospheric corrosion [6,9,10]. In view of the disadvantages of field exposure test, several simulated atmospheric corrosion tests enabling the acceleration of corrosion have been developed in the last decades [2,16]. Wet/dry cyclic corrosion test (CCT) [14,19], based on saltwater spray followed by drying, can simulate atmospheric corrosion under controlled relative humidity (RH) and temperature. The present study was focused on the corrosion resistances of MnCuP weathering steel in simulated coastal atmosphere, industrial atmosphere, and coastal–industrial atmosphere submitted to CCTs. Besides, the anti-corrosion mechanism of MnCuP weathering steel was discussed by X-ray photoelectron spectroscopy (XPS), potential (E)–pH diagrams and electron probe microanalyzer (EPMA) analysis.

2. Experimental

16Mn steel, Q235 steel, MnCu steel, and MnCuP steel were employed in this investigation with their composition being listed in Table 1 [23]. The steel was embedded in epoxy resin, schematic diagram in Fig. 1, and then the sample was ground with SiC paper down to 600 grade emery paper. After being cleaned with ethanol, the samples were stored in a desiccator for 24 h, and then subjected to the wet/dry cyclic corrosion test [14,19]. It consisted of [16]: (I) Weighing the initial sample; (II) Wetting the sample surface with $40 \mu\text{L cm}^{-2}$ corrosion electrolyte; (III) Drying the sample in a chamber maintained at 30°C and 60% RH for 12 h; (IV) Re-weighing the sample after drying; (V) Rinsing the sample with distilled water to prevent progressive salt accumulation and drying them before fresh application of corrosion electrolyte; (VI) Repeating the above steps from (II) to (V) for different CCT numbers. One N (CCT number) equals to a half day. The electrolytes were: 0.1 mass% Na_2SO_3 with pH = 4.0 (simulating an industrial atmosphere), 0.3 mass% NaCl (simulating a coastal atmosphere), and 0.3 mass% NaCl + 0.1 mass% Na_2SO_3 with pH = 4.0 (simulating a coastal–industrial atmosphere). The rusted sample for cross-sectional analysis was observed using EPMA (electron probe microanalyzer, EPMA-6010) for detecting the distribution of P element at test condition of $U = 15 \text{ kV}$, $I = 100 \text{ nA}$.

3. Results and discussion

3.1. Atmospheric corrosion resistance of MnCuP weathering steel

For extensive tests, the atmospheric corrosion kinetics of steels can be expressed by following Equation [6,8,14,15]:

Table 1
Chemical compositions of the steels tested (mass%).

Sample	C	Si	Mn	P	S	Cu
16Mn steel	0.16	0.47	1.53	0.014	0.018	0.05
Q235 steel	0.21	0.21	0.58	0.017	0.036	0.02
MnCu steel	0.17	0.31	1.50	0.019	0.012	0.29
MnCuP steel	0.14	0.41	1.38	0.066	0.011	0.32

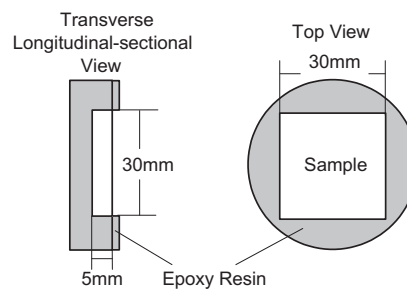


Fig. 1. Schematic diagrams of the sample used for wet/dry cyclic corrosion test.

$$\Delta W = AN^n \quad (1)$$

where ΔW is weight gain (mg), N is CCT number (corrosion time), A and n are constants. In log–log coordinates, this corrosion kinetics can be fitted by Eq. (2) produced by taking the logarithm of Eq. (1):

$$\log \Delta W = \log A + n \log N \quad (2)$$

Moreover, the first derivative of Eq. (1) gives the instantaneous corrosion rate V_i ($\text{mg cm}^{-2} \text{ d}$) Eq. (3) [14,15]:

$$V_i = 2 \frac{d\Delta W}{dN} = 2AN^{n-1} \quad (3)$$

It is obvious that A is equivalent to the weight gain when the CCT number is unity, and A is therefore considered a measure of the initial corrosion resistance of the sample. Conversely, the exponent n reflects the characteristic of the corrosion kinetics, that is to say, $n < 1$ means a corrosion deceleration process; $n > 1$ means a corrosion acceleration process, and $n = 1$ means the corrosion rate is constant [4]. A smaller n value indicates a lower corrosion tendency during the stage.

