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## Effect of Cr<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> on the Structure of Rust Layer Formed on Steels by Atmospheric Corrosion

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**Abstract:** The effect of chromium ion (Cr<sup>3+</sup>) and sulfate ion (SO<sub>4</sub><sup>2-</sup>) on the structure of the rust layer formed by thin electrolyte-film corrosion of low-alloy steels has been examined. By using X-ray diffraction spectroscopy, it was found that coexistence of Cr<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> in the electrolyte film covering the steel surface quickly forms the Cr-goethite ( $\alpha$ -(Fe<sub>1-x</sub>Cr<sub>x</sub>)OOH) layer which has been known as the final protective rust layer. Scanning vibrating electrode measurements showed that the rust layer formed under the electrolyte film containing Cr<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> possesses higher protective ability against the aggressive chloride environment. Mössbauer spectroscopy revealed that most of the Cr-goethite formed by corrosion of the Fe-5at%Cr alloy under thin electrolyte-film containing SO<sub>4</sub><sup>2-</sup> was the superparamagnetic ultra-fine Cr-goethite. It can be said that the Cr-goethites possess the high protective ability against aggressive corrosives.

**Keywords:** atmospheric corrosion, electrolyte film, ion species, rust layer, goethite

### Introduction

Atmospheric corrosion of steels strongly depends on the nature of oxide or rust layer on the steel surface [1]. Thus, we expect the rust layer to give certain beneficial effects for prevention of degradation of the steels. It is well-known that the so called "protective" rust layer formed on a weathering steels which contain a small amount of Cr, P, and Cu has strong protective ability for atmospheric corrosion of the steel. Thus, weathering steels possess high corrosion resistance, approximately twice as good as carbon steels, and therefore has been widely used as a structural material in an atmospheric corrosion environment.

Because formation of the protective rust layer usually takes time, the initial corrosion rate of the weathering steel is not substantially low and the initial unprotective

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rust contaminates the steel surfaces and other enviring materials. In addition, the protective rust layer cannot form in the coastal environment where the amount of air-borne salts is relatively high. These are significant problems to reduce maintenance tasks for structures made of weathering steel.

According to the recent understanding of the protective rust layer, the main constituent of the rust layers is changed with the exposure period from lepidocrocite ( $\gamma$ -FeOOH) (less than a few years), via amorphous substance (several years), to goethite ( $\alpha$ -FeOOH) type phase (decades). The corrosion rate of the weathering steel decreases with these phase transformations. The protective rust layer possesses the structure of Cr-goethite ( $\alpha$ -(Fe<sub>1-x</sub>Cr<sub>x</sub>)OOH) [2], which might be formed due to concentration of Cr in the rust layer after long-term exposure. By this Cr concentration in the goethite structure, the Cr-goethite possesses a densely packed structure that provides higher protective ability and prevents penetration of aggressive corrosive anions in the atmosphere. It is also pointed out that the Cr-goethite possesses cation selective ability. Therefore, the protective rust layer of the Cr-goethite impedes the penetration of aggressive corrosive anions such as Cl<sup>-</sup>, as well as its densely aggregated structure, which provides the resistance against a corrosive penetration.

Based on the above basic knowledge, the Cr-goethite is a highly protective rust that is useful for obtaining corrosion-resistant steels. It has been found that chromium sulfate (Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) is effective for obtaining the protective Cr-goethite rust layer in a short period [3]. Because of the quick formation of the protective layer, this effect of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> can be a key technology which prevents the damage by the briny air. It is now very important to know how Cr<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> contribute the quick formation of the Cr-goethite. In this paper, we try to understand the effect of Cr<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> on the detailed rust structure of steel.

## Experimental Method

### Specimen

Specimens employed were 0.5%Cr-0.3%Cu-0.06%P-0.5%Ni steel disks 15mm diameter and 5mm thick. The surfaces of the specimens were polished until #1500 emery paper.

