Corrosion Behavior of Silicon-Bearing Steel in a Wet/Dry Environment Containing Chloride Ions

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The rust of Si-bearing steel was analyzed by EPMA, XRF, XPS and TEM, and the electrochemical behavior of the rusted steel was investigated by the electrochemical impedance spectroscopy (EIS) method after wet/dry cyclic corrosion test with chloride ions.

The 2.0 mass% Si-bearing steel showed high corrosion resistance compared to carbon steel (SM) in the corrosion test. EPMA and XPS showed that Si existed as an intermediate oxidized state such as Si^{2+} in the inner rust layer for Si-bearing steel. TEM showed that nano-scale complex oxides containing Si were formed in the inner rust of the Si-bearing steel.

EIS measurement was taken to estimate the rust resistance (R_{rust}) and corrosion reaction one (R_t) of the rusted steel. It was found that R_{rust} and R_t of Si-bearing steel were much larger than those of SM after the rust formation. The corrosion of Si-bearing steel could be suppressed by the formation of the nano-scale complex oxide containing Si in inner rust layer to prevent the penetration of Cl ions.
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1. Introduction

Recently it is very important to use the weathering steel to reduce the maintenance cost of infrastructure facilities. In addition there are many steel structures in coastal areas, it is necessary to use high resistant steels against the corrosion caused by air-borne salt particles.¹⁾ Thus Ni-bearing weathering steels²⁾ that can be used in coastal environments have been proposed. However, Ni is a rare metal and hard to use for the recycle of steels.

While there have been many analyses of rust on the steels in mild environments,^{3–10)} there are many problems that remain unclear regarding the basic mechanisms of the rust formation¹¹⁾ and the effect of alloy elements^{12–14)} in saline environments. Therefore, in order to obtain the corrosion guidance for weathering steels that can be used in coastal environment, the thermodynamic stability of various rusts (Fe-X system) was investigated using a binary-phase potential-pH diagram.¹⁵⁾ Finally, it was indicated that Al and Si had the possibility to form stable complex-oxides with Fe. Moreover, Si does not prevent the recycle-use of steels that will be necessary in the future to take into the consideration of LCA (Life Cycle Assessment). However, there have been few reports about the effect of Si^{16,17)} on the atmospheric corrosion of steels in saline environment. In this study, the process of the formation and the electrochemical behavior were investigated on the rust of Si-bearing steels formed in a cyclic wet/dry condition. Specially, the chemical state of Si in the rust for Si-bearing steel was examined by using EPMA, XRF, XPS and TEM. Moreover the electrochemical behavior of the rust was investigated by the electrochemical impedance spectroscopy (EIS) method after wet/dry cyclic corrosion test with chloride ions. Finally, relation between the formation and electrochemical behavior of the rust was discussed for Si-bearing steel.

2. Experimental Procedures

2.1 Wet/dry cyclic corrosion test¹¹⁾

The corrosion test consisted of 2 steps. 1st step was wetting process by putting on the sample surfaces with 0.4 Litter/m² of a 0.5 mass% NaCl solution. And 2nd step was drying process by keeping the specimen in a chamber maintained at 25°C, 60% RH for 12 hours. Immediately before dropping a solution, the specimen was washed in distilled water and dried to prevent progressive salt accumulation. The sample materials were Si-bearing steel and carbon steel (SM), which composition was 0.05C-2.0Si-0.7Mn-0.01P-0.003S-0.03Al-0.003N-0.002O-Fe, and 0.05C-0.2Si-0.7Mn-0.01P-0.003S-0.03Al-0.003N-0.002O-Fe, respectively.

2.2 Physical analysis of the rust^{12–15)}

For the analysis of the rust, Electroprobe X-ray microanalysis (EPMA), X-ray Fluorescence Spectroscopy (XRF), X-ray photoelectron spectroscopy (XPS) and Transmission electron microscopy (TEM) were used. The EPMA was carried out using a JEOL JXA-8600MX, with an acceleration voltage of 15 kV, an irradiation current of 1×10^{-7} A, and a beam diameter of 1 μm . After the steel was mounted in the resin, it was mirror polished using emery papers, diamond paste and Al_2O_3 powder. Then carbon was evaporated onto the specimen in order to compensate the charging effects. A cross section of the rusted steel was examined. The distribution of Si in the rust was measured to identify the existing location of Si. Moreover the chemical state of Si in the rust was measured by using Si $K\alpha$ and $K\beta$ characteristic X-Ray. This new method has an advantage to investigate the chemical state of element in local area under 1 μm of the diameter by using electron beam source.

