

# Nanoscopic Mechanism of Protective Rust Formation on Weathering Steel Surfaces

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## Abstract

*Weathering steel, when exposed outdoors for a few years, forms a protective layer resulting in reduction of the corrosion rate. The state of rusts is fundamental for understanding its mechanism, but the structure and its relationship with the mechanism have not been understood. In this study, a new approach was applied to reveal nano-structure of rusts with using of X-ray synchrotron radiation. It has been shown that additional elements alter the corrosion process in its early stage, resulting in formation of protective rusts.*

## 1. Introduction

Weathering steel<sup>1,2)</sup> is a kind of low-alloy steel mainly containing alloying elements such as Cu and P. It is characterized by protective rust that forms on the surfaces, significantly reducing the rate of corrosion, after a few years' use without paint coating at inland locations where there are lower levels of airborne salt. The rust forming on the surfaces of weathering steel is divided into two layers under observation through a polarized light microscope. The inner layer on the steel substrate side is a rust layer not showing polarization (dark layer); the enrichment of Cu and P in the layer has been confirmed<sup>3)</sup>. However, no direct and quantitative information regarding the structure of the inner rust layer has been made available, and its change over time has not been studied in detail, either. The lack of information has made clarification of corrosion protection mechanisms difficult.

With conventional weathering steels, the protective rust does not form in a coastal environment containing considerable levels of airborne salt, thus corrosion proceeds. A new type of weathering steel (3% Ni advanced weathering steel) has been developed to solve the problem<sup>4,5)</sup>. It is a steel based on the concept of preventing airborne salt from coming close to the steel substrate by adding Ni to the steel to control the ion selectivity of rust layers, and the steel has exhibited excellent weatherability in regions of salt damage<sup>4,5)</sup>. However, many aspects related to the details of the weatherability mechanisms of the steel remain yet to be clarified.

Clarification of the corrosion resistance mechanisms of alloying elements is very important for quantifying environmental conditions

under which the weathering steel is used and estimating long-term service life of structures made of weathering steel. For the purpose of clarifying the corrosion protection mechanism, the authors examined the mechanisms of the corrosion reactions of weathering steel by nanoscopic analysis methods employing the X-ray synchrotron radiation<sup>6,7)</sup>. As a result, they opened up the possibility of comprehensively understanding the structure of the rust that formed on weathering steels and its historical change<sup>8-12)</sup>. This paper reports the analysis results.

## 2. Corrosion Reactions under Nanoscopic Observation

Corrosion occurs in the environment of atmospheric exposure as a result of reactions whereby metal ions that have dissolved during the cycles of wetting and drying turn into  $\text{Fe}(\text{OH})_x$ , precipitate from the solution, and finally form rust layers ( $\text{FeOOH}$ ) through grain growth. What is important for understanding the reaction mechanisms are (A) an electrochemical viewpoint to consider the reactions as electron exchange reactions resulting from the dissolution of metal ions and (B) a colloid chemical viewpoint to consider them as the processes of growth of ions into fine particles and then rust<sup>13)</sup>. **Fig. 1** is a schematic illustration of the processes from nanoscopic structural changes of ions to the formation of rust seen from the above viewpoints.

The first stage of rust formation reactions (Stage I) consists of a nucleation process wherein metal ions dissolve in a solution in a wet environment and form  $\text{Fe}(\text{OH})_x$  and then rust cores ( $\gamma\text{-FeOOH}$ ) (see Fig. 1). The next stage (Stage II) consists of a growth process wherein

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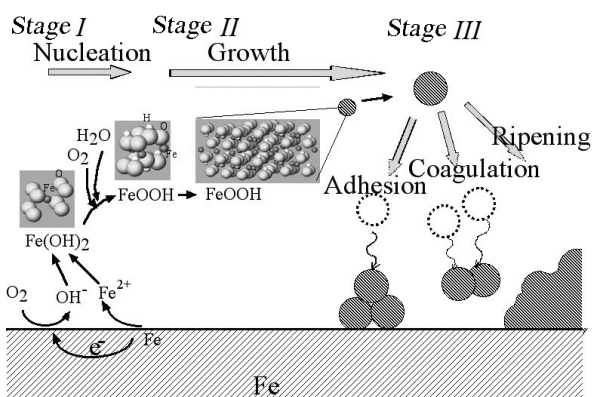


Fig. 1 Schematic diagram showing nanoscopic reaction of rust formation. The diagram was based on the reference<sup>13)</sup>.

the rust cores grow into fine particles up to 1 nm or so in size. Then the fine particles undergo changes such as adhesion, coagulation and ripening under repeated cycles of wetting and drying to form layers of rust particles several nanometers to 100 μm in size (Stage III).

