Formation of Corrosion Protective Rust on Steel Exposed to the Atmosphere

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ABSTRACT

Corrosion protection of infrastructures such as bridges, steel towers sending electricity and buildings made of steel is very important from the viewpoint of their life expectancy. Extension of their lives is possible by selection of appropriate corrosion preventive methods. Usage of weathering steel or adoption of appropriate coating etc. is useful for this purpose.

It has well been known that corrosion protective rust formed on steel will increase the atmospheric corrosion resistance. Atmospheric corrosion resistant weathering steel containing small amounts of chromium, nickel, copper or phosphorus forms corrosion protective rust in several years of exposure

This paper deals with the development of a method for accelerating formation of corrosion protective rusts on steel with a paint containing inorganic and organic compounds. The paint helps corrosion protective rusts grow on metal surface only after a few year exposure in the marine environment。 The main constituent of corrosion protective rusts is a fine grained structure of α-FeOOH.

Key words: Atmospheric corrosion, Thin water layer, Rust layer, Corrosion protective rust, Weathering steel, Paints, Synchrotron radiation, XZFS.

INTRODUCTION

Steel is one of the major constructional materials for infrastructures such as brides, highways, steel towers, etc. It is not expensive and strong as well as good in workabilities compared with other metals and alloys. However, it has some drawbacks. One of them is gradual deterioration in the atmosphere. Therefore, many efforts have been done for extending the atmospheric corrosion resistance. New corrosion preventive methods have currently been developed.

The following is the sequence of the development of atmospheric corrosion resistant steels.

Carbon steel

When Carbon steel is exposed to the atmosphere, it corrodes with formation of rusts such as α-FeOOH, γ-FeOOH, β-FeooH, δ-FeOOH and magnetite. α-FeOOH, a stable rust termed as goethite, makes steel corrosion resistant according to its fine grained rust structures. Whereas γ-FeOOH termed as lepidcrosite is not stable, it is easily reduced to magnetite. Therefore, γ-FeOOH may acts as a cathodic depolarizer in a corrosion local cell, inducing atmospheric corrosion. β-FeooH is formed in the marine atmosphere, and non-corrosion protective.

Weathering steel

Weathering steel contains small amounts of copper, nickel, chromium, and sometimes phosphorus. It has shown a good atmospheric corrosion resistance as much as up to five times than that of carbon steel. Fine grained rust formed on weathering steel retards oxygen diffusion through the rust, resulting in less corrosion in weathering steel than carbon steel. Chromium substituted goethite (CrxFe1-x)OOH in the rust is the major components of the rusts in making fine grained and compact corrosion protective rust.

Specially painted steel

Painting is carried out for the purpose of decoration as well as corrosion protection of base steel from the atmosphere. Generally speaking, paint on the steel has not shown good long time corrosion resistance under water because of corrosion under paint. Currently developed or developing corrosion preventive methods use special paints to carbon or weathering steel solely for acceleration of corrosion protective rust formation. The paints have special chemical compounds within the paints, which combine with dissolved metal cations dissolving from the base metal. A few years later, painted steel surface changes to atmospheric corrosion protective rusts.

FEATURES OF ATMOSPFERIC CORROSION

When steel is immersed in water, it is corroded in not a small amount. Rust is formed quickly on the surface of steel, however, the rust does not have any corrosion protective effect. On the other hand, steel is able to have corrosion protective property when steel is exposed to the atmosphere. Atmospheric corrosion is the phenomenon that iron and steel are corroded in the atmosphere intermittently under wetted and dried conditions. Fig.1[1] is the schematic showing the effect of water thickness on the corrosion of steel. Dip condition means that steel is immersed in bulky water. Steel corrodes no to a small extent. Rust formed on steel is voluminous and of many voids, therefore is unable to retard corrosion.

The stage of dew and wet conditions make steel corrode faster due to the higher transportation of oxygen from water to the metal surface. However, time goes on, rust formed accumulates on metal surface, resulting in retardation of corrosion. Rust formed on steel under the dew and dip conditions is corrosion protective one.

