

Evaluation of Corrosion Behaviors of Austenitic Stainless Steel Exposed in Marine Atmosphere of South China Sea

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Abstract: Austenitic stainless steel 304 and 316L were exposed to actual atmospheric environments of South China Sea for half one year, and the influences of microstructures on atmospheric corrosion behavior of the two stainless steels were investigated. The results showed that the average corrosion rate of the two stainless steels were about $10^{-3} \sim 10^{-4}$ mm/a, while the depth of pitting hole was up to $\sim 10 \mu\text{m}$, the number and area of pitting corrosion for the 316L are less and smaller than that of 304, the result of potentiodynamic polarization shows that the pitting potential of 316L is higher than that of 304, which indicates that atmospheric corrosion resistance of 316L is excelled to 304.

Introduction

Austenitic stainless steel (SS) demonstrates high corrosion resistance due to the formation of a passive layer markedly enriched chromium (Cr) content. Hence, such steel is used commercially in various industrial applications. However, in a marine atmospheric environment, airborne sea salts with moisture deposits to form a thin electrolyte film and/or droplet in a wide range of relative humidity. Under such condition of highly concentrated aggressive chloride anion on the surface, stainless steels suffer from pitting corrosion even below the relative humidity, at which general atmospheric corrosion of carbon and weathering steel can occur ^[1]. According to the results of investigation on the islands in South China Sea, much pitting has been observed on the surface of the petrochemical equipment and pipes of 304 stainless steel, which threatens the safety and application of the equipment seriously.

The addition of molybdenum improves 316L stainless steel pitting corrosion resistance compared to 304. 316L stainless steel has been extended to many applications in marine and industrial environments due to good strength and excellent corrosion resistance. However, in the conditions of high chloride concentration and high temperature, it is inevitable for the stainless steel to be attacked

by localised corrosion leading to the perforation of its surface, reducing the service life of the structure. Corrosion is an undesirable process that may result in the destruction of a metal, influencing its serving life ^[2]. Many studies have reported that pitting corrosion has been considered as a critical problem for the applications of stainless steel^[3], the cost of corrosion have been studied to analyse the effect on the developed global economy ^[4].

Atmospheric corrosion of metals is different from the other forms of corrosion due to exposure of metals to different atmospheres rather than immersion in electrolytes. The corrosion rate of metals exposed to a wet atmosphere is similar to that observed during immersion in aerated water in the presence of dissolved oxygen ^[5]. Marine atmospheres are the extreme in atmospheric corrosion due to chlorides from sea water and salts being swept by winds. Chlorides create the most corrosive environment and are a great concern to offshore platforms and vessels. In marine environments, the temperature drops and relative humidity (RH) rises at night, the moisture in the air may condense and form droplets or a thin solution layer containing chloride ions on metals surface. In contrast, an evaporation process, which increases the chloride ion concentration in the droplets, occurs as the daytime temperature increases and the RH decreases^[6]. The chloride ions adsorb on the outer surface of the passive film, permeate through the passive oxide film, and interact with the underlying metal ^[7,8,9].

In order to understand the corrosion behavior of steel as a function of type of steel and exposure time, the morphologies of the surface, the polarization and pitting potential have been studied on many occasions. This paper compares and investigates the anticorrosion of austenitic stainless steels 304 and 316L in terms of marine atmosphere of South China Sea.

Experiments

For this investigation, the steel specimen was cut into coupons of dimensions 100mm×100mm×5mm. The coupons were abraded to 800 grade emery paper, cleaned ultrasonically in acetone rinsed with distilled water, dried, weighed and stored in a moisture free desiccators prior to use. Atmospheric corrosion tests were under taken at island of South China Sea. The metal test panels were positioned at 45° to the horizontal, with skyward surface directed toward the sea to emphasize the marine fog effect. The exposed time is 1,3 and 6 months respectively. The chemical composition of the investigated stainless steels are shown in Table 1.

Table 1 Chemical composition of the investigated stainless steels (wt.%).