### Corrosion under Electrolyte Film

In order to obtain atmospheric rust layers on the steel surfaces, the steel disk specimens were corroded under thin layer of electrolytes of Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> or sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) at concentration of 3.5% each for 24 hours. The thickness of the electrolytes,  $h$ , was supposed to be 1-100

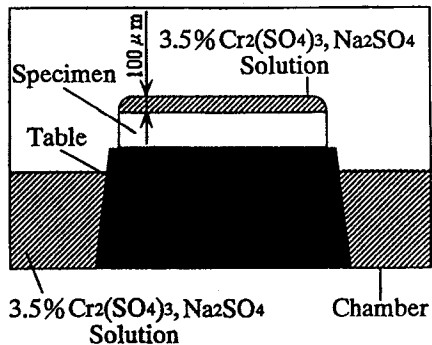


Figure 1 - Schematic illustration of electrolyte film corrosion chamber.

$\mu$  m by adjusting the amount of the electrolytes and relative humidity of the surrounding air in an electrolyte-film corrosion chamber, as shown in Figure 1. The rust layers formed under the  $\text{Cr}_2(\text{SO}_4)_3$  and  $\text{Na}_2\text{SO}_4$  electrolyte-films will be referred to in the remainder of this report as the CS and SS layers, respectively.

#### *Measurement of Corrosion Current Distribution*

The specimens with the rust layers formed under the 100  $\mu$  m thick electrolyte film on the steel disks were immersed in 3.5%NaCl solution at ambient temperature, and then the corrosion currents were measured using the scanning vibrating electrode technique (SVET). The probe of the SVET was Pt wire with diameter of 0.05mm. The measurements were done after certain immersion periods,  $t_i$ , of 0, 3, and 5 hours in the 3.5%NaCl solution. The amplitude and frequency of probe vibration were controlled to be 10  $\mu$  m and 130Hz, respectively.

#### *Measurement of Corrosion Rate*

Specimens with the CS layer formed on the steel disks were corroded under 3.5%NaCl solution film with the same thickness of the electrolyte film,  $h$ , employed to obtain the rust layers. The corrosion rate during this NaCl solution film corrosion was measured by oxygen consumption measurement [4], that measures the oxygen partial pressure decreased by oxygen consumption as a cathodic reaction in the tightly sealed corrosion chamber. The purpose of this measurement is to know the effect of the electrolyte-film thickness on the protective ability of the rust layer.

#### *Metallographic Cross Sections*

Metallographic cross sections were prepared by shearing cross sections and mounting in two-part, room temperature-curing epoxy. The mounts were ground repeatedly with successively finer silicon carbide, and finished with alumina powder. The cross sections of the rust layers were characterized by optical microscopy and by electron probe microanalyzer to determine the distribution of some important elements.

#### *Structural Analysis of Rust Layer*

Rust layers formed on the steel were removed by a razor until the steel surface appeared, and then ground into powder. The powdered rust samples were desiccated for a week in advance of the analysis. The powdered samples were characterized by means of X-ray diffraction spectroscopy employing a Co target. The quantitative determination of rust constituents comprising goethite, lepidocrocite, akaganeite, magnetite, and the X-ray amorphous substances was carried out by measuring the diffraction intensities and comparing that of KCl powder that had been mixed with rust samples as an internal standard. The remainder other than the above crystalline constituents was considered as the X-ray amorphous substances in this quantifying

estimation because the amounts of other crystalline materials and air-borne dusts might be very small.

### Fe-Cr Alloy Film

Since the role of Cr as an alloying element on the formation of rust layer is very important to discuss the protective ability of the rust layer, the rust layer formed from Fe-5at%Cr alloy was also examined using Mössbauer spectroscopy. Fe-5at%Cr alloy film with a thickness of 100nm was vapor-deposited on a Si(100) single crystal substrate. The surface of the alloy film was covered with 100  $\mu$ m-thick (0.1mol/l  $\text{Na}_2\text{SO}_4$  + 0.005 mol/l  $\text{H}_2\text{SO}_4$ ) film for 200h at ambient laboratory temperature, so that all the alloy film was corroded and finally the uniform rust layer was formed. Because the alloy film was corroded in a short period, the rust layer formed is categorized as an initially formed rust layer.

