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Research Article

The monitoring of pitting corrosion in stainless steel in the simulated corrosive conditions of marine applications

Thee Chowwanonthapunya*

Faculty of International Maritime Studies, Kasetsart University, Chonburi 20230, Thailand

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Abstract

This paper describes the monitoring of pitting corrosion in ferritic and austenitic stainless steel under the simulated acidic conditions of marine applications. The monitoring dealt with corrosion weight loss and metallurgical investigation. The results indicated that stainless steel with passive film shows good corrosion resistance to the simulated corrosive environment for all test periods. In contrast, stainless steel without passive film cannot provide an inhibiting effect for the whole test period. After 24 h. of testing, both of the stainless steels were locally attacked. Pitting corrosion was observed on the surface of both stainless steels. In small pits, self-accelerating corrosion can occur. Therefore, longer immersion times were attributed to the higher corrosion rates of both stainless steel in simulated acidic conditions.

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1. Introduction

Stainless steels are one class of high alloy steel, containing more than a 12 % (Wt) chromium content, and have been widely used in marine applications (Jiménez-Come et al., 2012). This is due to the combination of their advantages, such as acceptable anti-corrosion and mechanical properties. Technically, the anticorrosive property of stainless steels can be enhanced by the presence of a thin chromium oxide layer, known as a passive film (Moayed & Golestanipour, 2005). This thin layer can protect the surface of stainless steels from the corrosive attacks from mild to intermediate acidic environments. Nevertheless, in marine applications, this film can be locally damaged by an increase in oxidizing agent power, the sudden reduction of pH, and mechanical abrasion (Chowwanonthapunya & Wiriyanon, 2015). In fact, locally damaged areas in stainless steel used in marine industries can lead to the premature failure of pipelines or equipment. Nowadays, there are 2 kinds of stainless steel which are often used in marine industries. The first kind is austenitic stainless steel, whereas the other is ferritic stainless steel. Both kinds of stainless steel can be protected by the presence of Cr-containing protective films. However, corrosion resistance to chloride and the recovery of the protective film are different, particularly when the passive film is locally damaged (Garcia et al., 2008). Hence, a monitoring study of both types of stainless steel exposed to the corrosive conditions of marine applications should be performed, especially when the protective film on the surfaces of both types of stainless steel is completely damaged.

In this study, monitoring of pitting corrosion in ferritic and austenitic stainless steel immersed in the simulated acidic conditions of sodium chloride acid was conducted and discussed.

*Corresponding author: Faculty of International Maritime Studies, Kasetsart University, Chonburi 20230, Thailand
E-mail address: thee.c@ku.th

2. Materials and methods

The chemical compositions of ferritic and austenitic stainless steels in this experiment are listed in **Table 1**. Specimens of both stainless steels were prepared, with dimensions of 15×15×1 mm³, then subjected to 2 kinds of conditions. The first test was conducted on stainless steel with a passive film, and the second one was performed on stainless steel without a passive film. To remove the passive film, the specimens were ground with Sic#800. The acidic conditions of marine applications can be simulated by the use of the NaCl acid with a concentration of 95 % weight. During the period of testing, changes in pH and in concentrations of both solutions were controlled by a pH meter and a Solinometer. The equivalent thickness loss of the specimens was then monitored with an electronic balance with a sensitivity of 0.001 g. The monitoring period was carried out at 12, 24, 36, and 48 h after the first immersion.

3. Results and discussion

3.1 Corrosion mass loss

The monitoring results of the corrosion weight loss of both types of stainless steel exposed to the simulated acidic conditions are given in **Figure 1**; both types of stainless steel with passive films showed no corrosion mass loss throughout the exposure time. However, when the passive film was removed, both types of stainless immersed in the simulated acidic conditions become significantly active after the first 24 h of exposure. Clearly, after this period, the metal dissolution of both grades increased during the rest of the exposure period.

From these results, it can be observed that the stainless steel with passive film effectively resisted the simulated corrosive environment for the whole test period. However, damage to the passive film promotes the active state of the stainless steel. Both types of stainless steel in the active state can inhibit the attack of chloride for the first 24 h of the exposure period only. The acidic conditions and the prolonged exposure time enhance the increase in corrosion mass loss at the exposure periods of 36 and 48 h.

3.2 The estimated corrosion rate

To clearly explain the anti-corrosion performance of both stainless steels, we estimate the average corrosion rate of them in the active state when exposed to the simulated acidic conditions from **Figure 1** in **Figure 2**. From **Figure 2**, the corrosion mass loss of austenitic stainless steel is obviously lower than that of ferritic stainless steel.

Table 1 Chemical compositions of specimens.

