JSTR
ASEAN Journal of Scientific and Technological Reports

Research article

Corrosion of Low Carbon Steel in Chloride Containing Environment

Tosapolporn Pornpibunsompob[1*], Sittha Saidarasamoot[2], Sawitri Phabjanda[3], Teeratas Pornyungyuen[4], Apirath Gositanon[5], Suradet Chalermboon[6] and Ploypilin Nakaracha[7]

[1] Metallurgical and Materials Engineering Laboratory, Research and Development Division, Defence Technology Institute, Nonthaburi, 11120, Thailand; tosapolporn.p@dti.or.th
[2] Metallurgical and Materials Engineering Laboratory, Research and Development Division, Defence Technology Institute, Nonthaburi, 11120, Thailand; sittha.s@dti.or.th
[3] Metallurgical and Materials Engineering Laboratory, Research and Development Division, Defence Technology Institute, Nonthaburi, 11120, Thailand; sawitri.p@dti.or.th
[4] Metallurgical and Materials Engineering Laboratory, Research and Development Division, Defence Technology Institute, Nonthaburi, 11120, Thailand; teeratas.p@dti.or.th
[5] Metallurgical and Materials Engineering Laboratory, Research and Development Division, Defence Technology Institute, Nonthaburi, 11120, Thailand; apirath.g@dti.or.th
[6] Metallurgical and Materials Engineering Laboratory, Research and Development Division, Defence Technology Institute, Nonthaburi, 11120, Thailand; suradet.c@dti.or.th
[7] Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand; ploypailin.nak@ku.th
* Correspondence: E-mail: Tosapolporn.p@dti.or.th

Abstract: This research aims to investigate the corrosion of low-carbon steel in a chloride-containing environment. The investigation started by preparing and studying the surface condition of the specimens. The mechanical properties, microstructures and chemical compositions were also comparatively investigated between standard and corroded specimens. The results showed that the surface of the corroded samples was rough and peeling, different from the standard specimens, which were relatively smooth and non-corrosive. The average ultimate tensile strength and average yield strength of normal specimens were higher than those of corroded specimens at 5.39% and 2.32%, respectively. The corrosion products developed on the surface of corroded specimens caused a high-stress concentration area. The specimen is more prone to cracks and breaks when subjected to tensile stress. The surface of the normal specimen was composed of iron, oxygen, carbon, and silicon. In contrast, the surface of the corroded specimen contained the same elements as the normal specimen except chlorine which was detected. The film layer of the corroded specimen was cracked in contrast with the normal specimen, where the film still covered the metal substrate. The chemical composition analysis found that the corroded specimen's film layer contained chlorine, which is not detected in the film layer of the normal specimen. This is because the film layer of hot-rolled steel remains porous even passing the hot-rolling process. These pores allow chloride ions to diffuse and react with the film layer and the metal substrate. This makes the film layer of the corroded specimen thicker and initiates cracks. When stable alpha-iron-oxyhydroxide is formed on the steel surface, it can help to suppress corrosion.

Keywords: Corrosion, Low alloy steel, Chloride environment

Citation:
Pornpibunsompob, T.; Saidarasamoot, S.; Phabjanda, S.; Pornyungyuen, T.; Gositanon, A.; Chalermboon, S.; Nakaracha, P. Corrosion of Low Carbon Steel in Chloride Containing Environment. *ASEAN J. Sci. Tech. Report.* **2022**, *25*(4), 21-29. https://doi.org/10.55164/ajstr.v25i4.247174.

Article history:
Received: August 2, 2022
Revised: November 9, 2022
Accepted: November 13, 2022
Available online: November 20, 2022

1. Introduction

Low-carbon steels have many good properties in engineering applications, such as medium strength, malleability and ductility. It can be easily used in hot-rolled conditions and, after subsequent cold-rolling, annealing, and possibly coating. Modern processing provides a high degree of control of chemistry and processing to enable a wide range of grades with different combinations of strength and formability. Close control of gauge, width, shape, and flatness is also achieved[1]. Hot forming is one of the favorite processes in manufacturing low-carbon steel. As a result of the hot-forming process, the size and shape of the product are easily obtained. Furthermore, the parent material chemistry significantly influenced oxidation's kinetics and affected the oxide films' microstructure and composition [2]. This film is formed on the surface of the workpiece during hot rolling and is generally made up of Wustite (FeO), Magnetite (Fe_3O_4) and Hematite (Fe_2O_3) with positions arranged from the steel surface to the outer surface contacting environment, respectively. Wustite is developed from a eutectoid reaction and transforms to Magnetite, so the oxide film results in only Magnetite and Hematite layers[3]. Moreover, the oxide film on the surface is also porous. However, the film layer is deformed by a hot rolling process and extruded to the desired shape and thickness. The film has a certain density and is sufficient to provide effective corrosion protection in some normal atmospheres. Therefore, studying and analyzing the root causes of such occurrences is necessary.

