Mechanical Properties of Native Rust Layer Formed on a Low Alloy Steel Exposed in Marine Atmosphere

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Low alloy steel panels, exposed in marine atmosphere for 4 years, formed a compacted rust layer which could suppress the penetration of corrosive electrolyte and lower the corrosion rate. But in practical applications, the protective reliability is limited by the mechanical properties of the rust layer under the action of various loads. This paper presented the first attempt to evaluate the variation of mechanical properties of the protective rust layer with the exposure term by means of micro-indentation testing. Based on the analysis of energy release during cracking, the fracture toughness and the adhesion strength of the rust layer were evaluated. Results showed that the fracture toughness and adhesion strength of the rust layer were improved with the prolongation of the exposure term, the adhesion strength of the rust layer was higher than the fracture toughness of the rust layer itself.

KEY WORDS: atmospheric corrosion; low alloy steel; micro-indentation; rust layer.

1. Introduction

In 1916, American Society of Testing Materials initiated the investigation of the atmospheric corrosion of materials.¹⁾ In the 1930s, U.S Steel Corporation discovered weathering steels with a good resistance to atmospheric corrosion in industrial and rural environments by adding certain amount of Cu, P and other alloying-elements.²⁾ But the weathering steels could not form protective rust layer and had a higher corrosion rate in the case of existence of Cl^- .^{3,4)} Yamashita^{5,6)} investigated the atmospheric corrosion of weathering steel containing certain amount of Cr exposed in marine atmosphere for over 20 years, and found that the native rust layer was composed of two layers, the inner layer was compacted and enriched with Cr. Literature⁷⁾ reported that such protective rust layer has a phase constituent of alpha Cr-substituted ferric oxyhydroxide ($\alpha\text{-(Fe}_{1-x}\text{Cr}_x\text{)OOH}$). Ion selective measurements indicated that the rust layer with the phase constituent of $\alpha\text{-(Fe}_{1-x}\text{Cr}_x\text{)OOH}$ and could suppress the penetration of Cl^- , which helped to accelerate the formation of compacted rust layer. However, in practical application most structures, such as bridges and containers, have to bear various loads. The rust layer with poor properties is easy to crack or to be peeled off from the substrate, resulting in a high corrosion rate just like before the protective rust layer formed. Therefore the protective performance and reliability of the compacted rust layer are limited by its mechanical properties, and it is meaningful to study the mechanical properties and adhesion strength of the com-

pacted rust layer formed on the substrate steel.

In this work, the fracture toughness of compacted rust layer, and bonding strength between rust layer and substrate steel have been evaluated by means of indentation testing based on the energy release during cracking.

2. Experiments

2.1. Atmospheric Exposure

The plates of low alloy steel (60 mm×100 mm×4 mm) and carbon steel (60 mm×100 mm×4 mm) facing south at an angle of 45° to horizon, were exposed for up to 4 years at the coast of Shanghai area in the southeast of China. The corrosion rate was calculated considering the total affected area, weight loss and metal density. The composition of the steels was given in **Table 1**, the meteorological data and atmospheric contamination data are given in **Table 2**.

2.2. Analysis of Rust Layer

Specimens were fixed using an epoxy resin, grounded on emery papers, and polished with diamond paste. The outer loose rust layer on the steel was easily descaled from the substrate, and the inner one was carefully scraped off from the substrate using a razor. The phase constituent of the rust was identified by means of XRD using Rigaku Dmax-rC X-ray diffractometer. Cross sections of the surface rust layers were observed using LEICA MEF4M optical microscopy. The EPMA was carried out using JOEL 733.

Table 1. Chemical composition (wt%) of steel exposed at the coast of Shanghai city in the southeast of China.

Steel	C	S	P	Mn	Si	Cr	Cu	Rare Elements
Low alloy steel	0.050	0.005	0.020	0.080	0.280	2.010	0.200	0.410
Mild Steel	0.200	0.007	0.010	0.010	0.400	-	0.150	-

Table 2. The meteorological data and atmospheric contamination data at testing area (1994–1999).