The XRF was conducted using Rigaku 3080 with a Rh X-ray source and beam diameter 20 mm. The chemical state of Si in the rust was measured by using Si $K\alpha$ and $K\beta$ XRF

spectra. XRF samples were prepared by using standard chemicals for Si and SiO₂ distributed in the resin.

For the XPS, a SSI SSX-100 was used, with an Al K α X-ray source and beam diameter 600 μ m. After the rust on the steels were scraped using a spatula of brass, the powder was mounted on a pure In plate. The sample for XPS was covered with a Ni mesh and electron with acceleration voltage of 1 V was irradiated in order to compensate the charging effects. Moreover, the chemical state of Si was investigated using its Si 2s and 2p spectrum, where the binding energy was corrected by that of the adventitious carbon (C 1s = 284.6 eV).

For the TEM observation with Philip CM30, the rust was cut by FIB (Focused Ion Beam) from the inner layer. EDXS (Energy dispersing X-ray) analysis was carried out using PV9900 (EDAX Co., Ltd) in order to identify the chemical composition of the rust and select the Si-rich oxides.

2.3 EIS measurement of the rust¹¹⁾

After the corrosion test, the electrodes were fabricated, and EIS measurements were carried out. EIS measurements were taken in 0.1 M Na₂SO₄ solution, under the following conditions: two electrodes system, measurement frequency range of 20 kHz to 0.3 mHz, and applied voltage of 10 mV. Because it takes 5 hours for EIS measurement to get all results up to 0.3 mHz, the rust is changing in the NaCl solution during measurements. By comparing the EIS values at 1.0 mHz after 0, 5, 24 hours, it was found that there were little changes in the EIS results of the rusted steel measured in Na₂SO₄ solution. Thus it need technically for using Na₂SO₄ solution to keep the rust condition in the EIS measurement.

3. Results and Considerations

3.1 Analysis of the rust on Si-bearing steel

The corrosion resistance of the Si-bearing steel was evaluated by 40 cycles of a wet/dry corrosion test. The amount of corrosion was measured by the weight loss of the steels after removing the rust. The rust was removed by the wire brush in the Ammonium hydrogen citrate solution (HOC(COOH)(CH₂COONH₄)₂) at 60°C. The amount of corrosion at 30 cycles for the Si-bearing steel was about 85% of that of carbon steel (SM). It was clear that the addition of Si had an effect in environments containing chlorides. In order to clarify the corrosion-resistance mechanism of Si-bearing steel, the structural state of the rust was investigated.

The surface layer of rust for a sample of Si-bearing steel was analyzed by EPMA. From the investigation of the distribution of Si in the rust layer, it was found that Si was concentrated in the inner part of the rust layer. Then the chemical state of Si in this concentrated layer was newly measured by using Si K α and K β characteristic X-rays of EPMA. Figure 1(A) shows the results of an analysis of a test sample subjected to 20 cycles of the corrosion test, and of the standard materials SiO₂ and metallic silicon (Si). The peak position of the K α characteristic X-ray for Si-bearing steel is different from that of the standard materials SiO₂ and metallic silicon, appearing middle position between the these two peaks. Furthermore, Figure 1(B) shows the same kind of results for an analysis using Si K β characteristic X-rays. The

Fig. 1 Characteristic X-rays spectra of (A) Si K α and (B) Si K β from the rust of Si-bearing steel and standard reference chemicals (SiO₂, Si) obtained by EPMA.

peak position of the Si K β characteristic X-ray appears between those of two materials. What is more, in comparison to the peak strength values of Si K β ' of these two standard materials, that of the Si-bearing steel is shown in the middle value between them. From these results, it is suggested that the Si in the rust layer is not in a metallic but an oxidized state, however it is in a different chemical bonding state to SiO₂.

As a small amount of characteristic X-rays spectra were analyzed, it was a little difficult to determine chemical state of Si based only on the above analysis. Thus we carried out a further analysis using XRF on the rust gathered from a sample after 20 cycles of the corrosion test. Figure 2(A) shows the results of an analysis of rust for Si-bearing steel and the standard materials. The peak position of the Si K α for test sample is different from that of the metallic silicon and similar to that of SiO₂. Figure 2(B) shows the spectrum of Si K β for the rust. The peak of the Si K β for test sample shows the position between those of Si and SiO₂. From these results, it is suggested that the Si in the rust layer is not in a metallic but an oxidized state.