The corrosion of hot-rolled low-carbon steel has been investigated for many years. However, the research on steel corrosion remains very interesting at present. Fundamentally, corrosion is due to moisture and dissolved oxygen but is accelerated by many contaminants, such as sulfur dioxide and chloride [4]. The corrosion products were quantitatively developed in a pollutant-free atmosphere depending on the exposure time and relative humidity. It had filiform corrosion characteristics. Meanwhile, cellular corrosion products grew on the filaments[5]. In the case of chloride environments, chloride plays an important role in accelerating corrosion reactions and rapid corrosion product formations. Various amounts of chloride depositions implied different accelerative corrosion mechanisms. The high amount of chloride over critical concentration is very significant for β-FeOOH formation. However, as to the low amount of chloride deposition, its effect was mainly conducive to transforming γ-FeOOH to α-FeOOH [6]. The corrosion will also deteriarate the mechanical properties of low alloy steel. A decrease in the sample cross-section governs the reduction of ductility. Additionally, the exfoliation was also a cause of degradation in terms of cracks. The random form of any pits on steel surface became progressively worse in the mechanical properties, related to mass loss and pit depth and extension[7-8].

In this study, some hot-rolled steel sheets showed many rusts on the surface of the storage area. Its quantity is larger than normal when observed visually. Moreover, when the rust was removed before being fabricated, it was deeper than usual. So, this research aims to analyze the cause of low-carbon hot-rolled steel corrosion by comparing normal and corrosion conditions. It will also introduce some suggestions for inhibiting and preventing corrosion.

2. Materials and Methods

Initially, two conditions of low-carbon hot-rolled steel specimens (normal specimens and corroded specimens) are received from a hot-rolled steel manufacturer in Thailand. The condition of the workpiece's surface was recorded after the visual inspection was examined. The three types of specimens were prepared: the three specimens for chemical composition testing (approximated to 50×50 mm), the three specimens for microstructural analysis (approximated to 10×15 mm), and the four specimens for mechanical properties testing (according to ASTM E8). To analyze microstructure and morphology, the specimens are performed by Carl Zeiss Sigma 500VP Field Emission Scanning Electron Microscope (FESEM). The microchemical analysis of both normal and corroded specimens was conducted by Oxford Aztec Ultim Max 60 Energy Dispersive Spectroscopy (EDS). The specimens for tensile testing were prepared by Wirecut & EDM machine and then mechanically tested by 100 kN Universal Tensile Testing Machine. Olympus DSX510 Digital Microscopes examined the fracture surface of two types of specimens. After analysis and testing, data collection and conclusion of the research results were collected. The process of analysis and testing is placed in Figure 1. The prepared specimen is shown in Figure 2. The chemical compositions were analyzed by BRUKER Q4 Optical Emission Spectroscopy (OES) and the results are shown in Table 1. They indicated that the specimen is low-carbon steel.

Table 1. Chemical composition of the specimens

Composition (%Wt.)	Conditions	Carbon	Silicon	Manganese	Phosphorous	Sulfur
Normal specimen	Specimen No.1	0.172	0.203	0.519	0.0035	< 0.005
	Specimen No.2	0.169	0.209	0.521	0.0029	< 0.005
	Specimen No.3	0.174	0.217	0.522	0.0029	< 0.005
	Average	**0.172**	**0.210**	**0.521**	**0.0031**	**< 0.005**
Corroded specimen	Specimen No.1	0.168	0.196	0.521	0.0019	< 0.005
	Specimen No.2	0.169	0.199	0.513	0.0019	< 0.005
	Specimen No.3	0.171	0.202	0.519	0.0017	< 0.005
	Average	**0.169**	**0.199**	**0.518**	**0.0018**	**< 0.005**

