Effect of Ni on the oxygen reduction reaction for low alloy steels in thin electrolyte layer conditions

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Abstract: The corrosion behavior of carbon and a Ni-containing steel is investigated in the environment of a thin electrolyte layer. Potentiodynamic cathodic polarization curves were determined using a thin electrolyte layer apparatus at ordinary and negative pressure environments. Oxygen reduction is an important cathodic reaction for carbon steel in the present study. However, the suppression of oxygen reduction occurred for Ni-containing steels. The inhibition of oxygen reduction was closely correlated with the formation of the amorphization of the corrosion product, which contained amount of Ni, formed on the Ni-containing steel.

1. Introduction

Low alloy steels are widely used in many application fields, such as construction, bridges and pipelines. The corrosion resistance of low alloy steels has attracted significant attention. Weathering steel is a kind of low alloy steel that is applied in construction and bridges. The nature of the corrosion product formed on weathering steel are receiving increasing attention [1–7]. Compared with carbon steel, the enhanced corrosion resistance of weathering steel is due to the compact rust layer formed on the surface. However, the corrosion of steel in marine atmosphere exposure is much higher than steel in other environment exposure. In recent years, a new type of advanced weathering steel containing 3 wt.% Ni has been developed and applied to bridges in some coastal areas where the air born salinity is higher than the upper limit for weathering steel [8].

Kimura [9] suggested that the excellent corrosion resistance of advanced weathering steel which contained 3 wt.% Ni, is achieved by adjustment the Fe(O, OH)₆ lattice structures of rust formed on its surface. The stabilized Fe₂O₃, i.e., Fe₃NiO₄, in the nano-network changes the ion-exchanging properties of rust from anion to cation selective. Similar results have also been reported by other researchers [10].

Chenet al. [11] suggested that Ni is enriched in the rust layer formed on weathering steel, especially in the inner rust layer, while Cl⁻ almost concentrated in the outer rust layer. Therefore, it was speculated that the cation selective property of the rust layer of Ni-containing weathering steel can be achieved by Ni concentration (the content of Ni exceeds 4 wt.%).

Diaz et al. [12] suggested that the higher content of Ni leads to higher corrosion resistance of advanced weathering steel. It can be attributed to the high proportion of nano-phasic goethite (particle size smaller than 15 nm) in the inner rust layer by concentration of Ni in the rust layer. These results are consistent with findings of Cano et al. [13], who pointed out that high Ni content steels exhibited excellent corrosion resistance after a 2-year.

It is well-known that the corrosion resistance of low-alloy steels can be improved by increasing their nickel content [12, 14, 15]. However, according to the research of Cheng [16], when the Ni content in
weathering steels exceeds 3.5 wt.%, the corrosion resistance improves slightly even with a considerable increase of Ni content. Therefore, 3.5 wt.% is the optimal Ni content in weathering steels to decrease the corrosion rate in industrial atmosphere.

In most previous studies, the ionselective property of rust layers containing Ni and the effect of Ni content on the corrosion resistance of low alloy steel have been the focus, with reports describing the influence of Ni on the electrochemical reactions of low alloy steels and the characteristics of corrosion products being rare. In the present study, the thin electrolyte layer method is preceded on a solution containing Cl-. The effects of Ni on the oxygen reduction reaction and on the characteristics of rust layer formation on low alloy steels are also analyzed. The propose of this study was to understand the role of Ni in improving the corrosion resistance of low alloy steel exposed in marine atmospheres with high humidity.

2. Experimental

2.1. Thin electrolyte layer apparatus

A thin electrolyte layer apparatus has been utilized in previous studies and the theory of the measurement of the electrolyte layer thickness that established a loop connected by a Pt needle, working electrode and ampere meter has been discussed [17–19]. According to this method, the distance between the Pt needle and electrode surface was determined to be 100μm in the present study. As shown in Figure 1, the apparatus discussed in previous studies was put into a chamber that isolated the air. An air pump was connected to the chamber. Therefore, the apparatus can prevent a negative pressure environment for the experiment.

![Figure 1. Schematic of thin electrolyte layer apparatus.](image)

The thickness of the thin electrolyte layer decreased with the time increasing. Once the thickness of the thin electrolyte layer was too low to touch the Pt needle, the current could not be observed by an ohmmeter. At this time, the peristaltic pump was turned on to put into the water until the current was observed by the ohmmeter alarm. It must be noted that when the thickness of the thin electrolyte layer was less than 90μm, the current was not observed because of the water tension. Therefore, the thickness of the thin electrolyte layer was controlled at the range of 85–110μm.

The experiments were performed in a NaCl solution (pH 6.8) at a temperature of 25ºC and the concentration of NaCl was 0.62mol/L (mass percent of 3.5 wt.%). The thickness of the thin electrolyte layer on the electrode surface approached 100μm.