The authors studied each of the above reaction stages to clarify the effects of alloying elements of weathering steels. The results of the studies are explained and discussed below, stage by stage.

### 3. Stage I: Nucleation of Metal Ions

In order to clarify the reactions in Stage I, the authors developed a technique that enables direct observations of the states of metal elements in a solution that was in direct contact with a metal surface<sup>14, 15)</sup>. Fig. 2 shows a reaction cell used in the developed technique. The cell makes it possible to observe, dynamically or in situ, the element concentrations and atomic structures in a solution under an environment in which diffusion and electrochemical reactions proceed simultaneously. To realize such observation, the authors also developed an observation method employing the X-ray absorption fine structure (XAFS) analysis using synchrotron radiation. The XAFS analysis is a structural analysis method taking advantage of the fact that minute change in the absorbance near the absorption edge energy of X rays reflects the environmental structure around an atom that absorbs X rays<sup>16)</sup>. The method makes it possible to examine the structure of neighboring atoms around atoms of a specific absorber element, without being affected by the crystallinity of the material in question.

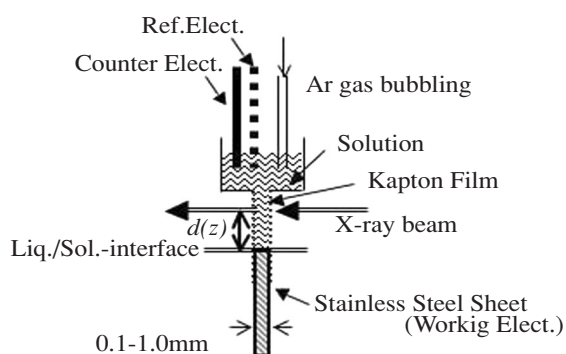


Fig. 2 A part of the system (a reaction cell) which was developed to observe atomic structure of solution adjacent to metal surface<sup>14, 15)</sup>

For the purpose of studying the effects of alloying elements, tests were carried out using specimens of a binary alloy (Fe-5.0mass%Cr). The structure of colloidal rust that formed after immersing the specimens in artificial seawater for 2 weeks was analyzed in a state of solution (wet) and after drying (dry). Rust that formed on the same steel after an atmospheric exposure for 15 years and specimens of rust powder ( $\alpha$ -FeOOH and  $\gamma$ -FeOOH) were also analyzed for comparison purposes. Fig. 3 shows the radial distribution functions (RDFs) around Fe atoms obtained by the XAFS analysis.

The first peak in the RDF (Radial Distribution Function) of the colloidal specimen after 2 weeks of corrosion (wet) corresponds to the nearest neighbor of Fe-O [1st NN], and its second peak to the nearest neighbor of Fe-Fe [1st NN] and the second nearest neighbor of Fe-O [2nd NN]. This indicates that Fe(O, OH)<sub>6</sub> unit nuclei corresponding to the  $\gamma$ -FeOOH phase form at an initial stage of corrosion. An Fe(O, OH)<sub>6</sub> unit nucleus is the smallest unit of the structure wherein six oxygen atoms (some of which being -OH) surround an Fe atom; these nuclei combine with each other into a network and grow as corrosion proceeds (see the right-hand side of Fig. 3).

When the colloidal rust is dried, the strength of the third peak ([Fe-Fe (1st NN)] and [Fe-O (2nd NN)]) of the RDF (dry) near  $r = 0.33$  nm increases. This indicates that the Fe(O, OH)<sub>6</sub> unit nuclei that have formed in a colloidal state grow during the drying process.

The RDF of the specimen after 15 years of corrosion is similar to that of the crystalline  $\alpha$ -FeOOH specimen. These results make it clear that the Fe(O, OH)<sub>6</sub> network develops, and a change from  $\gamma$ -FeOOH to  $\alpha$ -FeOOH takes place during a long period of corrosion under repeated cycles of wetting and drying.