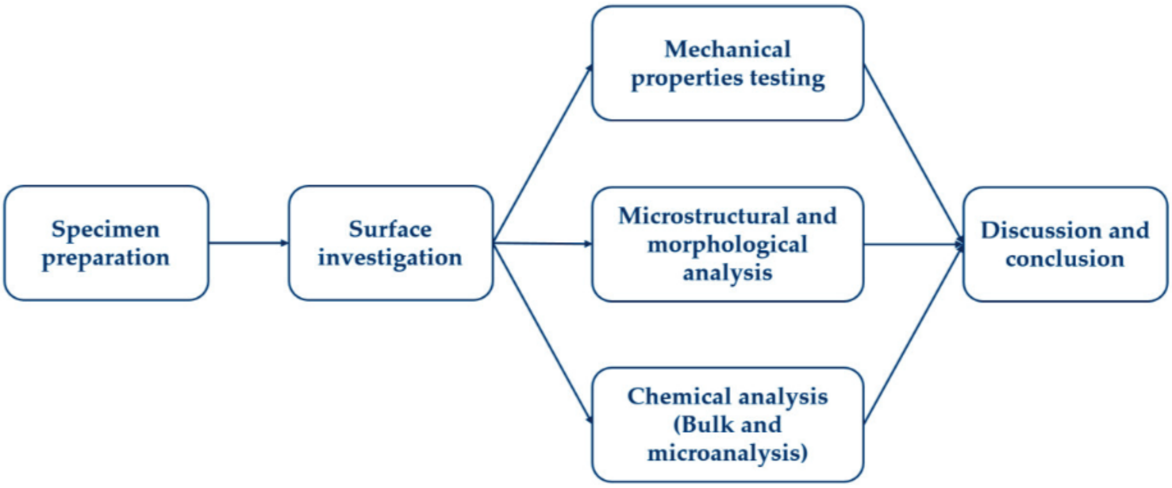


Figure 1. Specimen preparation and testing procedure

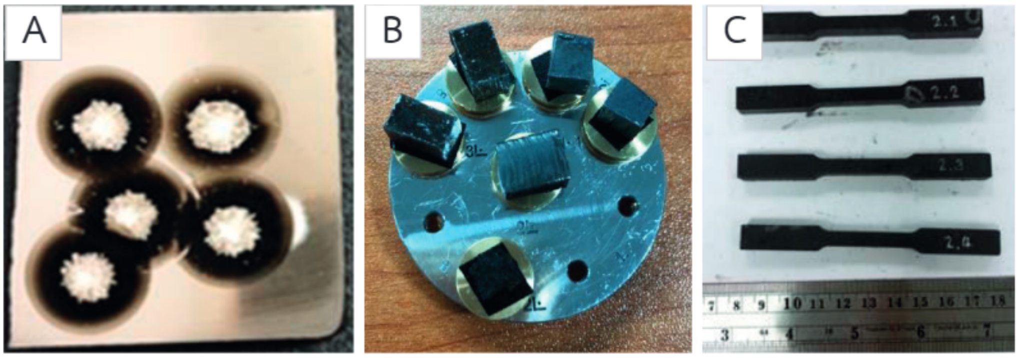


Figure 2. Testing and analysis specimen (A) chemical composition analysis specimen, (B) microstructure and morphology analysis specimen, and (C) specimen for tensile testing

3. Results and Discussion

The corrosion of low alloy steel in chloride containing atmosphere was studied in three approaches:

3.1 Mechanical properties approach

The tensile testing results of two types of specimens were placed in Table 2.

Table 2. Tensile testing results of normal and corroded specimens

Mechanical properties	Specimen type	Test results (MPa)				
		Specimen No.1	Specimen No.2	Specimen No.3	Specimen No.4	Average
Ultimate tensile strength	Normal	455.52	444.94	446.50	444.47	447.86
	Corrosion	423.80	429.25	421.88	424.85	424.95
Yield strength	Normal	295.19	286.99	282.08	291.36	288.91
	Corrosion	280.37	272.89	284.83	291.10	282.30

It was found that normal specimens have an average maximum tensile strength of 447.86 MPa, which is higher than that of corroded specimens with an average maximum tensile strength of 424.95 MPa. In the same way, the average yield strength of normal specimens is 288.91 MPa, while the average yield strength of corroded specimens is 282.30 MPa. Therefore, the average mechanical properties of normal specimens are higher than those of corroded specimens, as shown in Figure 3. If it is calculated as a percentage, it will be concluded that normal specimens have the average maximum tensile strength and the average yield strength higher than corroded specimens at 5.39% and 2.32%, respectively. Because the surface of corroded specimens is very rough due to corrosion products, tension loads acting on the corrosion pits will cause stress concentration and decrease the strength[8]. When the workpiece is subjected to tensile stress, it is easier to propagate some cracks. It can be noticed from the cracked surface, and it is a sharp tooth mark, as shown in Figure 4(A). When the tensile strength increases, the crack will propagate until the workpiece is completely fractured. While normal specimens do not have corrosion products on the surface, the fracture is caused by the ductile failure mechanism. The fracture surface is shown in Figure 4(B). Thus, it has a strength higher than the corroded workpiece.