Station	T	RH	Rain	C(Cl)	C(SO ₂)	C(Cl ⁻ in rain)	C(SO ₄ ²⁻ in rain)
	(°C)	(%)	(mm·y ⁻¹)	(mg·dm ⁻² ·d ⁻¹)	(mg·dm ⁻² ·d ⁻¹)	(mg·m ⁻³)	(mg·m ⁻³)
Qingdao	20.3	77.8	912.9	0.364	0.347	5914	6405

2.3. Indentation Testing

Indentation testing was performed using Fischerscope[®] H100VP X-PROG Microhardness tester. The apparatus comprises two distinct components, a measuring head for performing indentations and an optical microscope for selecting a specific sample site prior to indentation. Both components are directly linked by an electro-mechanical position system that allows movement along two perpendicular horizontal axes with a lateral displacement resolution of 1 μm . The system has a load resolution of 0.4 mN and a displacement resolution of less than 10 nm. The indentations and the corresponding crack images were observed using Nanoscope IIIa, Nanoscope Digiter Ltd.

3. Results and Discussion

3.1. Corrosion Rate

Figure 1 shows the variation of the thickness loss of the steels with the exposure term. The thickness loss is obtained from the formula $W/\rho A$, where the W is the weight loss, ρ is the density of the steel, and A is the exposed area of the sample. In the term of the first year, both low alloy steel and carbon steel showed a higher corrosion rate. Two years later, the corrosion rate of low alloy steel is obviously lower than that of carbon steel. Through regression analysis on the corrosion data (as shown in Fig. 2) following a bi-logarithmic equation: $\log d = M + N \log t$ (where d is corrosion depth in μm , t is exposure term in y), it can be seen that value of N for low alloy steel, 0.52, is much smaller than that for carbon steel, 0.77. Literature⁸⁾ explains that for the corrosion process controlled by an ideal diffusion process, N is equal of 0.5. The constant for carbon steel is much greater than 0.5, indicating that the rust layer can not inhibit the penetration of corrosive electrolyte, and substrate steel has a higher corrosion rate. The constant for weathering is approximately equal to 0.5, indicating that the rust layer could protect the substrate steel from rapid corrosion, and the corrosive electrolyte can only act on the steel following diffusion mechanism.⁸⁾

3.2. Morphology of the Rust Layer

Figure 3(a) showed the morphology of rust layer on the surface of carbon steel exposed for 4 years observed using optical microscope, it was found that there existed many cracks and voids in the rust layer acting as the transferring

Fig. 1. Variation of corrosion depth of steels with the exposure term in marine atmosphere.

Fig. 2. Regression analysis on the corrosion data following the bi-logarithmic equation, $\log d = M + N \log t$, it can be seen that value of N for low alloy steel, 0.52, is much smaller than that for carbon steel, 0.77.

path for the electrolyte liquid. Similarly, the rust layer on the surface of low-alloy steel exposed for one year had a loose structure just like that of the carbon steel (as shown in Fig. 3(b)). Two years later, the compacted rust layer had formed as shown in Figs. 3(c) and 3(d), which is to say that the formation of protective rust layer is a gradual process consonant with the opinions of other literatures.^{9,10)} Analysis of XRD shows that the rust layer of carbon steel

Fig. 3. The metallography observation of rust layers on the surface of both carbon steel and low alloy steel exposed in marine atmosphere. a) Carbon steel, 4 years, b) low alloy steel, 1.5 years, c) low alloy steel, 2 years, d) low alloy steel, 3 years.

Fig. 4. The XRD spectra of both carbon steel and low alloy steel. a) Rust power on the surface of carbon steel exposed for 4 years; b) outer loose rust products on the surface of low alloy steel exposed for 4 years; c) inner compacted rust layers on the surface of low alloy steel.

panels exposed for 4 years is composed mostly of α -FeOOH and γ -FeOOH (as shown in Fig. 4(a)). However, although the outer rust products has the same phase constituents as that of carbon steel (as shown in Fig. 4(b)), the inner compacted rust layer on the surface of low alloy steel exposed for 4 years is composed of α -FeOOH (as shown in Fig. 4(c)). At the same time there exists the enrichment of Cr element in the compacted rust layer by the analysis using EPMA (as shown in Fig. 5). It is well known that the diameter of Cr is similar to that of Fe, both of them has same valence electron number, so it is reasonable that Cr ions could partly substitute the Fe ions in α -FeOOH to form a new phase α -(Fe_{1-x}Cr_x)OOH, as has been reported by Yamashita *et al.*^{5,6)} Literature⁷⁾ reported that the rust layer with phase constituent of α -(Fe_{1-x}Cr_x)OOH has cation selective performance, and could suppress the penetration of Cl⁻. Therefore, the low-alloy steel panel with such compacted rust layer has a lower corrosion rate than carbon steel panels, which explained the variation of corro-