Fig. 2 shows the weight gain results for 16Mn, Q235, MnCu, and MnCuP steels in simulated coastal atmosphere as a function of CCT number in log–log coordinates. MnCu steel shows better corrosion resistance than 16Mn steel and Q235 steel, respectively and this is in accordance with the field exposure test [21]. After 20 CCT, MnCuP steel shows the lowest weight gain compared with other three steels, indicating the best resistance of MnCuP steel among the four to corrosion in simulated coastal atmosphere. Besides, for each of the steels, the whole corrosion process can be divided into two stages: a higher slope for the first segment line and a lower slope for the second segment line. The fitting equations and correlation coefficient (R^2) of different stages are shown in Table 2. During the first stage, the n value for MnCuP steel is lower than 1, but the n values for the other steels are all higher than 1, indicat-

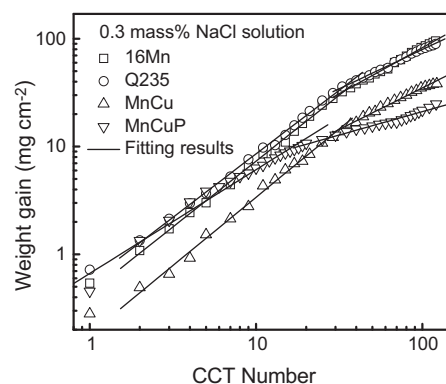


Fig. 2. Corrosion weight gain results of different steels exposed to simulated coastal atmosphere.

ing the best corrosion resistance of MnCuP steel during the initial corrosion stage. During the second stage, the n values for the steels are all lower than 1, indicating the corrosion deceleration process. Also, MnCuP steel has the lowest n value, showing its best corrosion resistance among the four steels.

Based on the fitting results in Table 2, Fig. 3 shows the fitted instantaneous corrosion rate results for the steels as a function of CCT number. It is evident that the corrosion rate of 16Mn, Q235, MnCu steels increases during the first corrosion stage with increasing the CCT number and then decreases after the transition point. However, the corrosion rate of MnCuP steel decreases during the whole corrosion process, although it is higher during the first corrosion stage than that after the transition point, indicating the best resistance of MnCuP steel to simulated coastal atmospheric corrosion during the whole test. Moreover, the transition point of MnCuP steel is earlier than that of other steels, indicating that a protective rust layer can be formed on MnCuP steel in a short exposure time.

Fig. 4 shows the weight gain results for Q235, 16Mn, MnCu, and MnCuP steels in simulated industrial atmosphere as a function of CCT number. Table 3 shows the fitting results in Fig. 4. During the first corrosion stage, MnCuP steel shows the highest n and A values, indicating that MnCuP steel exhibits worse corrosion resistance than MnCu, 16Mn, and Q235 steels. However, during the second corrosion stage, MnCuP steel shows the lowest n and A values, indicating that MnCuP steel exhibits better corrosion resistance than MnCu, 16Mn, and Q235 steels. MnCu steel shows almost the same corrosion weight gain with Q235 steel, and their resistances are better than that of 16Mn steel in simulated industrial atmosphere. This is in accordance with the exposure test results reported by Yan et al. [21].

The fitted corrosion rate results for Q235, 16Mn, MnCu, and MnCuP steels in simulated industrial atmosphere are shown in Fig. 5. The corrosion rate of Q235, 16Mn and MnCu steels increases gradually with increasing the CCT number during the first corrosion stage, and then decreases gradually after the transition point. However, for MnCuP steel, the corrosion rate decreases gradually during the whole corrosion stage. Besides, it can be seen that the corrosion rate of MnCuP steel during the first corrosion stage is higher than that of the other steels. The higher corrosion rate of MnCuP steel during the first corrosion stage can contribute to the uniform corrosion of the steel, promoting the formation of a compact and protective rust layer on the whole steel surface. So, we can conclude that MnCuP steel shows much higher atmospheric corrosion resistance than Q235, 16Mn, and MnCu steels in simulated industrial atmosphere. Moreover, the transition point of MnCuP steel is earlier than that of other steels, indicating that a protective rust layer can be formed on MnCuP steel in a short exposure time.