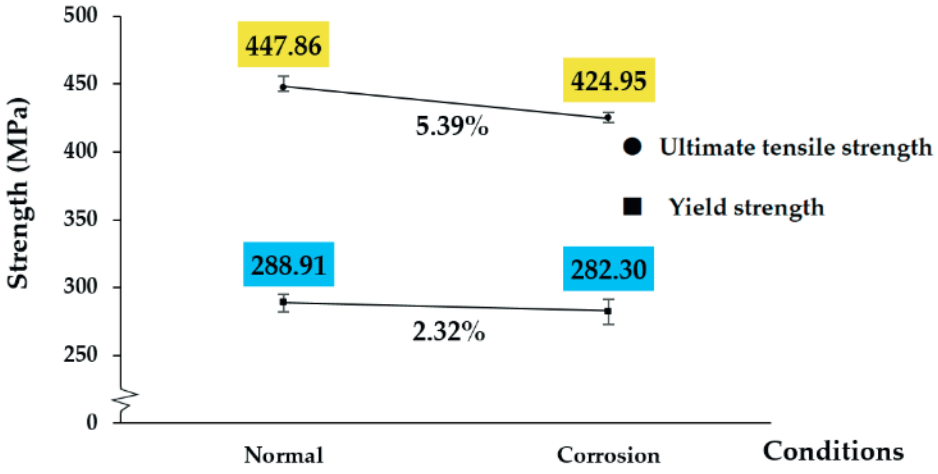


Figure 3. Average mechanical properties comparison between normal and corroded specimen

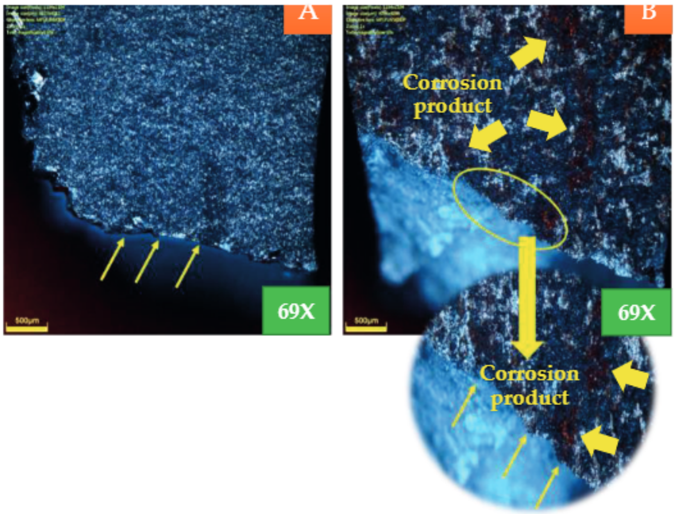


Figure 4. Fracture surface analyzed by optical microscope comparison between (A) Normal specimen and (B) Corroded specimen

3.2 Surface study approach

The surface condition of normal and corroded specimens, observed with visual and light microscopy, is shown in Figure 5. It can be seen that the normal specimens' surface is matte and does not peel off. As for the corroded workpiece, the surface of the workpiece is rough, and some area of the specimen's surface is peeled off. Also, it is found corrosion products when examined by scanning electron microscopy. As shown in Figure 6, it was found that the surface of the normal specimen is smooth and dull. Small scabs may be found on the surface in some places resulting from the hot rolling process. As for corroded parts, the workpiece's surface is rough and peeled off.

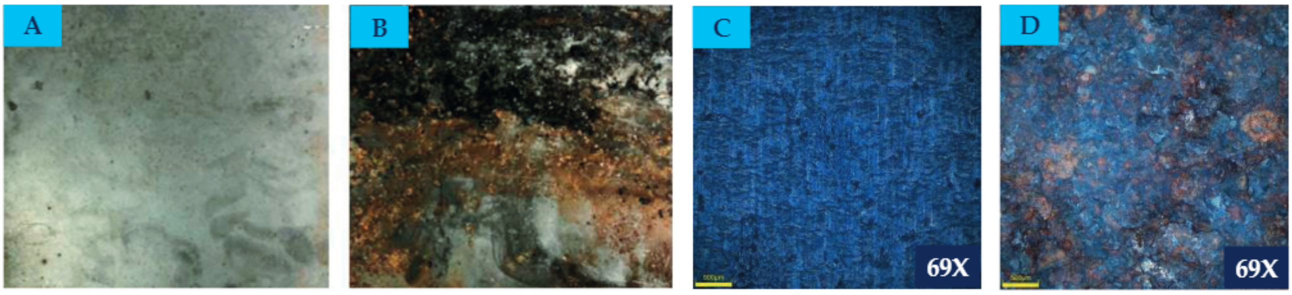


Figure 5. Surface investigation of specimens by visual examination (A) normal specimen, (B) corrosion specimen, and by optical microscope (C) normal specimen (D) corroded specimen

