Effect of Cr on the Characteristic of Rust Layer Formed on Low Alloy Steels Immersed in Flowing 3.5%NaCl Solution

Jianwei Yang1,2, Shan Jiang1,2,* and Feifan Xu1,2

1 Shougang Research Institute of Technology, Beijing 100043, China; 2 Beijing key Laboratory of Green Recyclable Process for Iron & steel Production Technology, Beijing 100043, China

*Corresponding author email: jiangshan@shougang.com.cn

Abstract. The role of Cr concentrated in rust layer formed on Cr-containing steels was investigated. Corrosion products formed on these steels were analyzed by using XPS, XRD, TEM, and Raman spectroscopy. The result indicates that amorphous Cr(OH)3 and (FeCr)3O4 formed on the Cr-containing steels resulted in the formation of ultrafine corrosion-product particles and, consequently, a compact rust layer with low electronic conductivity. The Cr-containing rust layer served mainly to inhibit the cathodic reaction of O2 reduction, thereby improving the flow-accelerated corrosion resistance of the low alloy steel.

Keywords: Chromium; Corrosion product; Amorphization; Cathodic reaction.

1. Introduction

The study of flow-induced corrosion of steels has been proceeded through years[1,2]. Most of the studies have investigated the corrosion resistance and corrosion behavior of Cu alloys, stainless steels, as well as the carbon steels. And yet there are reports indicate the corrosion rate of steels, in a stagnant environment, is much lower than that in a flowing environment While Low alloy steels tend to be more widely used in all kinds of industrial facilities. Some facilities even operate in a fluid environment inevitably, especially these ballast pipes served in vessels. However, the characterization of rust formed on low alloy steels exposed in flowing environment is rarely reported.

In the research field of atmospheric corrosion of weathering steel, amorphous substance is often seen as the main product of rust layer which formed on steel surface[3-9]. And the amorphous substance also benefits the protection of rust layer. In the flowing condition, the diffusion rate of oxygen can be increased by fluid flow. Hence, oxygen could easily penetrate the corrosion product, the formation of disordered Fe(OH)3 or amorphous FeOOH can easily occur in the process of corrosion[6,7]. It worths mentioning that Stratmann[10] also propose that amorphous FeOOH is a type of primary corrosion product.

In the previous study[11], Cr concentrated in the inner rust layer formed on weathering steel promote the amorphization of rust layer. By the reason of the increase of Cr content in the rust layer, it results in a formation of α-FeOOH with small crystalline structure doping Cr. The fine structure of α-FeOOH actually could improve the compactness of rust layer. And the Cr-goethite also exhibited cation selectivity[11], and Yamashita determined the role of Cr in the structure of α-FeOOH[13].

It is essential to build the knowledge framework of the correlation between the Cr concentration of the rust layer, which forms on the low alloy steel after exposure to a flowing NaCl solution, and the formation of amorphous substances. And the role of Cr in the rust layer is also important but unclear.
Therefore, in the present study, the corrosion product formed on Cr containing steels under the condition of flowing 3.5%NaCl solution were examined to investigate the role of Cr in the rust layer, and the relationship between Cr concentration and the formation of amorphous substances in the rust layer were also discussed.

2. Experimental Method
The rotating cylinder apparatus used in the present study has been mentioned in our previous study[14]. The chemical compositions of experimental steels are list in Table 1. The corrosion experiment on those steels was performed on the rotating cylinder apparatus. All the specimens were immersed in flowing 3.5%NaCl solution with rotating speed at 200rpm for 384h. Prior to exposure, the specimens were polished, rinsed with acetone, and air-dried. The area of exposure surface for each working electrode was 3.01cm².

| Table 1. Chemical composition of experimental steels, wt%. |
|-------------|-----|-----|-----|-----|-----|
|             | C   | Mn  | Si  | P   | S   | Cr   |
| Carbon steel| 0.082 | 0.63 | 0.24 | 0.012 | 0.0036 | -    |
| Fe-0.5Cr steel | 0.075 | 0.61 | 0.24 | 0.011 | 0.0030 | 0.46 |
| Fe-2Cr steel  | 0.078 | 0.60 | 0.21 | 0.018 | 0.0020 | 1.98 |
| Fe-5Cr steel  | 0.082 | 0.60 | 0.15 | 0.0012 | 0.0040 | 4.94 |

2.1. Test Solution
This experiment was performed in a 3.5% NaCl solution (pH: 6.8). The average temperature of solution is about 25 °C. Because of the recirculation, the solution temperature was in the rage of 23 °C to 26 °C.