Fig.2 [2] shows the difference in the corrosion behavior for steel between the bulky water and thin water layer. Under ①bulky condition steel is corroded in the active dissolution potential region. Corrosion product formed on metal surface does not exert any corrosion protective performance.

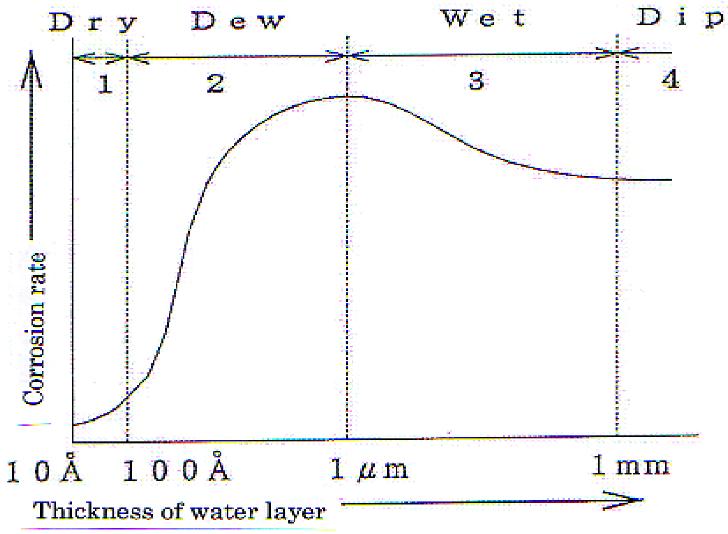

Fig. 1 Relationship between water thickness and corrosion rate for steel.

Steel continues being active at the corrosion potential of Ecorr.,1, resulting in getting corroded at a high corrosion rate. Whereas, under ②thin water layer condition, steel is passivated at the corrosion potential of Ecorr.,2 due to the corrosion protective performance of rust formed on metal surface. The corrosion rate of passivated steel is remarkably less than that of actively dissolving steel.

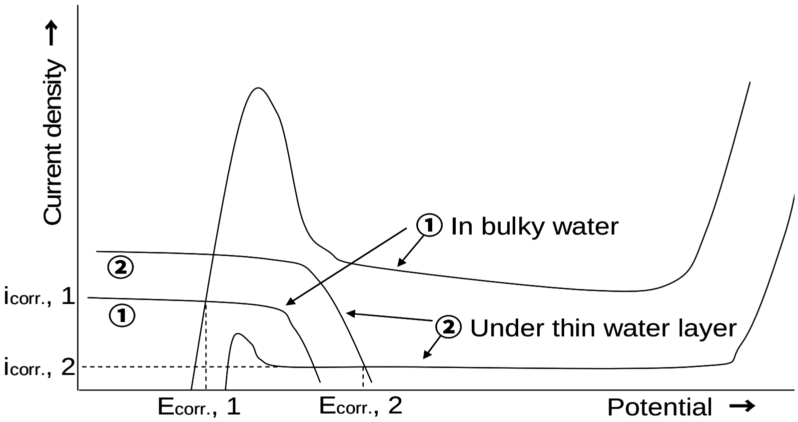

Fig. 2 Corrosion behavior for steel in different water conditions.

Fig. 3 [3]shows exposure test results in the atmosphere for carbon and weathering steels.

Corrosiveness of the atmosphere is larger in the order of marine atmosphere ＞ industrial atmosphere＞ rural atmosphere. As for corrosion resistance, weathering steel is much better than carbon steel.