Fig. 6 shows the weight gain results for Q235 and MnCuP steels in simulated coastal–industrial atmosphere. Q235 steel exhibits an abnormal weight gain behaviour during the wet/dry cyclic corrosion test. As can be seen from the fitting results in Table 4, during the first corrosion stage, the n value for Q235 steel is 0.74 and, during the second corrosion stage, the n value is 0.94. The two n values are lower than 1, indicating the corrosion deceleration tendency

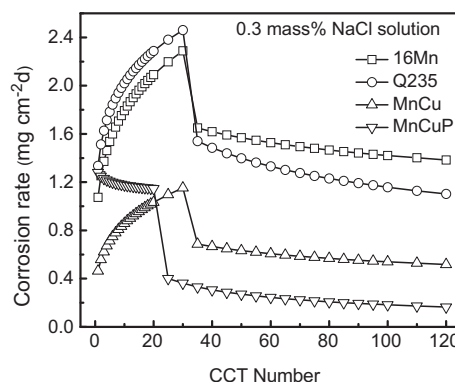


Fig. 3. Corrosion rates of different steels exposed to simulated coastal atmosphere.

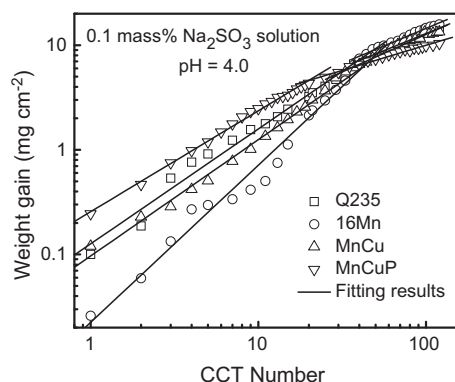


Fig. 4. Corrosion weight gain results of different steels exposed to simulated industrial atmosphere.

Table 3
Regression coefficients of the corrosion data in Fig. 4.

	The first segment	The second segment
Q235 steel	$y = -3.90 + 1.10x, R^2 = 0.99$	$y = -3.18 + 0.65x, R^2 = 0.99$
16Mn steel	$y = -4.65 + 1.50x, R^2 = 0.99$	$y = -3.18 + 0.67x, R^2 = 0.99$
MnCu steel	$y = -4.01 + 1.11x, R^2 = 0.99$	$y = -3.33 + 0.72x, R^2 = 0.99$
MnCuP steel	$y = -3.59 + 0.97x, R^2 = 0.99$	$y = -2.96 + 0.48x, R^2 = 0.99$

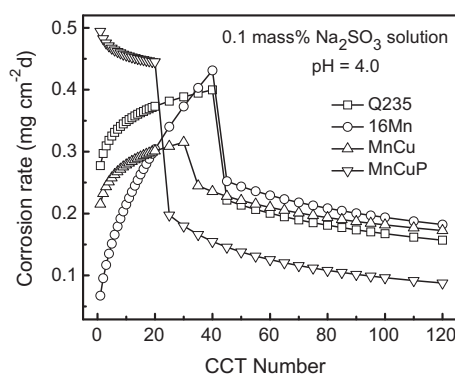


Fig. 5. Corrosion rates of different steels exposed to simulated industrial atmosphere.

Table 2
Regression coefficients of the corrosion data in Fig. 2.

	The first segment	The second segment
16Mn steel	$y = -3.36 + 1.22x, R^2 = 0.99$	$y = -2.80 + 0.86x, R^2 = 0.99$
Q235 steel	$y = -3.25 + 1.18x, R^2 = 0.99$	$y = -2.56 + 0.73x, R^2 = 0.99$
MnCu steel	$y = -3.74 + 1.27x, R^2 = 0.99$	$y = -3.00 + 0.77x, R^2 = 0.99$
MnCuP steel	$y = -3.18 + 0.96x, R^2 = 0.99$	$y = -2.54 + 0.43x, R^2 = 0.99$

during the first stage and the second stage, respectively. But, the higher n value for the second stage than the n value for the first stage, indicating that the corrosion rate of Q235 steel during the second stage is higher than it is during the first stage in simulated

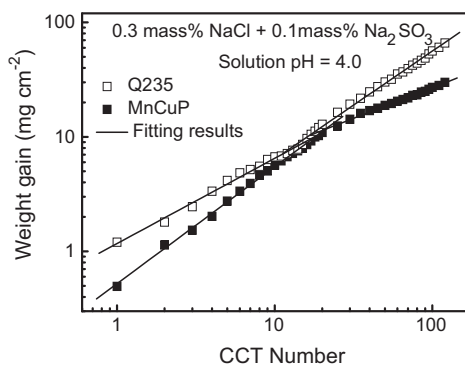


Fig. 6. Corrosion weight gain results of different steels exposed to simulated coastal–industrial atmosphere.