In order to identify separately the iron oxides that were either superparamagnetic at 300K or magnetically ordered between 300 and 77K, the transmission Mössbauer spectroscopy was used. The powdered sample of the rust layer on the Si substrate was mixed with BN powder and pressed into a 1cm diameter tablet. The Mössbauer spectra were recorded using a  $^{57}\text{Co}$  in rhodium source at room temperature 300K and 77K in a liquid nitrogen cooled cryostat. A commercial proportional counter filled with the mixture of xenon and carbon dioxide gases was used.

## Results and Discussions

### Corrosion Current Distribution

A large number of cracks were observed in the loosely packed SS layer by the optical and scanning electron microscopies. On the contrary, densely aggregated structures were found in the CS layer. The corrosion current distributions are shown in Figure 2. Many corrosion current peaks were observed over the SS layer. However, little corrosion current was measured in the CS layer; this indicates that the CS layer possesses high protective ability against corrosives even in the aggressive chloride environment.

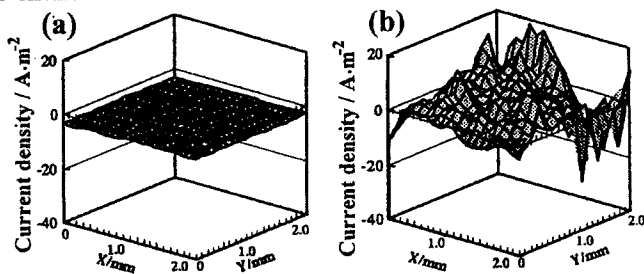


Figure 2 - Corrosion current distributions over the steel specimens covered with the rust layers formed under the  $\text{Cr}_2(\text{SO}_4)_3$  (a) and  $\text{Na}_2\text{SO}_4$  (b) electrolytes, in the NaCl solution ( $t_i=0$ h).

The X-ray diffraction spectroscopy revealed that main phase of rust constituents is goethite, as shown in Figure 3. It has been pointed out that lepidocrocite is an initial unprotective rust on the weathering steel, as was mentioned above. The large amount of goethite in the CS and SS layers, therefore, implies that  $\text{SO}_4^{2-}$  accelerates the rust formation and leads the formation of goethite-phase rust. It was found using electron probe microanalysis that the CS layer contains Cr in its rust. It can be said that coexistence of  $\text{Cr}^{3+}$  and  $\text{SO}_4^{2-}$  preferentially forms Cr-goethite which has been known as the final protective rust layer [2,3]; probably  $\text{Cr}^{3+}$  positions  $\text{Fe}^{3+}$  lattice site of goethite structure as a substitutional ion and forms stable goethite structure. It was pointed out that  $\text{Cr}^{3+}$  precipitates as hydroxide much faster than  $\text{Fe}^{2+}$  during air oxidation [5]. Thus, a large number of nuclei of hydroxide might be formed at the  $\text{Cr}^{3+}$  precipitation sites, which may result in formation of very fine particles of the Cr-goethites. Aggregation of this ultra-fine Cr-goethite causes higher protective performance of the rust layer.

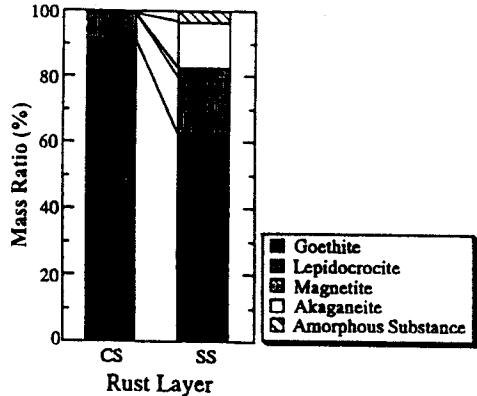


Figure 3 - Mass ratio of rust constituents evaluated after the SVET measurement by X-ray diffraction intensities of the rust layers formed under the  $\text{Cr}_2(\text{SO}_4)_3$  (CS) and  $\text{Na}_2\text{SO}_4$  (SS) electrolytes ( $t_i=5h$ ).