Fig. 5. Observation of alloying elements in the rust layer on weathering steel exposed for 4 years using JOEL 733 EPMA, and the enrichment of Cr is observed in the rust layer.

sion rate of steels with the prolongation of the exposure term as discussed in section 3.1.

It is well known that compacted rust layer is difficult to form on the surface of low alloy steels in the environment with higher Cl⁻ content. But at the same time other elements have the influence on the atmospheric corrosion process, just like temperature, relative humidity and corrosion time. Another key element is the composition of steels. Keiser *et al.*,¹¹⁾ Stockbridge *et al.*,¹²⁾ Cohen and Hashimoto *et al.*¹³⁾ have studied the distribution of alloying elements during the formation of compact rust layer as follows: (1) The presence of alloying elements can retard the growth of rust and suppresses the supply of oxygen to the steel surface. (2) Alloying elements would reduce the conductivity of the rust. (3) Alloying elements could precipitate and cover the steel surface. (4) Alloying elements could retard the crystallization of rust and contributes to a uniform dissolution of the steel and formation of a rust layer at the initial stage. (5) Many effects of alloying elements are still ambiguous. Therefore the composite effect of above elements result in the formation of the compact rust layer formed on the surface of the steel panels with higher alloying elements even at the higher Cl⁻ content.

3.3. Fracture Toughness of Rust Layers

The hardness of the compacted rust layer on low alloy steel was measured by means of cross-section indentation testing. The test was conducted at a peak indentation load (5 mN) low enough to avoid destroying the rust layer. The Vickers hardness (Hv) of the rust layer is got by the formula $-0.1891(5 \times 10^{-3}/l^2)$, where l is the size of imprints diagonal measured in the corresponding AFM images. Calculation results show that the hardness of rust layer exposed for 3 years (837.43), is much higher than that of the rust layer exposed for 2 years (781.68 Mpa), but lower than

Fig. 6. The indentation load-displacement curve and corresponding AFM image of compacted rust layer for different time. a) 2 years, b) 3 years, c) 4 years.

that of the rust layer exposed for 4 years (872.38 MPa), *i.e.*, the hardness of the rust layer is increased with the exposure term. We had investigated the low alloy steels containing different alloying-elements,¹⁴⁾ and reported that the rust formed on the low alloy steel has different phase constituents with the corrosion term, generally, the amount of amorphous rust is reduced, and Cr-goethite is increased accordingly. Yamashita *et al.*⁵⁾ investigated the protective rust layer formed on weathering steel by atmospheric corrosion during a quarter of a century, they pointed out that the rust layer of Cr-goethite is much more densely aggregated, which results in higher density of rust layer, and accordingly the hardness of the rust layer would be increased.

For measuring the fracture toughness of rust layer, the indentation test is conducted at a peak load (20 mN) high enough to crack the rust layer. Figure 6 showed the load-displacement (L-D) curves of indentations and corresponding AFM images. A step could be observed in each L-D curve of which corresponding images showed the cracks had propagated from four corners. During indentation, the fracture of rust layer made an abrupt change of the dis-

placement but the indentation load did not increase, which resulted in a step in the L-D curve, and obviously the load at the step corresponded to the critical load initiating the fracture of the rust layer. Further observation shows that the critical load to crack the rust layer exposed for 3 years is higher than that of the rust layer exposed for 2 years, but slightly less than that of the rust layer exposed for 4 years.