Element	Ni	Cr	Si	C	Mn	Fe
Austenitic stainless steel	8.54	17	0.55	0.12	1.42	76.15
Ferritic stainless steel	-	12.9	0.38	0.08	0.37	86.3

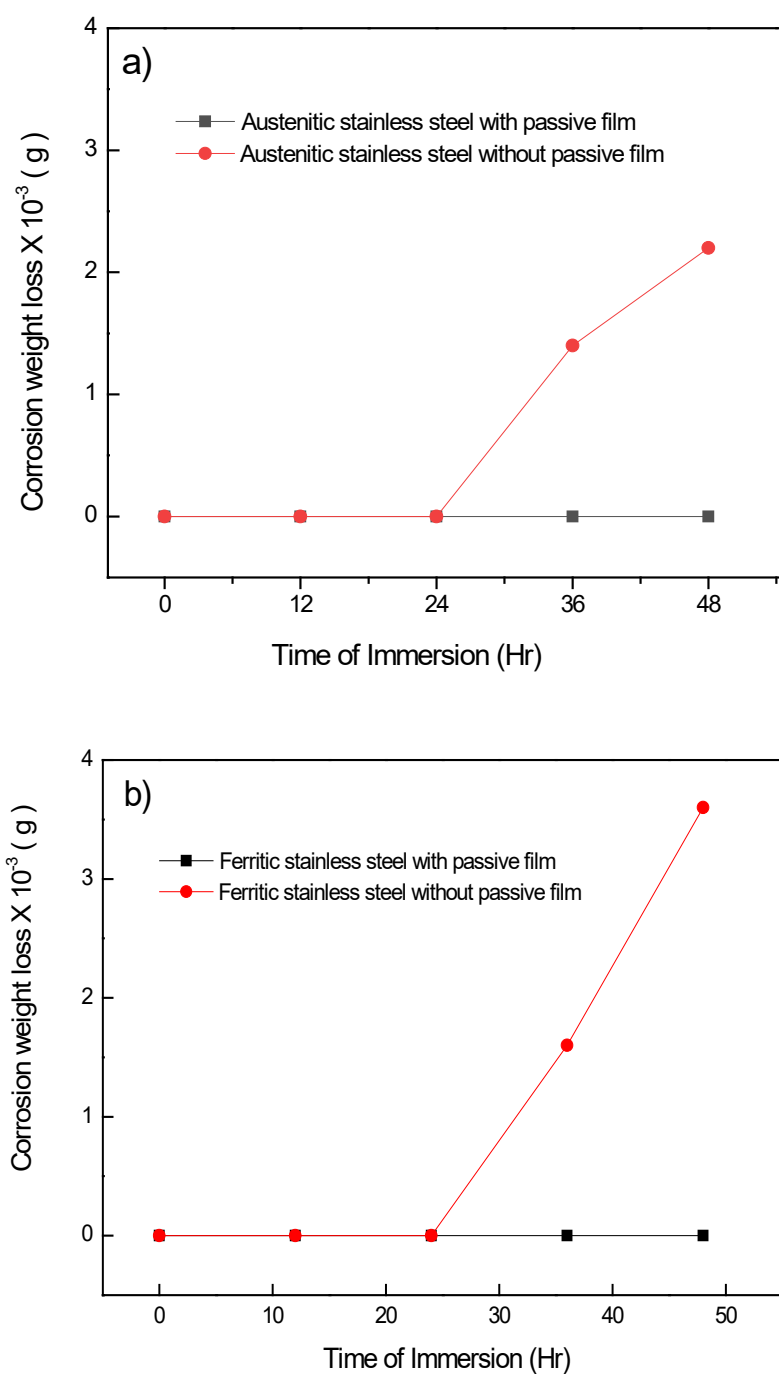


Figure 1 Corrosion performance monitoring of specimens in simulated acidic conditions (a) austenitic stainless steel and (b) ferritic stainless steel.

This information indicates that the anti-corrosion ability of austenitic stainless steel is better than that of ferritic stainless steel, even in high acidic conditions, such as NaCl solution.

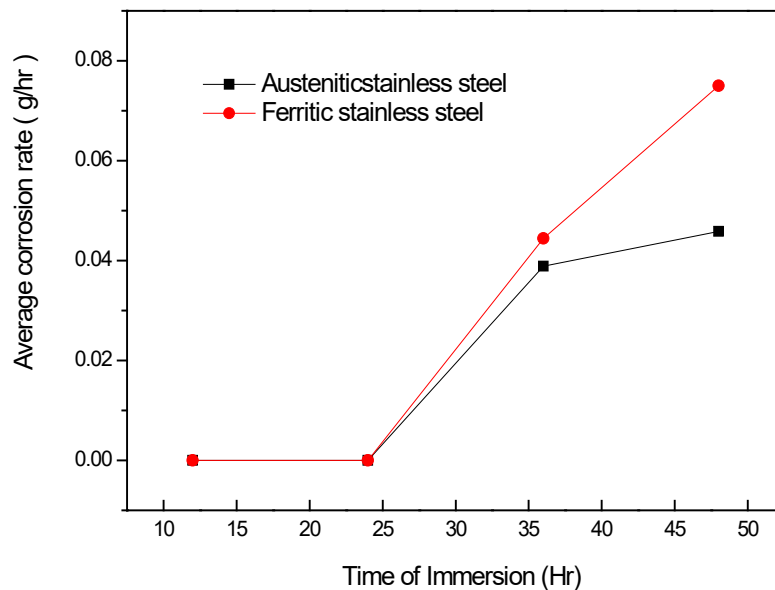


Figure 2 Corrosion rates of specimens in simulated condition (simulated NaCl solution).