Table 4

Regression coefficients of the corrosion data in Fig. 6.

	The first segment	The second segment
Q235 Steel	$y = -2.93 + 0.74x, R^2 = 0.99$	$y = -3.14 + 0.94x, R^2 = 0.99$
MnCuP Steel	$y = -3.28 + 1.02x, R^2 = 0.99$	$y = -2.64 + 0.54x, R^2 = 0.99$

coastal–industrial atmosphere. However, MnCuP steel shows higher n and A values than Q235 steel during the first corrosion stage, it shows lower n and A values than Q235 steel during the second corrosion stage, indicating that MnCuP steel exhibits higher resistance than Q235 steel to corrosion in simulated coastal–industrial atmosphere containing Cl^- and SO_2 . Moreover, as indicated in Fig. 6, from 10 CCT to 20 CCT, especially around the transition point, the weight gain results are not linear, indicating the transition process during this short duration. This may be responsible for the sudden change in the fitted corrosion rate at the transition point in Fig. 7.

Fig. 7 shows the fitted corrosion rate results for Q235 steel and MnCuP steel. During the first corrosion stage, the corrosion rate of Q235 steel is lower than that of MnCuP steel. But, after the transition point, during the second corrosion stage, the corrosion rate of MnCuP steel is much lower than that of Q235 steel, indicating that the rust layer formed on MnCuP steel is protective and this effect becomes prominent with increasing the CCT number. The higher corrosion rate of MnCuP steel during the initial corrosion stage can contribute to the uniform corrosion of the steel, promoting the formation of a compact and protective rust layer on the whole substrate surface. So, it can be concluded that MnCuP steel shows

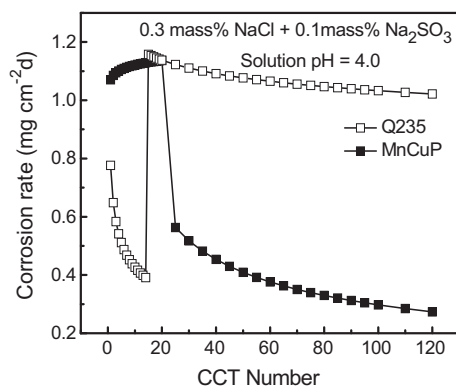


Fig. 7. Corrosion rates of different steels exposed to simulated coastal–industrial atmosphere.

much higher atmospheric corrosion resistance than Q235 steel in simulated coastal–industrial atmosphere.

3.2. Anti-corrosion mechanism of MnCuP weathering steel

It is believed that the formation of a protective rust layer on weathering steel is responsible for its higher corrosion resistance [24,25], and the alloy elements are usually accumulated in this layer [26,27]. To illustrate the chemical states of Mn and Cu elements in the rust, XPS analysis in Fig. 8 have been conducted. The result of Mn 2p_{3/2} peak around 641 ± 0.1 eV indicates its bivalent state Mn(II) corresponding to the presence of MnFe_2O_4 [28], and the result of Cu 2p_{3/2} peak around 932.6 ± 0.1 eV indicates its univalent state Cu(I) corresponding to the presence of CuFeO_2 [29]. Potential (E)-pH diagram has been employed to further understand the stable region for MnFe_2O_4 , CuFeO_2 , and Fe_3O_4 . Table 5 shows the equilibrium equations used in the present calculations of E -pH diagram. Compounds or species considered and their standard Gibbs free energy $\Delta G^0(298.15)$ values are listed in Table 6 [30–32]. The E -pH relationships are calculated by Nernst's Equation (4):

$$E(T) = E^0(T) + \frac{RT}{nF} \ln \frac{a_O}{a_R} = \frac{\sum \nu \Delta G^0(T)}{nF} + \frac{RT}{nF} \ln \frac{a_O}{a_R} \quad (4)$$