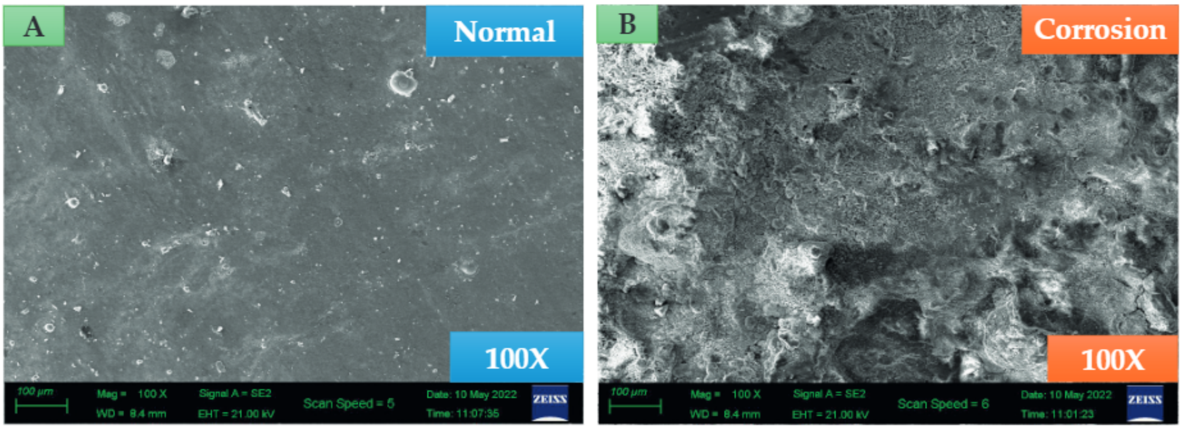
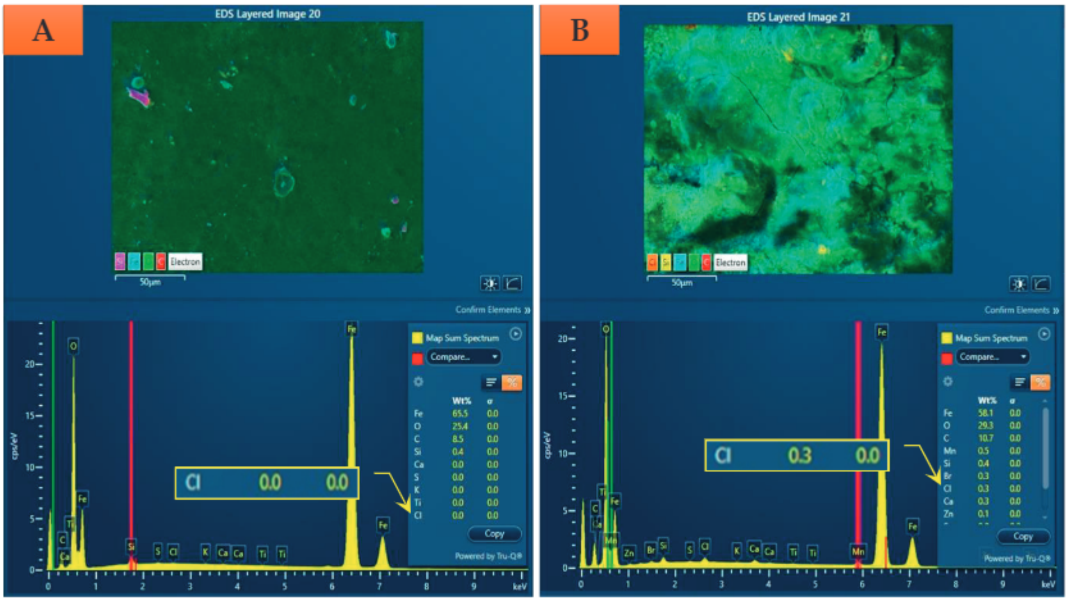


Figure 6. Surface morphology analyzed by FESEM (A) normal specimen (B) corroded specimen

The microchemical composition examined by EDS is depicted in Figure 7. It shows that the normal surface of the specimen is composed of iron, oxygen, carbon, and silicon, while the surface of the corroded specimen contains the same elements as the normal specimen except chlorine. It was detected on the surface of the specimen. Chlorine is one of the main elements that potentially cause corrosion in steel [6]. The effect of chlorine on corrosion is studied next.