### Corrosion Rate

Figure 4 shows the relationship between the electrolyte-film thickness,  $h$ , to form the rust layer and the corrosion rate of the steel with the CS layer under the NaCl solution film with the same thickness. Even though the corrosion rate of the steel with the CS layer was very low when  $h$  is large, the corrosion rate peak in its electrolyte-film thickness dependence was observed at  $h$  of about  $4 \mu\text{m}$ . This indicates that the protective ability of the CS layer might be low when  $h$  is very small. The existence of the corrosion rate peak was due to increasing in oxygen diffusion rate to the surface resulting in acceleration of the cathodic reaction. The decrease in the corrosion rate

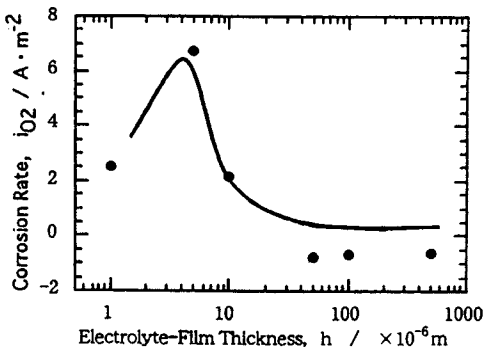


Figure 4 - Relationship between the electrolyte-film thickness,  $h$ , to form the rust layer and the corrosion rate of the steel with the CS layer under the NaCl solution film with the same thickness ( $t_i=0h$ ).

below 4  $\mu\text{m}$  of the thickness might be due to passivation of the corroding surface.

#### Rust Layer of Fe-Cr Alloy Film

Mössbauer spectra of the powdered sample of the rust layer on the Si substrate are shown in Figure 5. The room temperature spectrum shows that almost all the spectral peak areas can be assigned to a deep doublet comprising of  $\gamma$ -FeOOH and superparamagnetic components. The superparamagnetic components would correspond to ultra-fine crystals that might show no clear X-ray diffraction peaks because they have a small number of crystal planes in the crystal grain.

From the low temperature spectrum, it is found that the quadruple splitting showing the doublet at room temperature was split out to the sextet of the magnetic splitting. By fitting the hyperfine parameters of iron oxides and oxyhydroxides, the sextet in the low temperature spectrum can be assigned to the superparamagnetic Cr-goethite (S1-goethite) with the crystal size of 8-15nm. In addition, the doublet at the low temperature can be assigned to both  $\gamma$ -FeOOH and the superparamagnetic Cr-goethite (S2-goethite) with the crystal size less than 8nm.

By considering relative recoil free fractions of ferric oxyhydroxides, the Mössbauer spectra indicates that the mass fraction of  $\gamma$ -FeOOH and that of all the superparamagnetic Cr-goethite (S-goethite = S1-goethite + S2-goethite) are 12% and 88%, respectively. Therefore, it is said that the rust layer contains a large amount of the X-ray undetectable superparamagnetic Cr-goethites corresponding to the X-ray amorphous substance.