Grade/ Composition	C	Mn	Cr	Ni	Mo	Fe
304	≤0.03	1.4108	18.0402	8.3071	0.0194	Blance
316L	≤0.03	1.1787	16.8839	11.3024	2.5156	Blance

Throughout the outdoor corrosion tests, the morphologies and the pits depth of the samples were acquired with a 3D microscope Atmospheric corrosion of metals is usually an electrochemical reaction between the metal and its surrounding environment. Again, electrochemical methods are very useful for evaluating the protectiveness of corrosion products formed on a metal matrix. Therefore, it is beneficial to adopt electrochemical techniques in investigating the corrosion mechanism of copper subjected to a simulated coastal-industrial atmosphere.

For potentiodynamic polarization measurements, the corroded samples were employed as working

electrode, and the measurements were performed with a PARSTAT 2273 potentiostat/galvanostat in a conventional electrochemical glass cell with a large platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The test solution used in all experiments was 3.5% NaCl solution prepared from reagent grade chemicals and distilled water. Before measurement, CO₂ gas was input into the solution to discharge the O₂ at the rate of 500 ml/min for two hours, the scanning rate of the potentiodynamic polarization measurements was 20 mV/min.

Results and discussion



Figure 1. Corrosion morphologies of 304 stainless steel after exposed in South Sea atmospheric for different time: (a)controlled samples, (b)1 month, (c) 3 months, (d)6 months.

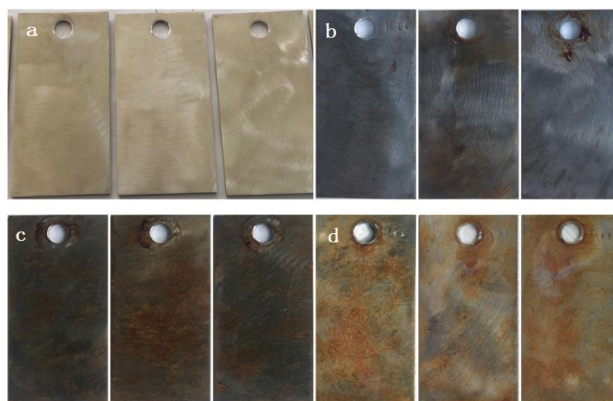


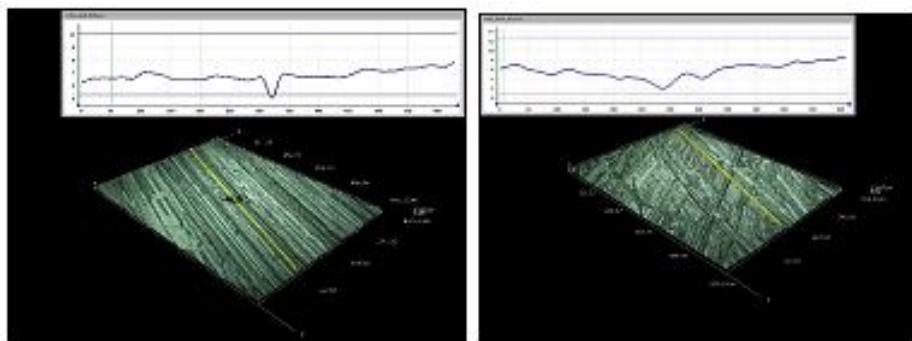
Figure 2. Corrosion morphologies of 316L stainless steel after exposed in South Sea atmospheric for different time: (a)controlled samples, (b)1 month, (c) 3 months, (d)6 months.

Figure 1 shows the macro-morphologies of 304 stainless steel exposed in South Sea atmospheric for different time. Figure 1a shows that the surface of the unexposed sample is smooth and, Figure 1b display that there are a few corrosion sites on the surface of one month exposed, and half of the surface has been corroded on the sample exposed for three months as seen in Figure 1c, most of the surface can be observed covered by corrosion sites for the sample by six months exposure as seen in Figure 1d.

Figure 2 shows the macro-morphologies of 316L stainless steel exposed in South Sea atmospheric for different time. The pre-exposed specimens had undergone corrosion to different extents, depending on the exposure time. Figure 2b displays that the corrosion on the 316L surface is observed after one month exposure, the local corrosion is mainly, which fragmentary distributes on the sample surface.

With exposure time increasing, the number of local corrosion and the corrosive area increase, the surface has been covered by the corrosion layer by the exposure time of six months, which indicates that the anti-corrosion ability of 316L is superior to 304. However, with exposure time increasing, localized corrosion arose eventually.