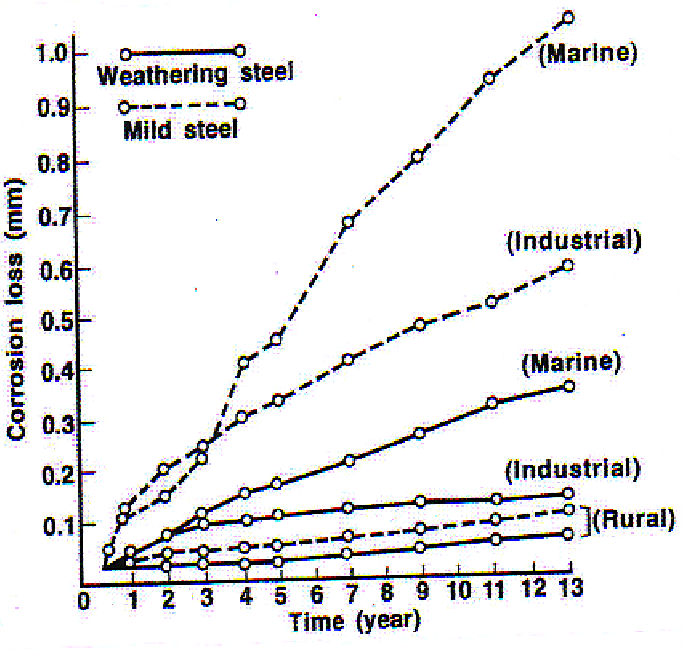

Fig.3 Atmospheric exposure test results for carbon and weathering steels.

STRCTURE OF PROTCTIVE RUST LAYER AND EFFECT OF METAL ION

A protective rust layer formed on the surface of a weathering steel which contains a small amount of Cr, P and Cu is responsible for the protection of the steel against corrosion in the atmosphere. The structure of the protective rust layers has been studied by various spectroscopies [4]-[13]. Those studies revealed that the protective rust layer consists of ultrafine crystals of ferric oxyhydroxides and the protective effect is derived from the dense aggregation of ultrafine goethite, α-FeOOH, which contains a certain amount of Cr. It has also been pointed out that this Cr-goethite possesses cation selectivity which prevents the penetration of corrosive anions such as chloride ions. The increase in Cr concentration in Cr-goethite results in a decrease in the crystal size[14] and emphasis on the cation selectivity[15], providing a high protective ability of the rust layer.

Here, the question is why the increase in Cr concentration causes the aggregation of small goethite particles with cation selectivity on weathering steel. The structure of the corrosion product of Fe-Cr alloy has been analyzed and it is pointed out that Cr^{3+} is not positioned at the Fe^{3+} site in the $FeO_3(OH)_3$ octahedra in the goethite crystal[16], [17]. It is infered that this Cr^{3+} site might explain the protective effect.

Here we mention the nanostructure of the protective rust layer on weathering steel exposed for a long term to an outdoor atmospheric environment. The rust layer examined was formed on the weathering steel containing 0.12C-0.39Si-0.9Mn-0.008P-0.006S-0.36Cu-0.61Cr-0.22Ni-0.014Nb (in mass%) exposed for 17 years to the atmosphere underneath the girder of a bridge in an industrial zone, with the airborne salt content and SO_2 content in the atmosphere of 0.041 mg/100cm^2/day (mdd) and 0.109 mdd, respectively[8].

A rust sample was removed from the skyward surface using a razor until the steel surface becomes visible, and then ground into powder. The powdered rust sample was desiccated for a week in advance of the analyses. We also prepared a pure goethite powder sample by an artificial method[14], [15]for reference. The structure of the rust was characterized by X-ray absorption fine structure (XAFS) analysis[18] using synchrotron radiation X-rays at BL27B of the Photon Factory in the Institute of Materials Structure Science of the High Energy Accelerator Research Organization in Tsukuba, Japan.

The Fourier transform of the Cr K edge EXAFS (the extended X-ray absorption fine structure) spectrum of the rust layer, and that of the Fe K edge EXAFS spectrum of pure goethite are shown in Fig. 4[18]. The Fourier transform is not phase-corrected; hence, the peak positions are shifted by approximately 0.06 nm in the negative direction from the actual distances. The strongest peak is shown at 0.14 nm in RSF around Cr^{3+}, the corrected distance of which is 0.20 nm. By considering the Cr^{3+} ionic radius of 0.07 nm, the nearest-neighbor atom with an ionic radius of 0.13nm can give this strongest peak.