Fig. 9 shows the E -pH diagram for Fe–Mn–Cu–H₂O system at 298.15 K. Black lines separate the stable regions for Fe_3O_4 ; blue lines separate the stable regions for MnFe_2O_4 ; red lines separate the stable regions for CuFeO_2 . The oxygen and hydrogen equilibria at 1 atm. are represented by dash line. The concentrations of the cations and anions are supposed to be 10^{-4} mol L⁻¹. Clearly, in the region where MnFe_2O_4 , CuFeO_2 and Fe_3O_4 overlap, the three compounds may coexist. It was assumed that Mn(II) and Cu(I) were involved in the formation of reverse spinel oxide Fe_3O_4 . Fig. 10 shows the structure of Fe_3O_4 crystal with one Fe(II)-centred octahedron (FeO_6), one Fe(III)-centred octahedron (FeO_6), and one

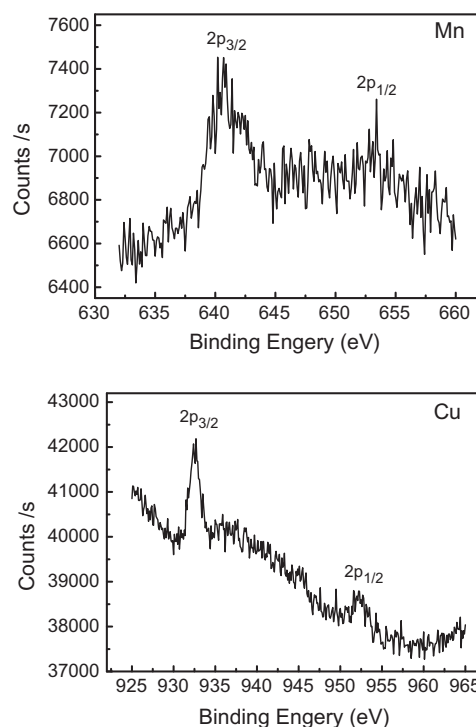


Fig. 8. XPS spectra of Mn and Cu elements in the rust layer on MnCuP weathering steel after 120 CCT in simulated coastal atmosphere.

Table 5Equilibrium equations for the stable ranges of Fe_3O_4 , CuFeO_2 , and MnFe_2O_4 used in E-pH calculations.

<i>Fe–H₂O system (Fe_3O_4)</i>		
(a)	$3\text{Fe}^{2+} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}$	$E = 0.8810 + 0.5 \times 0.0592 \times (-3\log[\text{Fe}^{2+}] - 8 \times \text{pH})$
(b)	$3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 2\text{H}^+ + 2\text{e}$	$E = -0.0477 + 0.5 \times 0.0592 \times (-2 \times \text{pH})$
(c)	$2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} = 3\text{Fe}_2\text{O}_3 + 2\text{H}^+ + 2\text{e}$	$E = 0.2339 + 0.5 \times 0.0592 \times (-2 \times \text{pH})$
<i>Fe–Cu–H₂O system (CuFeO_2)</i>		
(d)	$\text{Cu}^{2+} + \text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{CuFeO}_2 + 4\text{H}^+$	$1.3824 = 4 \times \text{pH} + \log[\text{Fe}^{2+}] + \log[\text{Cu}^{2+}]$
(f)	$\text{Cu} + \text{Fe}^{2+} + 2\text{H}_2\text{O} = \text{CuFeO}_2 + 4\text{H}^+ + 2\text{e}$	$E = 0.3802 + 0.5 \times 0.0592 \times (-\log[\text{Fe}^{2+}] - 4 \times \text{pH})$
(e)	$3\text{Cu} + \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} = 3\text{CuFeO}_2 + 4\text{H}^+ + 4\text{e}$	$E = 0.1299 + 0.25 \times 0.0592 \times (-4 \times \text{pH})$
(g)	$\text{CuFeO}_2 + 2\text{H}_2\text{O} = \text{FeOOH} + \text{CuO}_2^{2-} + 3\text{H}^+ + \text{e}$	$E = 2.9575 + 1 \times 0.0592 \times (\log[\text{CuO}_2^{2-}] - 3 \times \text{pH})$
(h)	$\text{CuFeO}_2 + \text{H}_2\text{O} = \text{FeOOH} + \text{CuO} + \text{H}^+ + \text{e}$	$E = 1.0580 + 1 \times 0.0592 \times (-1 \times \text{pH})$
(i)	$\text{CuFeO}_2 + \text{H}^+ = \text{Cu}^{2+} + \text{FeOOH} + \text{e}$	$E = 0.6227 + 1 \times 0.0592 \times (\log[\text{Cu}^{2+}] + 1 \times \text{pH})$
<i>Fe–Mn–H₂O system (MnFe_2O_4)</i>		
(j)	$\text{Mn}^{2+} + 2\text{FeOOH} = \text{MnFe}_2\text{O}_4 + 2\text{H}^+$	$13.4724 = 2 \times \text{pH} + \log[\text{Mn}^{2+}]$
(k)	$2\text{Fe}_3\text{O}_4 + 3\text{Mn}^{2+} + 4\text{H}_2\text{O} = 3\text{MnFe}_2\text{O}_4 + 8\text{H}^+ + 2\text{e}$	$E = 1.5472 + 0.5 \times 0.0592 \times (-3\log[\text{Mn}^{2+}] - 8 \times \text{pH})$
(l)	$3\text{Mn}(\text{OH})_3^- + 2\text{Fe}_3\text{O}_4 + \text{H}^+ = 3\text{MnFe}_2\text{O}_4 + 5\text{H}_2\text{O} + 2\text{e}$	$E = -1.4914 + 0.5 \times 0.0592 \times (-3\log[\text{Mn}(\text{OH})_3^-] + 1 \times \text{pH})$
(m)	$3\text{MnFe}_2\text{O}_4 + 4\text{H}_2\text{O} = 6\text{FeOOH} + \text{Mn}_3\text{O}_4 + 2\text{H}^+ + 2\text{e}$	$E = 0.6173 + 0.5 \times 0.0592 \times (-2 \times \text{pH})$