2.2. Rust-layer Analysis
The rust layers formed on experimental steels were scraped off by a razor and then were ground into powder. The powdered samples obtained from rust were prepared for XRD analyses. The XRD (Bruker Model D8 Advance, Cu target) measurements were performed at a scanning speed of 1°min⁻¹. The specimens covered by a rust layer were inlaid in an epoxy resin. Before buffing, the cross-section of the specimens was mechanically polished on emery papers (grades 150–1000). Subsequently, the cross-section of the corrosion products was tested by Raman spectroscopy.

The corrosion product of inner rust layer was separated by using ultra-sonic vibration in an ethanol solution for 1h. The solution containing inner layer corrosion product was dripped on a carbon film. After the ethanol evaporated, the corrosion products were observed by using a FEI FECNAI G² F20 microscope. The content of Cr in the inner rust layer was determined via X-ray photoelectron spectroscopy(XPS) (energy resolution: 0.5eV, anodic target: Al, high vacuum: 6.7×10⁻⁸Pa).

3. Results
3.1. Concentration of Cr in the Rust Layer
Fig.1 shows the content of Cr in the rust layer formed on the carbon steel and Cr-containing steels. These results suggest that the Cr content of rust layer is much higher than that of steel. In addition, the Cr content of rust layer increases with the increasing of Cr content of steel.
Figure 1. The content of Cr in the rust layer formed on the carbon steel and Cr-containing steels.

3.2. XRD Analysis of the Rust Layer
The XRD spectrum result of the inner rust layers formed on steels after flow accelerated corrosion experiments are shown in Fig.2. As the figure shows, peaks of the corrosion product formed on the Cr-containing steels are closely to those of the carbon steel correspondingly, and other chromium oxide phases were absent. Results of XRD also reveal that the increase of Cr content is resulted in amorphization of the corrosion products, and the position of corresponding characteristic peaks may indicate that the rust layer contained Fe₃O₄.

Figure 2. Analysis of XRD of the inner rust layer formed on experimental steels exposed to flowing 3.5% NaCl solution.
3.3. Influence of Cr on the Transformation of Corrosion Products

TEM observations revealed the structure of non-Cr oxide and the Cr-containing oxides with various Cr content, as shown in Fig.3. The oxides formed on the carbon steel and Cr-containing steels reveal the spindle and needle shape. The particle size of non-Cr oxide in the rust layer formed on the carbon steel is larger than that of the Cr containing oxides formed on the Cr-containing steels. Moreover, the spinal particle size of Cr-containing oxides decreased with the increasing of Cr content in the steel.

![Figure 3. TEM analysis of corrosion products formed on experimental steels.](image)

The interaction between iron oxide and the Cr concentrated in the rust layer was confirmed and the possible Cr species in the rust was determined via Raman spectroscopy of the same sample. As shown in Fig.4, the corresponding results reveal negligible shifting of the peaks occurring near 390 cm$^{-1}$ and 1300 cm$^{-1}$ of the main corrosion product formed on carbon steel and Cr-containing steel. A new peak occurs at 850 cm$^{-1}$. Rahman[15] and Ren[16] also mentioned that a new peak was detected near 850 cm$^{-1}$, respectively. Moreover, Weckhuysen[17]found that Raman peaks corresponding to chromium compounds occurred at Raman shifts of 800–1030 cm$^{-1}$. In the present study, the peak near 850 cm$^{-1}$is associated to a corrosion product containing chromium. This result is consistence with the reports suggested by Rahman and Ren.