Figure 3 shows the results of an XPS analysis on the rust for Si-bearing steel. Figure 3(A) shows the Si 2s XPS spectra of standard materials and the test sample. The peak position of the Si 2s of test sample is existing between those two

Fig. 2 XRF spectra of (A) Si K α and (B) Si K β from the rust of Si-bearing steel and standard reference chemicals (SiO₂, Si).

standard materials. Figure 3(B) shows similar results for a Si 2p analysis. Here, because the Si 2p spectrum is close to the Fe 3s peak, the Fe 3s spectrum taken from a standard test sample of Fe₃O₄ was used to separate the Si 2p spectrum of test sample. It is found that the position of the Si 2p peak for the Si-bearing steel appears between that for the SiO₂ and the metallic silicon. In summary, it was also observed from evaluation using XPS that the Si in the rust layer was in an oxidized, but in a different state of chemical bonding to that of SiO₂.

Combining the results of the chemical analyses using EPMA, XRF and XPS, it can be stated that in the rust of Si-bearing steel, the Si is existing in an oxidized, not metallic, state, but in a different form of chemical bonding to that of SiO₂. The peak positions of each spectrum are summarized in the Table 1. Moreover the chemical shifts from the peak of metallic Si are estimated in the Table 1. The chemical shifts of Si-bearing steel from the peak of metallic Si are showing the almost half value than those of SiO₂. Maekawa¹⁸⁾ stated

Fig. 3 XPS spectra of (A) Si 2s and (B) Si 2p from the rust of Si-bearing steel and standard reference chemicals (SiO₂, Si).

that in analysis of Si based oxide compounds by XRF spectra, this peak appeared between that of SiO₂ and metallic silicon, which was the same as our results. Since generation of XRF only differs by excitation source, and since it is created by the same process as the emission of characteristic X-rays, it is considered that the spectrum are showing the similar chemical shift between XRF and EPMA. Furthermore, Hollinger¹⁹⁾ stated that the chemical shifts of Si were depending on mainly the value of the valence of Si, and that of Si²⁺ was showing half value than that of SiO₂ from the peak of metallic silicon. In our results, the chemical shifts of Si-bearing steel were showing almost half value than that of SiO₂. Thus the chemical shift is thought to depend mainly on the valence of Si, and Si is existing as a intermediate oxidized state such as Si²⁺ in the inner rust of Si-bearing steel.

In order to investigate the structure of the inner rust, TEM observation was conducted as shown in Fig. 4. The inner rust layer was cut by FIB (Fiber Ion Beam) as shown in Fig. 4(A). The rust containing Si is able to selected by EDXS analysis as in Fig. 4(B). From EDXS analysis, as the oxides contain both Si and Fe, they make complex oxides of Fe-Si type. Moreover, the oxides which contain Si are observed as white particles in the bright field image as shown in Fig. 4(A). It is understood that the sizes of oxide particles which contain Si are nano-meter level, and there are enriched layers of white

Table 1 Summary of the peak positions and chemical shifts for each spectra.

		Peak position (eV)			Chemical Shift (eV)	
		test sample	standard chemical		from the peak of metallic Si	
			Si-steel	Si	SiO ₂	
EPMA	Si K α	1740.5	1739.7	1741.2	0.8	1.5
	Si K β	1834.8	1836.6	1833.1	-1.8	-3.5
XEF	Si K α	1741.3	1740.4	1741.3	0.9	0.9
	Si K β	1833.8	1836.3	1832.8	-2.5	-3.5
XPS	Si 2s	152.9	150.9	154.8	2	3.9
	Si 2P	101.6	99.4	103.4	2.2	4

Fig. 4 FIB-TEM observation of the rust from the inner layer of Si-bearing steel. (A: bright field image, B: EDXS analysis)

particles. Thus these nano-scale complex oxides containing Si are enriched in the inner rust. From EPMA, XRF, and XPS analysis Si was identified as a intermediate oxidized state such as Si²⁺ and had a different chemical bonding to that of SiO₂. Probably Si made complex oxides with Fe as Si²⁺ state in the inner rust, and chemical bonding was different from that of SiO₂. Moreover, these nano-scale complex oxides (Fe-Si²⁺-O) could increase the corrosion resistance of the Si bearing steel. In this way, it can be understood that nano-scale complex oxides are possibly made in the rust of Si-bearing steel, and they can increase the corrosion resistance of the steels.