Table 6

Thermodynamic data of used species.

Species	$\Delta G^0(298.15 \text{ K})$ (J mol ⁻¹)	Source	Species	$\Delta G^0(298.15 \text{ K})$ (J mol ⁻¹)	Source
H ₂	0	[31]	O ₂	0	[31]
H ⁺	0	[31]	H ₂ O	-237191	[32]
Fe	0	[31]	Fe ²⁺	-78900	[32]
FeO	-256354	[31]	Fe ₂ O ₃	-740986	[31]
Fe ₃ O ₄	-1015450	[31]	FeOOH	-485300	[30]
HFeO ₂ ⁻	-379183	[31]	Cu	0	[31]
Cu ²⁺	65490	[32]	CuO	-129700	[31]
CuO ₂ ²⁻	-183600	[31]	CuFeO ₂	-479900	[31]
Mn ²⁺	-228100	[32]	Mn(OH) ₃ ⁻	-744200	[31]
Mn ₃ O ₄	-1283200	[31]	MnFe ₂ O ₄	-1121790	[31]

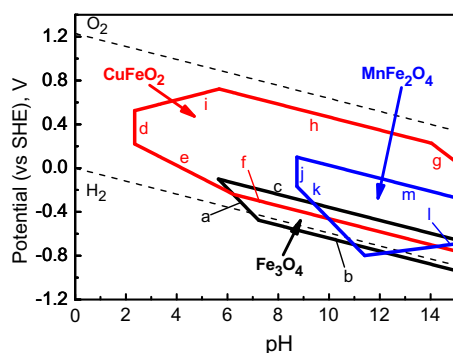


Fig. 9. E-pH diagram for the Fe–Mn–Cu–H₂O system at 298.15 K. Black lines separate the stable regions for Fe_3O_4 ; blue lines separate the stable regions for MnFe_2O_4 ; red lines separate the stable regions for CuFeO_2 . The oxygen and hydrogen equilibria at 1 atm. are represented by dash line. The concentrations of the cations and anions are supposed to be $10^{-4} \text{ mol L}^{-1}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fe(III)-centred tetrahedron (FeO_4) [33]. One Mn(II) substitutes one Fe(II) and occupies in the octahedral centre of Fe_3O_4 crystal. One Cu(I) substitutes one Fe(III) and occupies in the tetrahedron centre of Fe_3O_4 crystal, leading to the electronegativity of the crystal [34]. Therefore, the rust can repel the penetration of chloride ions, contributing to the cation-selectivity of the rust layer in the presence of chloride ions.