A

	Wt%	σ
Fe	65.5	0.0
O	25.4	0.0
C	8.5	0.0
Si	0.4	0.0
Ca	0.0	0.0
S	0.0	0.0
K	0.0	0.0
Ti	0.0	0.0
Cl	0.0	0.0

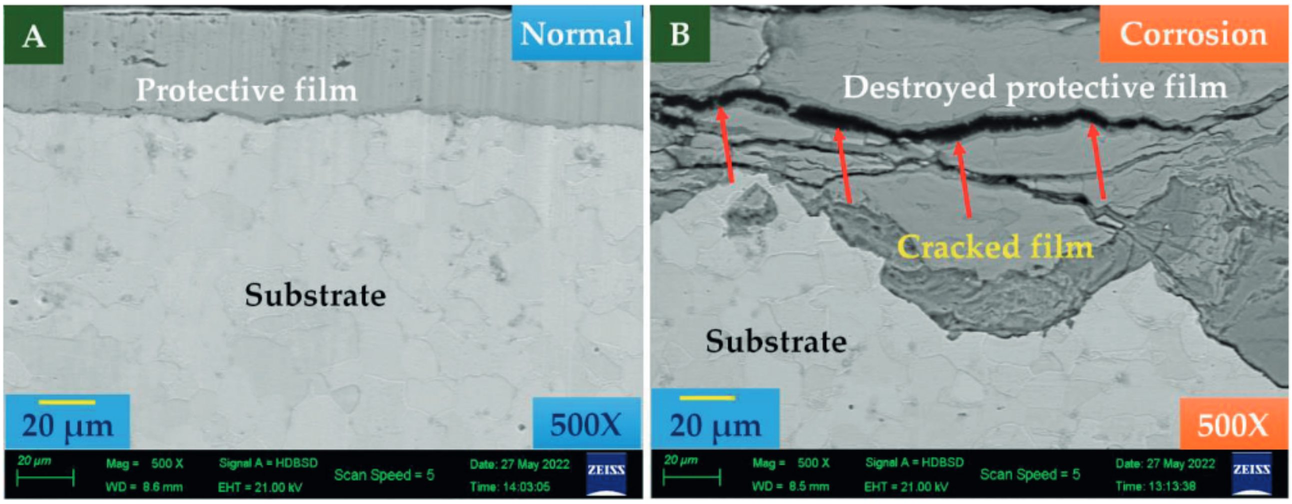
B

	Wt%	σ
Fe	58.1	0.0
O	29.3	0.0
C	10.7	0.0
Mn	0.5	0.0
Si	0.4	0.0
Br	0.3	0.0
Cl	0.3	0.0
Ca	0.3	0.0
Zn	0.1	0.0

Figure 7. Microchemical composition of the specimen surface analyzed by EDS (A) Normal specimen (B) Corroded specimen

3.3 Protective film approach

A detailed investigation of the surface, especially at the protective film, was performed, as shown in Figure 8. It was found that normal specimens have a protective film coating on the surface. An oxidation reaction formed the film layer during the hot rolling process (Figure 8(A)). In contrast with corroded specimens, the protective film is destroyed. The film contains several cracks separating the protective film from each other. This phenomenon allows the metal surface to contact the corrosive environment directly. Therefore, oxidation reactions still occur continuously. So, the film layer of the corroded specimen is not only a result of the hot rolling process, but it is also caused by an oxidation reaction when the substrate is exposed to the corrosive environment. That explanation can also explain why the film thickness of the corroded workpiece is greater than the normal specimen.



Mag = 500 X WD = 8.6 mm Signal A = HDBSD EHT = 21.00 kV Scan Speed = 5 Date: 27 May 2022 Time: 14:03:06 ZEISS

Mag = 500 X WD = 8.5 mm Signal A = HDBSD EHT = 21.00 kV Scan Speed = 5 Date: 27 May 2022 Time: 13:13:38 ZEISS

Figure 8. Morphology of protective film analyzed by FESEM (A) normal specimen (B) corroded specimen

The microchemical composition of normal specimens is shown in Figure 9. It was found that the protective film formed by the hot-rolling process was mainly composed of iron and oxygen. It is ferrous oxide. Moreover, it was observed that the iron content in the oxide film region was greater than that in the substrate. The substrate is composed of many elements within it. Therefore, as a proportion, the iron content is greater in the film layer area.