As was mentioned above, the main constituent of the initial rust layer within a few year exposure on a weathering steel is  $\gamma$ -FeOOH and the protective rust layer

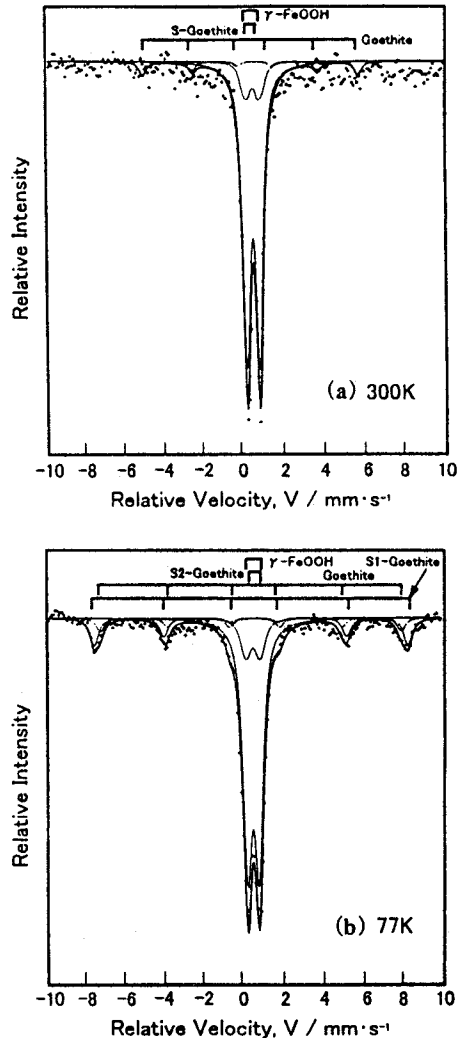


Figure 5 - Mössbauer spectra of the powdered sample of the rust layer formed by corrosion of Fe-5at%Cr alloy film covered with the sodium sulfate solution film.

obtained after long-term exposure, depending on the atmosphere and steel composition, has the Cr-goethite structure. However, most of rust constituents on the present Si substrate was the superparamagnetic ultra-fine Cr-goethite. This quick formation of the ultra-fine Cr-goethite might be due to the high Cr concentration in the Fe-Cr alloy film. Usually, the weathering steel contains 0.3-0.5 mass% Cr, which concentrates in the rust layer during long-term corrosion and helps formation of the Cr-goethite [6,7]. On the other hand, the Cr concentration in the Fe-Cr alloy was much higher than that in the weathering steel. This higher concentration of Cr in the Fe-Cr alloy, inevitably in its rust layer too, would result in the quick formation of the ultra-fine protective Cr-goethite phase.

In the case that the Cr concentration in the Cr-goethite is more than 5mass%, the crystal size becomes less than 10nm [8]. This agrees well to the present result that shows high concentration of Cr results in the formation of the ultra-fine Cr-goethite. In addition, it has been pointed out that the cation selective property is appeared when the Cr content exceeds approximately 3 mass% [9]; i.e. the Cr-goethite impedes the penetration of aggressive corrosive anions such as  $\text{Cl}^-$ . Thus, the ultra-fine Cr-goethite possesses the high protective ability against aggressive corrosives. Finally, it is said that the results obtained in this research can be directed toward development of new technologies which enable us to obtain the protective rust layer on the weathering steel very quickly.

## Conclusions

The effect of  $\text{Cr}^{3+}$  and  $\text{SO}_4^{2-}$  on the structure of rust layer on steels by atmospheric corrosion under thin electrolyte film has been examined using the scanning vibrating electrode method, X-ray diffraction and Mössbauer spectroscopy. The rust layer formed under the electrolyte film containing  $\text{Cr}^{3+}$  and  $\text{SO}_4^{2-}$  possesses higher protective ability against corrosives even in the aggressive chloride environment. Coexistence of  $\text{Cr}^{3+}$  and  $\text{SO}_4^{2-}$  in the electrolyte film covering the steel surface quickly forms the Cr-goethite,  $\alpha\text{-(Fe}_{1-x}\text{Cr}_x)\text{OOH}$  layer which has been known as the final protective rust layer. Most of the Cr-goethite formed by corrosion of the Fe-Cr alloy under thin electrolyte film containing  $\text{SO}_4^{2-}$  was the superparamagnetic ultra-fine Cr-goethite. It can be said that the Cr-goethites possess the high protective ability against aggressive corrosives.

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