Effect of Scratches on Passive Anti-corrosion in Cr-Mn Ferroalloy

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Abstract. To study the scratch effect on the metal corrosion, some special scratches on the Cr-Mn ferroalloy were formed by rubbing a sandpaper on the sample surface. Two environmental cases are considered, that is, a humidity air, and a humidity air bottomed with alkaline–organic solution successively. The micro-surfaces of the samples are observed by Energy dispersive spectrometer, and the elementary contents are analyzed on an area and a line. Special scratches on the surface of Cr-Mn ferroalloy do not accelerate the metal corrosion in a humid organic alkaline environment. On the contrary, it would play a positive role in the sample passive anti-corrosion process. Chromium oxide and manganese oxide particles are produced by the oxidation of metals in a humidity air would gather in the grooves caused by the scratches. The relative study is less reported till now.

1. Introduction

Owing to the huge economic losses caused by the destruction of metal structures, the scientific community has devoted increasing attention to the corrosion phenomenon in recent decades. The impact of corrosion on the domestic economy of countries is as high as 3% of their GDP [1]. Ferroalloy containing Cr are widely used in industrial production and daily life, and they may be corroded more quickly when there are scratches and other damage to their surfaces [2–4]. When a metal is in a non-neutral environment, the corrosion process of the metal mainly involves H+ or OH− [5], and the metal is oxidized very quickly [6, 7]. However, when there are oxide films or grooves on the metal surface that can hold Cr or Mn, and the metal system contains organic matter that can be oxidized, the metal will be corroded more slowly by OH− [8]. This is common in wet, alkaline soil, in which there is always organic matter that can be easily oxidized [9, 10], and when metal comes into contact with it, the above passive anti-corrosion system is established. Though there some studies have been reported about the corrosion of metals with scratches on their surfaces [6, 7], there less studies were done about the effect of scratches or grooves on anti-corrosion of metals in an alkaline–organic humidity environment.

The focus of this study is to explore the scratch effect on the Cr-Mn ferroalloy anti-corrosion. Two environmental cases were considered: a humidity air, and a humidity air and alkaline–organic solution successively.
2. Mechanism
The corrosion mechanism was studied after two different stage treatments. The samples were treated in a humidity air and alkaline–organic solution. After some preliminary experiments, we found that when the above treatments were carried out alternately, the metal corrosion rate on the sample surfaces could be slowed down.

If the samples were only treated in a humidity air, the oxide films would form on the Cr-Mn ferroalloy surfaces, and the reactions are as follows.

\[
4\text{Cr} + 3\text{O}_2 \rightarrow 2\text{Cr}_2\text{O}_3 \quad (1)
\]

\[
2\text{Mn} + \text{O}_2 \rightarrow 2\text{MnO} \quad (2)
\]

As there are loose ferric hydroxide, ferrous hydroxide, and ferric oxide in the oxide film, the oxide film on the sample surfaces would quickly fall off, and then the metal surfaces would be exposed. The oxide film in a groove would be retained by the groove protection. EDS analysis around some grooves of the sample surfaces after a humidity air treated found that the relative content of element O in the grooves is higher than that in other areas, and element O should be belong to Cr2O3 or MnO, meaning that the grooves have the ability to retain the Cr, Mn oxide films or their oxide aggregates.

If the samples were treated in a humidity air and alkaline–organic solution successively, the following phenomena would occur. When the Cr-Mn oxides retained in the grooves met the organic functional groups in the alkaline–organic solution, the Cr-Mn oxides would catalyze the organic functional groups of the alkaline–organic solution. The organic functional groups were oxidized to release free H⁺, and the free H⁺ would react with the OH⁻ to form H₂O. The pH value of the liquid films near the grooves tended to neutral for consuming the OH⁻ of the alkaline liquid–organic solution, which resulted in the corrosion rate around the grooves being slowed down compared with other surface areas without grooves. The reactions mentioned above were presented in Equation 3 and 4. The anti-corrosion process in the grooves was shown in Figure 1.

\[
\text{Cr}_2\text{O}_3 - \rightarrow -2\text{Cr}^{2+} + \text{H}^+ + \text{H}_2\text{O} \quad (3)
\]

\[
\text{MnO} - \rightarrow -\text{Mn}^{2+} + \text{H}^+ + \text{H}_2\text{O} \quad (4)
\]