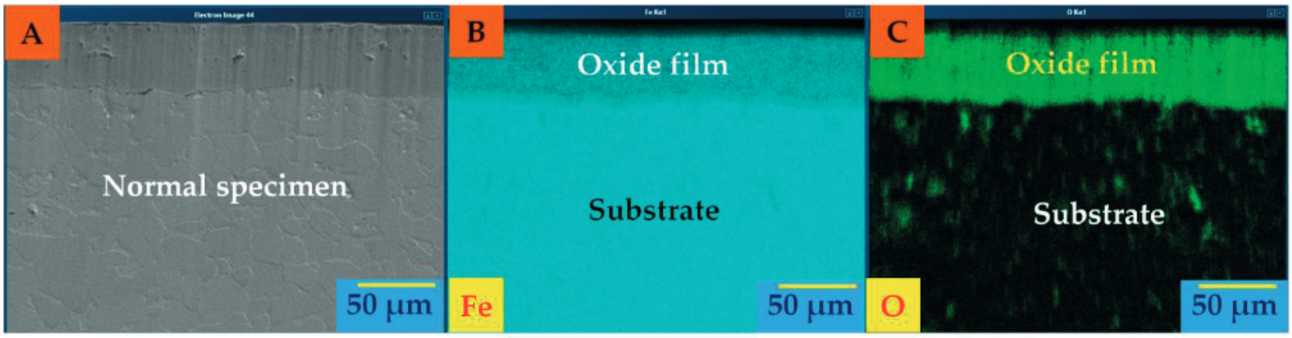


Figure 9. EDS mapping of cross-section's surface normal specimen (A) SEM micrograph (B) iron (C) oxygen

The oxide film layer is cracked in corroded specimens. However, the chemical composition is not quite similar to the normal specimens. Iron, oxygen, and chlorine are found in the oxide film. It remains similar to the composition of the corroded specimen's surface, as shown in Figure 10. Therefore, the oxidation of steel, despite the presence of chlorine, will continue to form compounds composed of iron and oxygen because the protective film is porous (Even though it has been hot rolled, making the film denser). This allows the chloride ions to easily pass through the film and react with the substrate resulting in a thicker and deeper oxidation film. However, if the oxidation layer is complete, it will inhibit chloride corrosion [6]. Chloride plays a vital role in catalyzing the oxidation of steel.

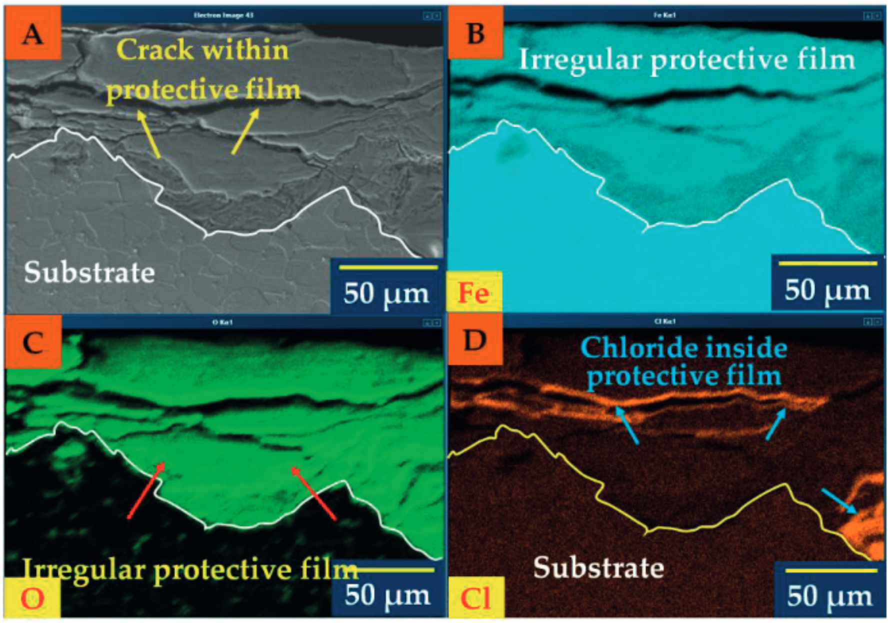


Figure 10. EDS mapping of cross-section's surface corroded specimen (A) SEM micrograph (B) Iron (C) Oxygen (D) Chlorine

Because the chloride ion catalyzes the oxidation reaction of steel, following Equations 1 – 2, resulting in an increment in both classification and quantity of corrosion product. This is consistent with the analysis results shown in Figure 10.

$$Fe \xrightarrow{\text{Anodic}} Fe^{2+} \xrightarrow{\text{Hydrolysis}} [FeOH]^{+} \xrightarrow[\text{precipitation}]{\text{Oxidation and}} \gamma\text{-FeOOH(s)} \tag{1}$$

In equation 1, Gamma-iron-oxyhydroxide (γ-FeOOH) is a corrosion product that develops earlier and then transforms to alpha-iron-oxyhydroxide (α-FeOOH) according to equation 2. Alpha-iron-oxyhydroxide is more stable and adheres to the surface than Gamma-iron-oxyhydroxide. So, this ferrous oxide helps suppress the corrosion process on steel specimens [9].

$$\gamma\text{-FeOOH(s)} \xrightarrow{\text{Chlorination}} FeO_x(OH)_{2\text{-}2x}Cl \xrightarrow{\text{Solid precipitation}} \alpha\text{-FeOOH(s)+HCl(g)} \tag{2}$$

The suggested methods for corrosion inhibition and protection are summarized below;

1. A suitable pre-treatment or surface coating on a bare carbon steel surface would help inhibit corrosion. It prevents the access of corrosive anions to the steel surface [10-12].
2. Avoiding direct exposure to chloride-containing atmospheres can suppress and prevent corrosion, even though low-carbon steel can be slightly corroded in the natural environment caused by humidity and dissolved oxygen [13-14].