Moreover, the presence of Cu retards the growth of rust and suppresses the supply of oxygen to the steel surface; Cu reduces the conductivity of the rust; Cu precipitates and covers the steel substrate; Cu retards the crystallization of rust and contributes to a uniform dissolution of the steel and the formation of a rust layer

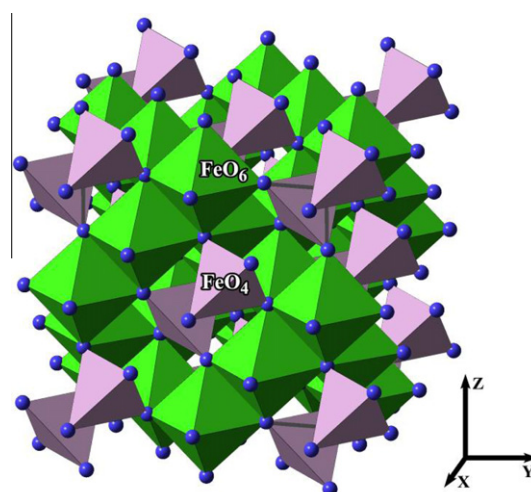


Fig. 10. Structure of Fe_3O_4 with Fe(III)-centred tetrahedron (FeO_4) and Fe(II)-centred octahedron (FeO_6).

at the initial corrosion stage [2]. It is believed that crystalline phosphate in the rust could be formed either in the presence of oxidizers or due to a large number of wet/dry cycles [34–36]. Fig. 11 shows the EPMA result of P element distribution in the rust layer on MnCuP steel with non-soluble phosphates being detected. With the progress of corrosion process, phosphorus can be oxidized into PO_4^{3-} [37], which may act as corrosion inhibitor contributing to the decreased anodic dissolution rate and cathodic reduction rate. Meanwhile, PO_4^{3-} can react with Fe^{2+} or Mn^{2+} to form non-soluble phosphates, which can lower the penetration of corrosive electrolyte to steel substrate. In addition, PO_4^{3-} has strong complexing action with H^+ , resulting in decreased cathodic hydrogen evolution rate and lower dissolution rate of H^+ to the steel [37,38].

4. Conclusions

- (1) The wet/dry cyclic corrosion test indicates that MnCuP weathering steel shows high resistance to corrosion not only in simulated coastal atmosphere, but also in simulated industrial atmosphere and in simulated coastal–industrial atmosphere.
- (2) During the three simulated atmospheres, the whole corrosion process of MnCuP weathering steel can be divided into two corrosion stages. The corrosion rate is higher during the first corrosion stage than it is during the second corrosion stage.

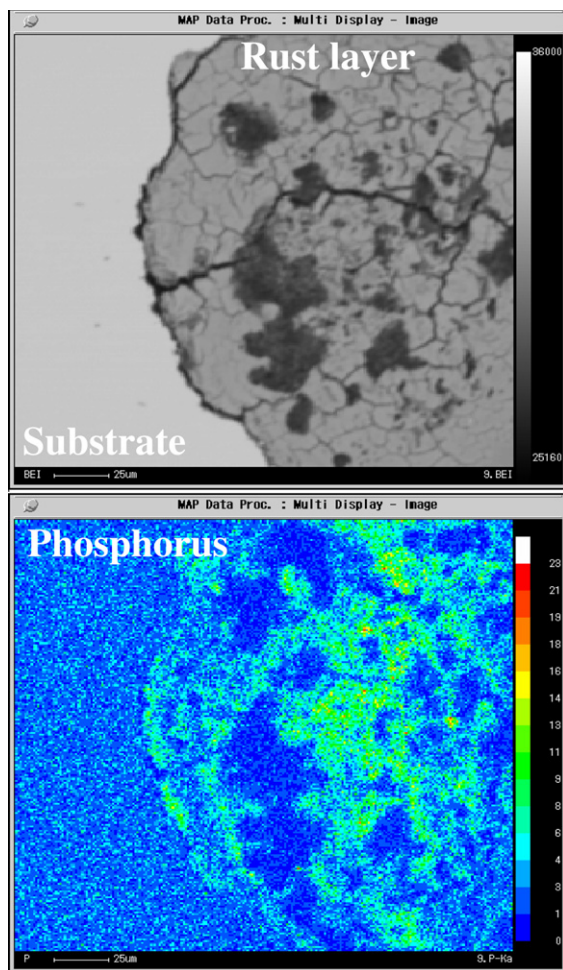


Fig. 11. EPMA mapping of phosphorus element in the rust layer on MnCuP weathering steel after 120 CCT in simulated industrial atmosphere.

- (3) Manganese and copper are identified in bivalent state and univalent state, respectively and may contribute to cation-selectivity of the rust layer in the presence of chloride ions. Phosphorus can promote the formation of non-soluble phosphates, which may act as corrosion inhibitor in the presence of hydrogen ions.

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