2.2. Specimens

Both of the Ni-containing steel and carbon steel were corroded in the thin electrolyte layer environment. Table 1 shows the chemical composition of experimental steels. The Dimension of exposure area was 12mm×8mm.
Table 1. Chemical composition of experimental steels, wt%.

|                | C    | Si   | Mn   | P    | S    | Ni  | Fe  |
|----------------|------|------|------|------|------|-----|-----|
| Carbon steel   | 0.060| 0.26 | 1.01 | <0.01| ≤0.005| -   | Bal.|
| Ni-containing steel | 0.054| 0.31 | 0.98 | <0.01| ≤0.005| 1.8-2.1 | Bal.|

2.3. Weight loss

Before corrosion test, the specimens were polished by emery paper, and then rinsed with ethyl alcohol. Samples after cleaning were weighed with an electronic microbalance. After corrosion test, the specimens were acid cleaning by immersed in pickling solution (500 mL HCl + 3.5g hexamethylenetetramine) and then specimens were cleaned by distill water and ethyl alcohol. Finally, the specimens were weighed again so that the weight loss of each specimens were calculated leading by corrosion test.

2.4. Electrochemical measurements

Potentiodynamic polarization test were carry out by using a Princeton Applied Research Model 4000+ potentiostat, and the scanning rate was determined as 1mV/s. Saturated calomel electrode was used as reference electrode.

2.5. Rust layer analysis

The corrosion products formed on Ni containing steel and carbon steel were removed from the steel surface, and then mechanical ground into a powder. The corrosion product powdered samples were used for XRD analyses. The XRD (Bruker Model D8 Advance, Cu target) measurements were carried out by a scanning rate at 1° min⁻¹.

The distribution of Ni in the rust layer was determined by using a cross-section specimen. The specimens containing rust layer were fixed by an epoxy resin. The cross-section specimens of rust layer of the fixed specimens were polished by emery paper grades form 150# to 1000#. Then, the cross-section of the corrosion products was characterized via electron probe micro-analysis (EPMA), Shimadzu Model EPM810 electron probe micro-analyzer (accelerating voltage: 15 kV, sample current: 0.1 μA).

The corrosion product from inner rust layer was separated from steel surface via ultrasonic vibration in ethyl alcohol for 1h. The ethyl alcohol containing corrosion product was dripped on a carbon film. After the ethanol evaporated, corrosion products were attached to carbon film. TEM analysis of the film were carried out on a FEI FECNAI G2 F20 microscope.

3. Results and discussion

3.1. Weight loss of experimental steels

Figure 2 shows the results of weight loss of experimental steels. In the initial stage, there was no significant difference in weight loss between the carbon steel and Ni containing steel. After 48h of corrosion, the carbon steel exhibited the highest weight loss. The weight loss of Ni-containing steel was accordingly less than that of the carbon steel, and the difference of weight loss between carbon steel and Ni containing steel increases with increasing corrosion period.

3.2. Potentiodynamic polarization curves

Figure 3 shows the cathodic potentiodynamic polarization curves of experimental steels tested in an ordinary pressure environment (with O₂) and in a negative pressure environment (without O₂). The current density associated with the cathodic shift of carbon steel tested in the ordinary pressure environment was much higher than that in the negative pressure environment. This phenomenon suggested that oxygen reduction played an important role in the cathodic reaction occurring on the rust layer formed on the carbon steel. However, the same phenomenon was not observed for Ni-containing steel.
steel. There was almost no difference in current density between the Ni-containing steel tested in the two environments.

Figure 2. Weight loss of experimental steels.

Figure 3. Cathodic potentiodynamic polarization curves of experimental steels tested in an ordinary pressure environment and in a negative pressure environment.

Figure 4. Anodic potentiodynamic polarization curves of experimental steels tested in an ordinary pressure environment and in a negative pressure environment.

Figure 4 shows the anodic potentiodynamic polarization curves of experimental steels tested in the two environments (with and without O₂). Observably, the anodic current density of carbon steel tested in the ordinary pressure environment was higher than that in the negative pressure environment. While,
the anodic current density tested in the ordinary pressure environment, for Ni-containing steel, was also higher than that in the negative pressure environment, but the difference between the current densities tested in the two environments was not obvious. These results indicate that oxidation of corrosion product formed on Ni containing steel was inhibited in the ordinary pressure environment.

It was clear that the main difference of electrochemical behavior between carbon and Ni-containing steel can be attributed to the addition of Ni in the Ni containing steel.

3.3. Distribution of Ni in the rust layer of the Ni-containing steel
Figure 5 shows the distribution of Ni in the rust layer formed on the Ni-containing steel. And these results suggest that Ni is enriched in the rust layer, and Ni content of the inner rust layer is a little higher than those of steel substrate and the outer rust layer. Therefore, the rust layer formed on Ni-containing steel existed concentration behavior of Ni[9,11–13]. The difference of electrochemical behavior between carbon steel and Ni containing steel was attributed to the amount of Ni in the rust layers.