3. Materials and Methods
Model 202 stainless-steel sheet with a size 1 cm × 1 cm × 1 mm was used in the experiment. A humidity air treatment stage was described as follows. Firstly, the samples were soaked in dilute nitric acid (0.05 mol/L) for 1 h to remove the original oxide film on the sample surface. Secondly, after the sample surfaces got dry, scratches on the sample surfaces were made by shifting a sandpaper (surface
particle size of 1 char) on the sample surfaces for 20 cm under 100 N pressure. Thirdly, the samples were laid aside for 48 h at a 95% humidity and 300 K atmosphere. Finally, the samples were dried at 330 K for 24 h. An alkaline–organic solution treatment stage was described as follows. Firstly, preparing the alkaline organic solution: Tartaric acid (0.03 g), sodium ascorbic acid (0.038 g), glucose (0.015 g), sucrose (0.03 g), citric acid (0.039 g), and ethanol (1 ml) were added to a distilled water (200 mL), using sodium carbonate to adjust the aqueous solution pH value to 9. Secondly, a skimmed cotton pad was immersed in the alkaline organic solution until it reached a saturation adsorption. Thirdly, the samples were laid side by side on the skimmed cotton pad for 168 h in a dustless environment (Humidity 100%; Temperature 300 K). Fourthly, the samples were immersed in a distilled water for 1 h. Finally, the samples were dried in a vacuum drying oven at 300 K for 0.5 h.

Energy dispersive spectrometer (EDS) analysis was carried out on the surface of the samples treated by a humidity air, or treated in a humidity air and alkaline–organic solution successively. The EDS analysis carried out in a line (7 μm – 10 μm), which crossed the grooves on the sample surfaces, and the step length used is 30 nm. The EDS analysis carried out in an area about 225 μm2 – 250 μm2. The elemental contents of the flat surface and the groove surface were analyzed separately, and they were calculated in an average based on two micro area elemental analysis of a sample.

4. Results and Discussion

Figure 2 shows the EDS analysis result of the samples that was treated in a humidity air. The average mass percentage of element O in the groove was 0.95%, element Cr 16.77%, and element Mn 1.33%. The average mass percentage of element O was 0.84%, element Cr 17.25%, and element Mn 1.37% on the flat surface. It was found that the relative content of O increased while the relative contents of Cr and Mn decreased. It was further found that the relatively flat surface in the groove has more Cr-Mn oxide. Considering the relative contents of elements due to O in the magnitude of the absolute value range from 0.01% to 0.05%, carbon and silica refractory erosion of inert-element relative content conforms to the trend, but the relative contents of elemental Cr and Mn are greater than 0.05%; therefore, the grooves in the process of retaining Cr-Mn oxide are slightly lost.

Next, EDS line analysis was carried out for the samples that were treated in a humidity air and alkaline–organic solution successively, and the results were shown in Figure 3. The mass percentage of oxygen at the groove is 1.60%, and 2.89 – 3.85% on the flat surface. The mass percentage of oxygen in the groove is lower than that in the other surface, and showed an increase tendency in the flat surface as the analysis point more and more distancing the grooves. But the increase tendency ended as the distance of the analysis point and the groove is too far. Based on the above oxygen distribution characteristic, the existing of the grooves on the sample surface made that the samples have a better anti-corrosion ability compared with the samples without grooves on their surface in an alkaline-organic humidity environment. For no relative studies were reported till now based on our knowledge, we did not give comparative discussion with others.

Comparing the oxygen mass percentages of the samples treated by a humidity air, or treated in a humidity air and alkaline–organic solution successively, they are higher when the samples only treated by a humidity air, indicating that the grooves on the sample surfaces can improve the sample anti-corrosion ability in the alkaline–organic humidity environment.
Figure 2. EDS photos and elemental spatial distribution analysis of micro areas on sample surfaces (Samples here were treated in a humidity air)

Figure 3. EDS photos and elemental spatial distribution analysis of some lines spanning grooves on sample surfaces (Samples here were treated in a humidity air and alkaline–organic solution successively)

5. Conclusions
The existing of the grooves on the sample surface would accelerate the sample surface corrosion in a moist environment. The existing of the grooves on the sample surface improved the sample anti-corrosion ability in an alkaline organic moist environment. The existing of the organic functional groups would tune the pH value of the alkaline liquid films near the grooves to neutral, which resulted in the anti-corrosion ability of the samples was improved.
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7. Reference
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