3.2 Evaluation of the electrochemical behavior of the rust by the EIS method

Figure 5 shows the results of EIS measurements on the

Fig. 5 Impedance and phase shift spectra of Si-bearing steel as a function of cycle of corrosion tests.

sample after the corrosion test. The resistance component at high frequencies more 1 Hz (Rh), the capacitance in the 1 mHz to 1 Hz region (C), and further the resistance component at frequencies less 1 mHz (Rl) can be recognized.¹¹⁾ As the amount of the rust increases with the number of test cycles, Rh also increases. Thus Rh can be related to the resistance of the rust (Rrust). Since the resistance of oxides is extremely high, it is considered that Rrust actually shows the resistance of the solution in the fine pores of the rust. On the other hand, the phase shift goes to 0 degree again at less than 1 mHz, showing the resistance component (Rl), which is considered to be the corrosion reaction resistance (Rt). When the amount of rust is small at 4 cycle, Rt can be verified at low frequency. Although when the amount of rust becomes large, Rt becomes difficult to recognize, it can be considered that impedance (Z) at very low frequencies reflects Rt. In the following, considering the actual time for the measurement, we have used Z at the 0.3 mHz to calculate Rt.

Fig. 6 Plots of impedance parameter (R_{rust} and R_t) of carbon steel (SM) and Si-bearing one (Si-steel) as a function of corrosion test cycle.

Figure 6 shows the results of EIS measurements on Si-bearing steel and SM conducted after the corrosion test, showing R_{rust} and R_t against the number of cycles. The Si-bearing steel shows a higher value of R_{rust} than SM in each number of cycles. Since R_{rust} is the resistance of solution in the pores of the rust, this fact shows that the rust of Si-bearing has a finer structure than that of SM.

Both the Si-bearing and SM show high values of R_t at the initial cycles, however, they have smaller R_t after 8 cycles. This fact is considered to correspond to the increase of the cathodic reduction of rust as the rust is created.¹¹⁾ R_t shows a constant value after 8 cycles because the anodic reaction is suppressed as the surfaces is covered by the rust. Furthermore, the Si-bearing steel has a larger value of R_t than SM after 8 cycles. The main reason for this fact is considered that nano-scale complex oxide containing Si is formed in inner rust, which suppresses the anodic reaction. This phenomenon can be verified from the measurement of R_{rust} . As the formation of the rust proceeds, the value of R_{rust} and R_t of Si-bearing steel show larger than those of SM, which depends on the fineness of the rust. Figure 7 shows the schematic diagram of the corrosion mechanism of the rust of Si-bearing steel. In general, the rust has many micro-defects (pores) through which the chloride (Cl) ions can penetrate to the base metal. However, the Si-bearing steel makes nano-scale complex oxides containing Si in inner rust at micro-defects, then increases the R_{rust} and R_t by the physical protection of the fine rust. Finally the Si-bearing steel could suppress the corrosion in saline environment.

The above corrosion test was conducted to form a thin film of rust using foils (2×10^{-5} m) of low alloy steel, and measured the rust membrane potential.^{18,19)} The results showed the rust film of SM had anion selective permeability,

Fig. 7 Schematic diagram for the corrosion mechanism of the rust of Si-bearing steel in wet/dry condition containing chloride ions.

however, that of Si-bearing steel had cation one. Thus the complex oxides containing Si made in the inner rust show possibly cation selective permeability and have the effect of preventing the passage of Cl ions through the rust. From this fact, it was understood that there was the effect of chemical prevention from the pass of Cl ions by making complex oxides containing Si.

In this way, there are two reasons why Si-bearing steel increases R_t and suppresses corrosion; 1) the effect of physical protection by the creation of nano-scale oxides at the micro-defects, and 2) the effect of chemical prevention from the pass of Cl ions by the change in selective permeability by making complex oxides containing Si.

4. Conclusions

A wet/dry cyclic corrosion test with Cl ions was performed on Si-bearing steel and the chemical state of Si in the rust and electrochemical behavior were analyzed.

- (1) In a wet/dry cyclic experiment, Si-bearing steel showed smaller corrosion content compared to carbon steel (SM), and had excellent corrosion resistance.
- (2) EPMA, XRF and XPS showed that Si in the rust of Si-bearing steel was mostly existing as an intermediate state such as Si^{2+} in the complex oxide in inner rust layer. TEM showed that nano-scale complex oxides containing Si were enriched in the inner rust of the Si-bearing steel.
- (3) An EIS measurement was taken of the corrosion test samples to find the rust resistance (R_{rust}) and corrosion reaction one (R_t), and the R_{rust} and R_t of Si-bearing steel were much larger than those of SM after the rust formation. In the Si-bearing steel, nano-scale complex oxides containing Si were formed in the inner rust, which could increase R_t and suppress the corrosion.

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