Figure 3 and Figure 4 show the 3D micro morphologies of samples after being exposed for different time in South Sea. With the exposed time increasing, the max depth of pit increases as shown in Figure 5, the average depth of pit is similar for 304 and 316L, the max pit depth of 316L is less than that of 304, which indicates that the ability of anti-pitting corrosion for 316L is excelled to 304.

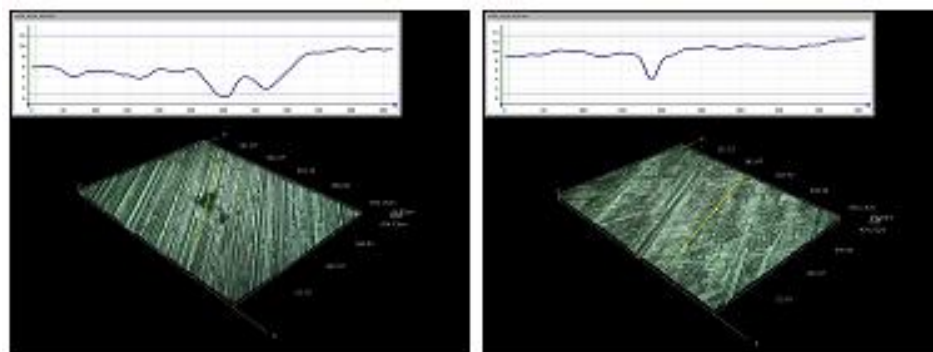


(a)

(b)

Figure 3. Micro morphologies of samples after exposed in South Sea for one month

(a) 304, (b) 316L stainless steel



(a)

(b)

Figure 4. Micro morphologies of samples after exposed in South Sea for six months

(a) 304, (b) 316L stainless steel

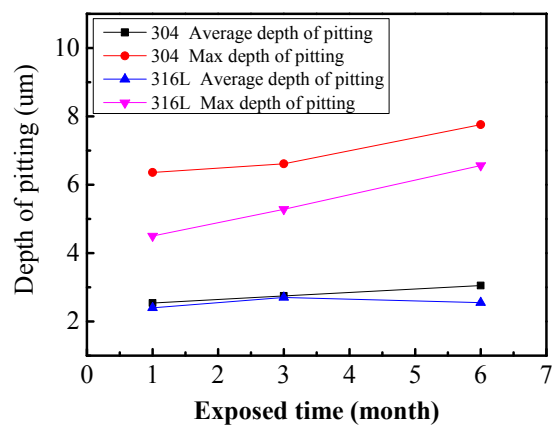


Figure 5. Maximum and average depth of pits with different exposed time

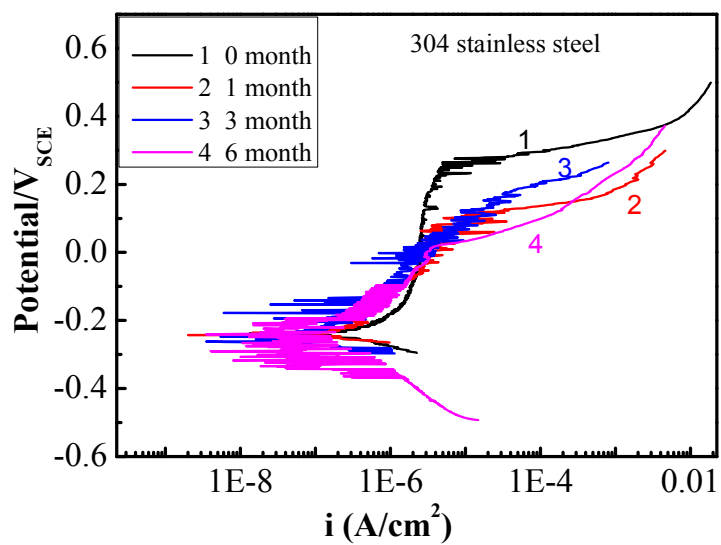


Figure 6 Potentiodynamic polarization curves of the unexposed and corroded 304 in 3.5% NaCl solution as a function of corrosion time.