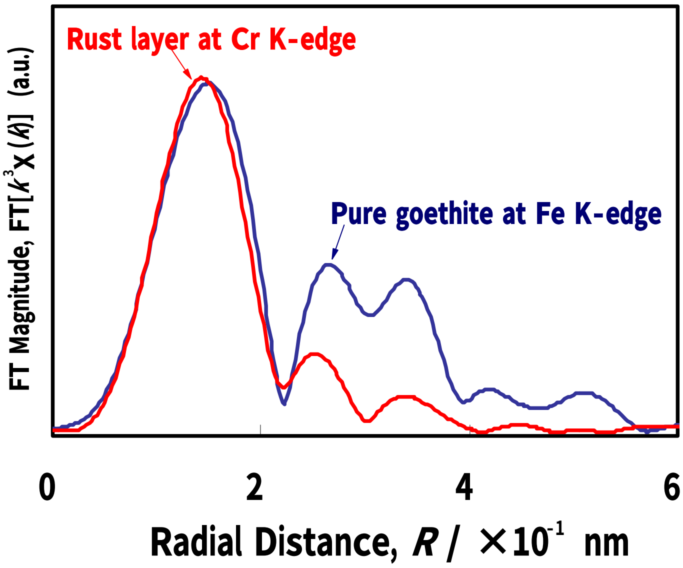

Fig.4 Fourier transform of the EXAFS spectrum, i.e., radial structure function, of the rust layer on weathering steel exposed horizontally to the atmosphere for 17 years underneath the girder of a bridge at Yokkaichi, at Cr K-edge, and that of pure goethite at Fe K-edge measured using PF synchrotron radiation X-rays.

The ionic radius of 0.13nm corresponds to O^{2-}, and the corrected distance is not markedly different from the nearest Fe-O bonding length, 0.196nm, in the goethite structure[16], which gives the strongest peak in Fig. 4 around Fe^{3+} in the artificial pure goethite. Thus, it is clear that Cr^{3+} in Cr-goethite of the protective rust layer is coordinated with O^{2-}.

The nearest-neighbor Fe-Fe distance is approximately 0.30-0.35nm in the goethite structure, which is clearly reflected by the two peaks at 0.26 and 0.32nm in Fig. 4 around Fe^{3+} in the artificial pure goethite. In contrast, those two peaks are not clearly observed around Cr^{3+} in Cr-goethite of the rust layer. This indicates that most of the Cr^{3+} does not substitute into the Fe^{3+} site at the center of the octahedron because the Fe^{3+} site should be strongly correlated to the neighboring Fe^{3+} sites, but is located in the double chains of vacant sites in Cr-goethite in the rust layer. It can be said that there is no fixed distance between Cr^{3+} in the double chains of vacant sites and the neighboring Fe^{3+} or Cr^{3+}.

Because there is no fixed distance between Cr^{3+} and the nearest neighbor cations, O^{2-} coordinated with and also strongly correlated to Cr^{3+} is not one in the $FeO_3(OH)_3$ octahedron. Generally, cation selectivity of materials can be interpreted in terms of the presence of fixed negative charges. Since Cr in goethite should be trivalent, the substitution of Cr^{3+} for Fe^{3+} or interstitial Cr^{3+} itself will not cause the fixed negative charge. Thus, it is noted that Cr^{3+} coordinated with O^{2-} in the double chains of vacant sites is expected to explain the ion selectivity.

If Cr^{3+} forms complex ions with a plural number of O^{2-}, the CrO_x^{3-2X} complex ion becomes negatively charged, exhibiting cation selectivity. Because of insufficient physical spacing, the CrO_x^{3-2X} complex anion cannot substitute for Fe^{3+} at the center of the octahedron, but is located in the double chains of vacant sites. Here, the CrO_x^{3-2X} complex anion has a much larger volume than Fe^{3+}, it can be inferred that the double chains of vacant sites are distorted or broken. In other words, the CrO_x^{3-2X} complex anion should be located at the surface and/or grain boundary of the Cr-goethite crystals, as schematically shown in Fig. 5[18]. This collapse of the double chains of vacant sites causes the formation of the ultrafine crystals of Cr-goethite.