The above findings suggest that austenitic stainless steel provides better corrosion resistance in simulated acidic conditions. As shown in **Table 1**, Cr content in austenitic stainless steel is higher than that in ferritic stainless steel. In addition, nickel content can increase pitting resistance in austenitic stainless steel. Therefore, the higher Cr content and the addition of Ni can account for the better corrosion resistance of austenitic stainless steel.

3.3 Corrosion mechanisms

Stainless steels have excellent corrosion resistance to mild acid, due to the formation of an adherent passive film. The thin and adherent passive film can provide a good barrier to surface attack from aggressive anions, i.e. chloride, as shown in **Figure 1**. However, the film is sometimes damaged by mechanical abrasive.

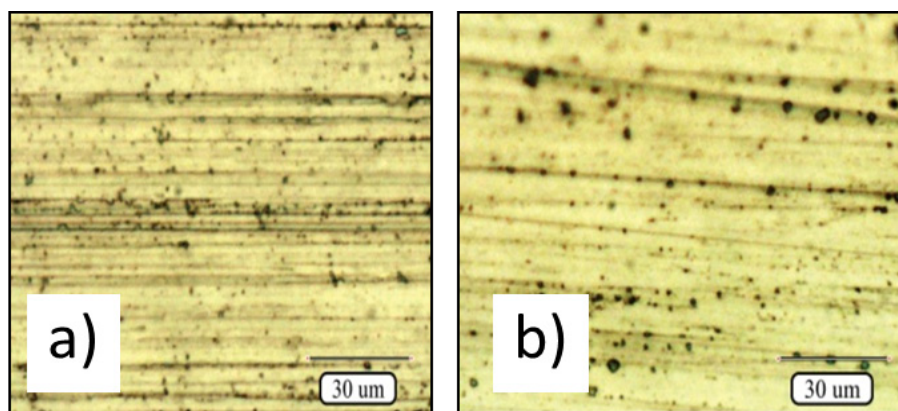


Figure 3 Change in the surface conditions of both stainless steels in simulated NaCl solution at 48 h; (a) austenitic stainless steel and (b) ferritic stainless steel.

Figure 3 shows the surface conditions of both grades of stainless steel after exposure to simulated acidic conditions at 48 h. From **Figure 3**, it is obvious that small pits were found on the corroded surfaces of both stainless steels. This finding suggests that stainless steel without passive film is locally attacked, and the shape of the corrosion is in the pitting form. In theory, active

stainless steel is corroded, and provides metal ions, as demonstrated in Eq. (1) (Moayed & Golestanipour, 2005; Chowwanonthapunya & Wiriyanon, 2015).



The heterogeneous sites, i.e. the grain boundary and carbide phases, in the surface of stainless steel are always susceptible to being locally attacked. This subsequently sets up a local electrochemical cell, composed of a small anode and large cathodes. The corrosion process still takes place at the same rate in the very small and narrow pits. This leads to excessive amounts of ferrous chloride. This kind of chloride can then be transformed into ferrous hydroxide and free acid, as clearly seen from Eq. (3) (Garcia et al., 2008).



The presence of the free acid (H^+Cl^-) can induce low pH conditions within pits and, thus, promote corrosion attacks (Xhoffer et al., 2004). A prolonged period of the immersion indicates a longer time for the attack. Therefore, longer periods of immersion can contribute to higher corrosion rates in both stainless steels in the simulated acidic conditions of marine applications.

4. Conclusions

The monitoring of pitting corrosion in ferritic and austenitic stainless steel in the simulated acidic conditions of marine applications was conducted. The results exhibit that stainless steel with passive film can resist simulated corrosive environments for the whole test period. Nevertheless, stainless steel after the removal of passive film can inhibit the corrosion attack for 24 h only. After this period, the surface of both types of stainless steel tested is locally corroded. The more aggressive NaCl solution can accelerate the corrosion process of both stainless steels. In the same simulated corrosive conditions, the corrosion resistance of austenitic stainless steel is better than that of ferritic stainless steel. This can be attributed to the higher chromium content of, and the addition of nickel in, austenitic stainless steel. Pitting corrosion was found on the surface of stainless steel in both grades. In small pits, accelerating corrosion attacks can occur. Thus, longer immersion time can account for the higher corrosion rate of both types of stainless steel in both acidic conditions.

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