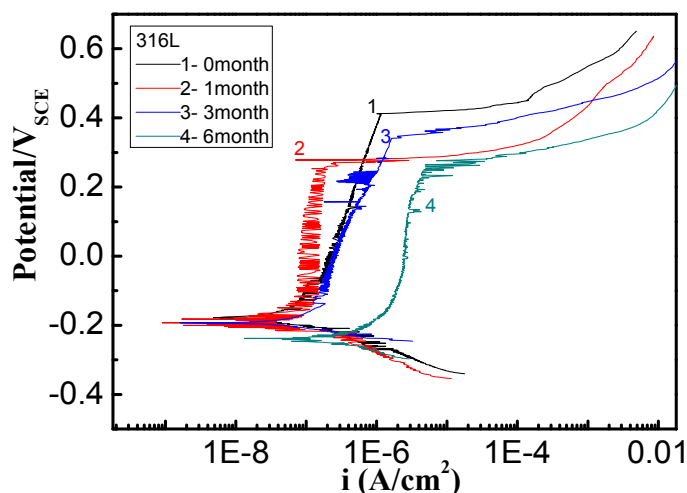


Figure 7 Potentiodynamic polarization curves of the unexposed and corroded 316L in 3.5% NaCl solution as a function of corrosion time.

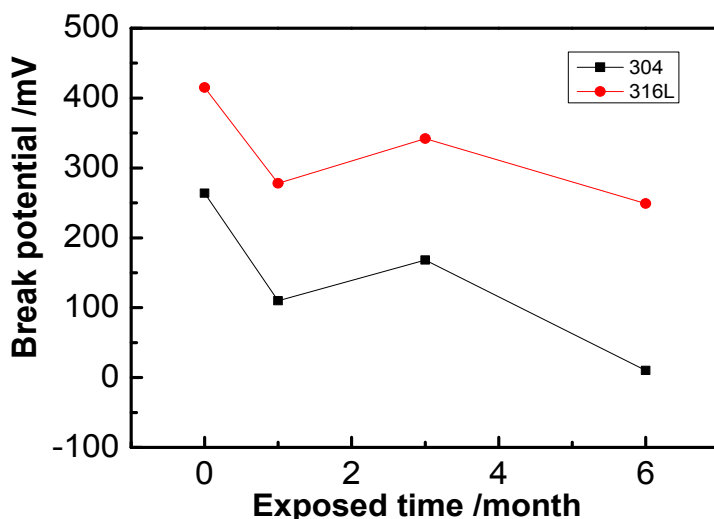


Figure 8 Pitting potential changes with the exposed time

Figure 6 and Figure 7 depict the potentiodynamic polarization curves of unexposed and pre-exposed samples in 3.5% NaCl solution as function of exposure time. For the unexposed and hence relatively un-corroded sample, the cathodic process was controlled by the dissolution of O₂, and the anodic process by the stainless steel passive reaction. The polarization curves for all systems have similar shapes, implying similarities in polarization behavior and hence corrosion mechanism. The E_{corr} is similar for the unexposed and exposed samples from one month to three months, and the E_{corr} of the sample exposed for six months decreases about 50 mV. The pitting potential of 316L and 304 decreases with the exposed time increasing, which indicates that the possibility of local corrosion occurring increases. The unexposed and pre-exposed samples of one to three months show the similar pitting potential, the passive zone of six months is different from the others, the trend of passive is not

completely, which implies that the poor passive layer owe to the occurring of pit corrosion. Figure 8 shows the pitting potential change with the exposed time increasing. The pitting potential of 316L is higher than that of 304, which indicates the trend of pitting occurring for 304 is easier than 316L.

Conclusion

Austenitic stainless steel 304 and 316L were exposed to actual atmospheric environments of South China Sea for half one year. The morphologies of samples were observed by 3D microscope, the results showed that the number and area of pitting corrosion for the 316L are less and smaller than that of 304, the results of potentiodynamic polarization shows that the pitting potential of 316L is higher than that of 304. The Ecorr of 316L keeps similar at exposed periods from one to three months, and decreases 50 mV with the exposed time increasing to six months, while the Ecorr of 304 samples decreases with the exposed time increasing, which indicates that, 316L shows better anticorrosion compared to 304, but it is necessary to evaluate the anticorrosion behavior in a longer period to decide whether 316L is appropriate for marine atmospheric environment of South China Sea.

Acknowledgements

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