4. Conclusions

Low-carbon hot-rolled steels were susceptible to corrosion under chloride-containing environments despite the protective film formed by the hot-rolling process. The phenomena caused the reduction of mechanical properties. The surface of the corroded specimen was rough and peeled off. Chloride ions penetrated the metal through the porous protective film and reacted with the substrate. It developed various compounds causing crack initiation and propagation in the film layer. When stable alpha-iron-oxyhydroxide was formed on the steel surface, it could help to suppress corrosion.

5. Acknowledgements

We would like to thank the Defence Technology Institute under the Ministry of Defence, Thailand, for supporting all expenses to attend the academic presentations.

Author Contributions: Sittha Saidarasamoot were the director of this project. Tosapolporn Pornpibunsompob wrote and submitted the article, coordinated with editor until the acticle had been accepted for publication. The specimens were prepared by Teeratas Pornyungyuen and Ploypilin Nakaracha. The tensile testing was performed by Suradet Chalermboon. Apirath Gositanon analyzed the specimen with Electron microscopy technique. Sawitri Phabjanda discussed and concluded the testing results.

Funding: This research was funded by Defence Technology Institute.

Conflicts of Interest: The authors declare that there is no conflict of interest regarding the publication of this article.

References

[1] Urabe, T. High Formability Steel In *Encyclopedia of Materials: Metals and Alloys, C. G. Francisca, M. Goro, 1st ed., Elsevier, Osaka, Japan*, 2021, 3-11.

[2] Ahmadi, D. *Oxide Scales Behaviour During Descaling and Hot Rolling*, Doctor of Philosophy in material science and engineering The University of Sheffield, England, June 2019, p. ii.

[3] Tanei, H.; Kondo, Y. Phase transformation of oxide scale and its control. *Nippon steel & Sumitomo metal technical report*, 2016, 111, March 2016.

[4] Fontana, M.G. *Corrosion engineering*, 3rd ed., McGraw-Hill, Singapore, 2001, 372-373.

[5] Lin, C.; Chen, S. Atmospheric corrosion behavior of mild steel in the initial stage under different relative humidity. *International journal of georesources and environment*, 2018, 4, 33-39.

[6] Ma, Y.; Li, Y.; Wang, F. Corrosion of low carbon steel in atmospheric environments of different chloride content. *Corrosion science*, 2009, 51, 997-1006.

[7] Martínez, C.; Briones, F.; Villarroel, M.; Vera, R. Effect of atmospheric corrosion on the mechanical properties of SAE 1020 Structural steel, *Materials*. 2018, 11, 1-17.

[8] Chen, Y. Y.; Tzeng, H. J.; Wei, L. I.; Shih, H. C. Mechanical properties and corrosion resistance of low-alloy steels in atmospheric conditions containing chloride. *Materials Science and Engineering A*, 2005, 398, 47-59.

[9] Tee, Ch. Atmospheric Corrosion of Steel: A Review and Case Study. *Journal of Science and Technology*, *Ubon Ratchathani University*, 2017, 19, 178-186.

[10] Etteyeb, N. et al, Corrosion inhibition of carbon steel in alkaline chloride media by Na_3PO_4. *Electrochimica acta*, 2007, 52, 7506-7512.

[11] Schuerz, S. et al. Corrosion behaviour of Zn–Al–Mg coated steel sheet in sodium chloride-containing environment. *Corrosion science*, 2009, 51, 2355-2363.

[12] Girciene, O. et al. The effect of phosphate coatings on carbon steel protection from corrosion in a chloride-contaminated alkaline solution. *Chemija*, 2013, 24, 251-259.

[13] Permsuwan, P. et al. Corrosion of different types of steel in atmospheric and tidal marine environment of Thailand. *Research and development journal*, 2011, 22, 17-24.

[14] Chowwanonthapunya, T. et al. A preliminary study of atmospheric corrosion performances of carbon steels in coastal and urban environments in Thailand, *Burapha university international conference* 2015, 10-12 July 2015, 625-632.