In addition, a weak signal occurred at the Raman band near 595 cm$^{-1}$ in the spectra associated with rust formed on Fe-5Cr steel. This broad band is associated with FeCr$_2$O$_4$, as shown in a previous study[18]. According to Wang[19], two peaks(at 545 cm$^{-1}$ and 718 cm$^{-1}$) occur in the Raman spectra of pure Cr(OH)$_3$ powders. The Raman band at 718 cm$^{-1}$, which is attributed to Cr(OH)$_3$, is close to the band at 701 cm$^{-1}$ that is attributed to Fe(OH)$_3$. Therefore, it can be concluded that Cr(OH)$_3$ is present in the rust layer formed on the Fe-5Cr steel surface.
3.4. Discussion

The results revealed that concentration of Cr in the rust layer results in the formation of a protective inner rust layer. This finding provides a guideline for obtaining high-performance steel by modifying the chemical composition of the low alloy steel.

Amorphous substances comprise one of the most important corrosion products in the rust layer. Okada[5] considered that the fine Fe3O4 was the main product composed of amorphous substance in the rust layer formed on steels exposed to atmosphere. However, a sharp X-ray diffraction pattern and characteristic infra-red absorption bands were obtained from the fine magnetite Fe3O4. In contrast, the amorphous ferric oxyhydroxide, exhibited a broad X-ray diffraction pattern[5]. Previous studies proposed that α-(FeCr)OOH was detected in the rust layer formed on weathering steel exposed in atmosphere for a long term exposure[11]. Therefore, α-(FeCr) OOH was the main product composed of amorphous substance in the rust layer formed on steels exposed to atmosphere. In a wet/dry cycle corrosion environment, the corrosion product was transformed periodically. However, reduction of α-FeOOH cannot occur in the wet/dry cycle corrosion condition, owing to the stable structure of α-FeOOH. Therefore, α-FeOOH can be saved and the inner rust layer is composed of α-FeOOH after the long term exposure of atmosphere. Cr concentrated in the rust layer participates in the transformation of corrosion product, and finally incorporated into α-FeOOH.

In the present work, the amorphous substance in the inner rust, which gives rise to a blurry diffraction pattern revealed via XRD, was identified as iron-chromium magnetite. Raman analysis also revealed that FeCr2O4 and Cr(OH)3 exist in the inner rust layer. And some studies have also pointed out that the main constituents of the rust contain Cr(OH)3[19]. Therefore, Cr(OH)3 can be detected. Owing to the formation of nanosized Cr-containing corrosion products can also give a broad X-ray
diffraction pattern, increasing Cr concentration results in amorphization of the inner rust layer. Therefore, these nanosized Cr-containing corrosion products was composed of FeCr$_2$O$_4$ and Cr(OH)$_3$. Formation of amorphous products in the rust can inhibit electron transport in the rust. Therefore, the rust cannot act as a large cathodic area and the cathodic reaction of oxygen reduction was suppressed. Fluid flow can accelerate the oxygen diffusion, thereby promoting the rate of cathodic reaction. However, the main effect of Cr concentrated in the inner rust layer is to suppress the cathodic reaction. Inhibition of the cathodic reaction leads to suppression of dissolution of metal, resulting in improving corrosion resistance of low alloy steel exposed to a flowing 3.5%NaCl solution.

4. Conclusions
The concentration of Cr in the inner rust layer affects the characterization of the corrosion product. This effect is manifested as amorphization of the inner rust layer, owing to the formation of ultrafine corrosion-product particles. The Cr-containing ultrafine corrosion-product particles, which are composed of amorphous Cr(OH)$_3$ and FeCr$_2$O$_4$, and some iron oxide, may lead to a reduction in the conductivity of the corrosion product. These effects suppress the cathodic reaction of O$_2$ reduction.

Acknowledgements
The authors acknowledge the support of National key research and development plan (No. 2016YFC0401205).