Taking the rust layer as monolithic bulk material, and the relationship among fracture toughness $-K_{IC}$, critical indentation load $-P$, residual stress at the surface $-\sigma$, and length of radial cracks $-c$, measured through AFM observation, can be expressed by following formulas.¹⁵⁾

$$\frac{xP}{c^{1.5}} = K_{IC} - 2\sigma \left(\frac{c}{\pi} \right)^{0.5} \dots\dots\dots (1)$$

where $x=0.016(E/H)^{0.5}$, H is the hardness of the rust layer, the elastic modulus of the rust layers (E) has been calculated by measuring the slope of the unloading curves. Because the native rust layer is self-formed on the substrates in natural environment for over 2 years, the residual stress σ

Table 3. Measurement results of indentation testing on the compacted rust layer on the surface of low alloy steel exposed in marine atmosphere for 2, 3, 4 years.

Sample	Hardness /MPa	E/GPa	$K_{IC}/\text{MPa}\cdot\text{m}^{0.5}$	$E_{int}/\text{MPa}\cdot\text{m}^{0.5}$
A	781.68	232.01	2.48	2.63
B	837.43	239.39	2.64	2.72
C	872.38	257.39	2.71	2.74

Note: sample A is referring to low alloy steel exposed for 2 years, B is for 3 years, and C is for 4 years.

Fig. 7. The L-D curves and corresponding AFM image tested at the interface between substrate steel and rust layer exposed for different time. a) 2 years, b) 3 years, c) 4 years.

could be neglected, then above formula is further simplified as following¹⁵⁾.

$$K_{IC} = \frac{xP}{c^{1.5}} \dots\dots\dots(2)$$

As list in **Table 3**, The value of fracture toughness of rust layer on low alloy steel exposed for 4 years is highest among all samples. The rust layer exposed for 2 and 3 years tends to more easily be destroyed under the action of the external loads although the rust is compacted enough to suppress the penetration of corrosive electrolyte.

3.4. The Adhesion Strength of the Protective Rust Layer

In order to characterize bonding strength of the rust layer to the steel substrate, the indentation spot is selected at the interface between the rust layer and substrate steel, and the peak load (20 mN) is high enough to peel off the rust layer from the substrate steel. Considering plastic deformation energy approximates to zero for more fragile material just like iron oxides, and fracture will occur when the strain energy release rate of the oxide layers equals the interfacial energy E_{int} . Then it is reasonable to use E_{int} to characterize the adhesion strength of the rust layer.

In each L–D curve (as shown in Fig. 7), two steps can be seen to correspond to the fracture of rust layer and interface respectively, further AFM observation shows that fractures had propagated both into rust layer and along interface between the rust layer and the substrate steel. Because of the better ductility, there was no cracks happened in the substrate steel. Chicot *et al.*^{15,16)} pointed out that the coatings on substrate cracked firstly when the indentation load approaches to its broken strength; in the following downloading process, because substrate and coating have different elastic properties there would exist a shearing stress at the interface, resulting in the fracture of the interface, and accordingly there is two steps in the L–D curves (Fig. 7). The interfacial energy (E_{int}) could be further deduced as follows.^{16,17)}

$$E_{\text{int}} = 0.015 \cdot \frac{P_C}{a_C^{3/2}} \left(\frac{E}{H} \right)_1^{1/2} \dots\dots\dots (3)$$

Where E and H are the composite properties of elastic modulus and hardness determined by rust layer and substrate steel together, a_C is the crack length measured from center of indent. The value of E_{int} was worked out as list in Table 3. The adhesion strength of the rust layer to the substrate steel is higher than that the fracture toughness of rust layer itself. Therefore, cracks will be generated in the rust layer firstly, not at the interface when bearing loads in practical application. Further propagation of cracks will make the loss of the protective effect of the compacted rust layer.

4. Conclusion

The low alloy steel panels formed protective rust layer on the surface exposed in marine atmosphere for 4 years, and had a lower corrosion rate. Based on the analysis of energy release during crack propagation in micro-indentation testing, K_{IC} and adhesion strength of the rust layer are calculated. The value of fracture toughness of the rust layer on low alloy steel exposed for 4 years is highest among all samples. For the panels exposed for 2 or 3 years, although the rust is compacted enough to suppress the penetration of corrosive electrolyte, its protective reliability is limited

under the action of the external loads in practical application. Furthermore, analysis on the L–D curves at the interface indicated that the adhesion strength of the rust layer to the substrate steel is higher than the fracture toughness of rust layer itself. The cracks would be easily generated in the rust layer firstly, not at the interface under the action of external load, and following propagation of cracks makes the loss of protective effect of the compacted rust layer.

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