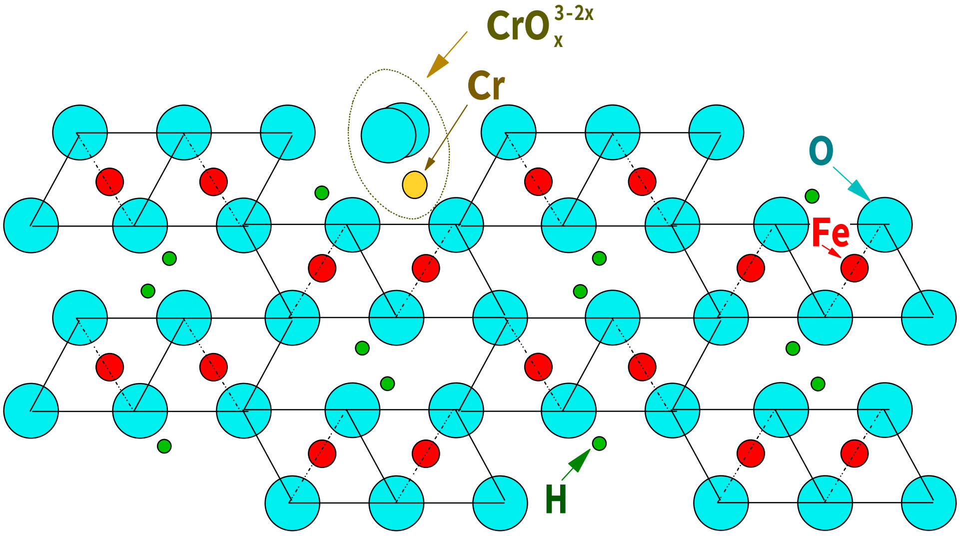

Fig.5 Schematic illustration of (001) projection of goethite crystal, where CrO_x^{3-2x} complex ion adsorbs at the surface.

The nanostructure of the protective rust layer on weathering steel is primarily comprised of ultrafine Cr-goethite crystals containing surface-adsorbed and/or intergranular CrO_x^{3-2X} complex anions.

Usually, it needs a certain exposure duration to form the protective rust layer on weathering steel. In addition, the steel exposed in a chloride environment, it is not easy to form the protective rust layer. For industrial use, it is expected to obtain the protective rust even in a relatively aggressive environment in a short period. It has been found that some metallic ions, like Cr[20], Al[21] ions, can promote the formation of the protective rust layer. Then we examined the use of those ions as oxides and sulfates contained in a resin to form a coating over the steel.

Figure 6 shows 2-year exposure appearance of the non-coated and coated steels. The coating prevents initial staining with red rust which is shown in the non-coated bare steel surface. However, rust is appeared on the surface of the coated steel, which indicates that the surface is covered with a rust layer. The corrosion loss of the coated steel is approximately 0.02 mm which is about one-fifth of that of the non-coated steel. This higher performance of the coated steel might be attributed to the formation of protective rust substance.

Fig.6 Surface appearance of non-coated (left) and coated (right) steels, after 2 years Corrosion. Air-borne salt content was 1.0 mdd.

CONCLUSIONS

Degradation of infrastructures made of steel is a critical issue from the viewpoint of their life extent. Rust layers formed on steel have important effects on the atmospheric corrosion of steel. Some kinds of iron rust accelerate corrosion, on the other hand other kinds of rust retard corrosion.

Atmospheric corrosion resistance of weatheirng steel bearing small amounts of Cu, Ni, and Cr depends on the fine grained, compacted and defect less rust of α-FeOOH. Synthetic acceleration of such corrosion protective α-FeOOH formation is possible with use of appropriate paints on steel or weathering steel.

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