Reference

[1] E.Sarver, M.Edwards, Effects of flow brass location, tube materials and temperature on corrosion of brass plumbing devices, Corros.Sci. 53(2011)1813-1824.
[2] J.A.Wharton, R.J.K.Wood, Influence of flow condition on the corrosion of AISI 304L stainless steel, Wear 256(2004)525-536.
[3] T.Misawa, T.Kyuno, W.Suetaka, S.Shimodaira, The Mechanism of Atmospheric Rusting and the Effect of Cu and P on the Rust Formation of Low Alloy Steels[J]. Corrosion Science, 1971, 11(1): 35-38.
[4] T.Misawa, K.Asami, K.Hashimoto, S.Shimodaira. The Mechanism of Atmospheric Rusting and the Protective Amorphous Rust on Low Alloy Steel[J]. Corrosion Science, 1974, 14(4): 279-289.
[5] H.Okada, Y.hosoi, H.Naito, Electrochemical Reduction of Thick Rust Layers Formed on Steel Surface[J]. Corrosion, 1970, 26(10): 429-430.
[6] M.Stratmann, K.Bohnenkamp, H.J.Engell, An Electrochemical Study of Phase-transitions in Rust Layers. Corrosion Science, 1983, 23(9): 969-985.
[7] U.R.Evans, C.A.J.Taylor, Mechanism of Atmospheric Rustiong. Corrosion Science, 1972, 12(3): 227-246.
[8] M.Stratmann, K.Hoffmann, In situ Mößbauer Spectroscopic Study of Reactions within Rust Layers, Corrosion Science, 1989, 29(11/12): 1329-1352.
[9] K.Inouye, K.Ichimura, K.Kaneko, T.Ishikawa, The effect of copper(II) on the formation of γ-FeOOH[J]. Corrosion Science, 1976, 16(8): 507-517.
[10] M.Stratmann, K.Bohnenkamp, T.Ramchandran, The Influence of Copper upon the Atmospheric Corrosion of Iron[J]. Corrosion Science, 1987, 27(9): 905-926.
[11] Yamashita M,MiyukiH,MatsudaY,etal., The long term growth of the protective rust layer formed on weathering steel by atmospheric corrosion during a quarter of a century[J]. Corrosion Science,1994,36(2):283-299.
[12] KamimuraT,NasuS,SegiT.Corrosion behavior of steel under wet and dry cycles containing Cr3+ I ion[J]. Corrosion Science,2003,45(8):1863-1879.
[13] Yamashita M,ShimizuT,Konishi, Structure and protective performance of atmospheric product of Fe-Cr alloy film analyzed by Mossbauer spectroscopy and with synchrotron radiation X-rays[J]. Corrosion Science,2003,45(2):381-394.
[14] Jiang S, Chai F, Su H, Yang CY, Influence of chromium on the flow-accelerated corrosion behavior of low alloy steels in 3.5%NaCl solution. Corrosion Science, 123(2017)217-227.

[15] Saidur Rahman Chowdhury, Ernest K. Yanful, Allen R.Pratt, Chemical States in XPS and Raman Analysis during Removal of Cr(VI) from Contaminated Water by Mixed Maghemite-magnetite Nanoparticles[J]. Jounal of Hazardous Materials, 2012, 235-236: 246-256.

[16] Zhongfei Ren, Xing Xu, Xi Wang, Baoyu Gao et al., FTIR, Raman, and XPS Analysis during Phosphate, Nitrate and Cr(VI) Removal by Amine Cross-linking Biosorbent[J], Journal of Colloid and Interface Science, 2016, 468: 313-323.

[17] B.M.Weckhuysen, I.E.Wachs, In-situ Raman Spectroscopy of Supported Chromium Oxide Catalysts: 18O2-16O2 Isotopic Labeling Studies[J]. Journal of Physics and Chemistry B, 1997, 101: 2793-2796.

[18] Ming Chen, Jinfu Shu, XiandeXie, Ho-kwang Mao, Natural Cat2O4-structured FeCr2O4 Polymorph in the Suizhou Meteorite and its Significance in Mantle Mineralogy[J]. GeochimicaetCosmochimicaActa, 2003, 67(20): 3937-3942.

[19] Bei Wang, Lining Xu, Jinyang Zhu, Hui Xiao et al., Observation and Analysis of Pseudopassive film on 6.5%Cr Steel in CO2 corrosion and environment[J]. Corrosion Science, 2016, 111: 711-719.