3.4. TEM analysis of rust layer formed on Ni-containing steel
A TEM image and EDS analysis of the inner rust layer corrosion product formed on Ni-containing steel is shown in Figure 6. The corrosion product revealed two remarkably different areas in terms of both composition and crystallinity, i.e., a Ni-containing area and a non-Ni-containing area. In the case of the non-Ni-containing area, the product gave rise to shape diffraction patterns. In contrast, in the case of the Ni-containing area, the corrosion product gave rise to a diffraction pattern of diffusion ring, which may indicate the existing of amorphous substance. Therefore, it can be speculated that Ni enrichment of the rust layer leads to the amorphization of the corrosion products.

3.5. XRD analysis of rust layer formed on experimental steels
Figure 7 shows the results of XRD analysis of corrosion products formed experimental steels. Both of the corrosion products formed on carbon steel and Ni containing steel were consist of $\alpha$-FeOOH, $\gamma$-FeOOH and Fe$_2$O$_4$, and Fe$_3$O$_4$ is the main corrosion product in the rust layers by comparing the intensity of the diffraction peaks. The main difference of the two corrosion products is that the Fe$_3$O$_4$ diffraction peaks of Ni containing steel were moving to a few higher diffraction angles than that of carbon steel. It is indicated that formation of NiFe$_2$O$_4$ may occur during corrosion process, in other words, Ni may distributed in the Fe$_3$O$_4$ in the rust formed on Ni containing steel. Therefore, the amorphous substance may consist of Fe$_3$O$_4$ doped Ni.
4. Discussion
The main difference in corrosion behavior between carbon and Ni-containing steels can be attributed to the corrosion product formed on the steels. As is mentioned in the previous study[20], magnetite and maghemite coexisted as a mixture of phases in the rust layer in desaerated corrosion medium, while lepidocrocite(γ-FeOOH) or ferrihydrite formation can be occured in aerated medium. Therefore, the difference of oxidation behavior of corrosion product formed on Ni containing steel between negative pressure environment and ordinary pressure environment was lower than that of carbon steel. It is indicated that formation of lepidocrocite or ferrihydrite in rust layer formed on Ni containing steel is more difficult than that in rust layer formed on carbon steel. However, this anodic electrochemical behavior may not impact corrosion rate of the steels directly.

Therefore, the rust layer plays an important role in O2 reduction which influence the corrosion rate of the steels directly. The rust layer is a type of porosint. There are many pores distributed on the surface of the rust layer. According to Hoerle[21] and Stratmann[22,23], when a certain amount of the γ-FeOOH is reduced to the conducting substance, namely reduced lepidocrocite(FeOHOH). The crystallographic structure of reduced lepidocrocite is consist with that of γ-FeOOH[24]. It coats the surface developed by the rust layer porosity. If a connection between the underlying metal exists, then the {FeOHOH} on the surface of the rust can act as a cathodic area. Oxygen reduction occurred on the surface of rust layer and on the inwall of the pores.

The thin electrolyte layer condition is similar with the condition of beginning of the drying stage of wet-dry cycles. Therefore, the oxygen diffusion can maintain a high rate through the corrosion period, leading to the high rate of oxygen reduction on surface of rust containing {FeOHOH}. The corrosion product acted as a wire to transport electrons from the metal surface to the surface of rust layer and the inwall of the pores. The corrosion product formed on the Ni-containing steels contained a certain amount of NiFe2O4, which belongs to the magnetite. As previous study mentioned[12], some nanosized corrosion products with a particle size smaller than 15 nm were attributed to the concentration of Ni in the inner rust layer. Owing to the formation of nanosized Ni-containing corrosion products, the incorporation of Ni into the Fe3O4 may lead to the formation of amorphization of the corrosion product, thereby decreasing the electronic conductivity of the corrosion product. Because of the poor conductivity of the amorphous corrosion product containing Ni, the process of transporting electrons was inhibited, thereby inhibiting the oxygen reduction reaction.

For the thin electrolyte layer conditions, the oxygen diffusion can maintain a high rate throughout the corrosion period. The concentration of Ni in the rust layer led to the inhibition of oxygen reduction occurring on the surface of the rust layer. Therefore, the addition of Ni can improve the corrosion resistance of low alloy steel exposed to thin electrolyte layer environments.

Figure 7. XRD analysis of corrosion products formed on the experimental steels.
Some aspects need to be understood clearly. For example, the proportion of oxygen reduction and corrosion product reduction occurring on rust formed on the carbon and Ni-containing steels, and the effect of Ni on the oxidation reaction of rust product should also be investigated in further detail.

5. Conclusions
The corrosion behavior of carbon and Ni-containing steel was investigated during thin electrolyte layer conditions with and without O₂. The main findings may be summarized as follows:

- The weight loss of Ni-containing steel was accordingly less than that of the carbon steel in the thin electrolyte layer condition.
- Oxygen reduction was inhibited for corrosion product formed on Ni containing steel;
- Concentration of Ni in the rust layer formed on Ni containing steel may lead to the formation of amorphous products;
- Ni distributed in the structure of Fe₃O₄ in the rust formed on Ni containing steel, thereby leading to the formation of amorphous products, this results in the inhibition of oxygen reduction during corrosion.

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