Conventional weathering steels contain small amounts of Cu, P and Cr. While the addition of Cr is believed to be effective in enhancing corrosion resistance in an environment of low salt damage (deposition of airborne salt of 0.05 mg-NaCl/dm<sup>2</sup>/day or less), there are reports to the effect that Cr accelerates corrosion in locations where the deposition of airborne salt is large<sup>5)</sup>. While it is necessary to clarify the mechanisms where the addition of Cr protects steel against corrosion for developing a reliable weathering steel, there are many arguments<sup>17-19)</sup> and the issue has not been settled.

Facing the situation, the authors made detailed analyses by the

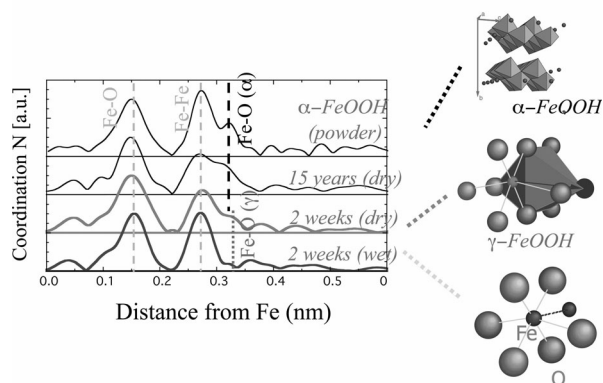


Fig. 3 Radial distribution functions around Fe atoms obtained by XAFS. From bottom, (1) the colloidal rust formed on Fe-5.0mass%Cr immersed in artificial seawater for 2 weeks (wet), (2) the dried powder of it (dry), (3) the rust formed on Fe-5.0mass%Cr exposed to atmosphere for 15 years, and (4) powder of  $\alpha$ -FeOOH. Corresponding atomic structures (network structures) are shown in right.

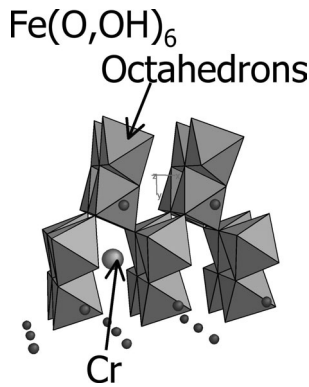


Fig. 4 The state of chromium in rust forming on weathering steel

XAFS method to clarify the involvement of Cr in the formation of the  $\text{Fe}(\text{O}, \text{OH})_6$  network during corrosion processes. The analysis revealed that, although Cr formed  $\text{Cr}(\text{O}, \text{OH})_6$  units, like the  $\text{Fe}(\text{O}, \text{OH})_6$  units of Fe, the sites Cr occupied in the network structure of  $\text{Cr}(\text{O}, \text{OH})_6$  were different from the sites that Fe usually occupies in the  $\text{Fe}(\text{O}, \text{OH})_6$  network structure (see Fig. 4). Thus, it became clear that the  $\text{Cr}(\text{O}, \text{OH})_6$  compound was not Cr-substituted goethite<sup>18)</sup>, that is, a compound in which the Fe sites in  $\alpha\text{-FeOOH}$  were partially substituted with Cr<sup>8,9)</sup>.

#### 4. Stage II: Formation of Atomic Network of $\text{Fe}(\text{O}, \text{OH})_6$

The  $\text{Fe}(\text{O}, \text{OH})_6$  unit nuclei that formed at Stage I grow under the wetting/drying cycles in the environment of atmospheric exposure to form fine crystals up to 1 nm in size that have a network structure of the  $\text{Fe}(\text{O}, \text{OH})_6$  unit nuclei. The authors investigated the influences of alloying elements on the formation processes of the network structure. The XAFS analysis using synchrotron radiation, the anomalous X-ray scattering method<sup>20)</sup> and the reverse-Monte-Carlo

(RMT) method<sup>21)</sup> were employed in combination for the precision structural analysis of the network at a nanoscopic level<sup>9)</sup> to clarify its atomic structure.

As examples of the network structure of rust clarified through the analysis, Fig. 5 shows the structures of (a) colloidal rust that formed on pure iron after immersion in artificial seawater for 2 weeks and (b) rust that formed on a weathering steel after atmospheric exposure at an inland location for 31 years. While the network structure of the former is similar to that of the  $\gamma\text{-FeOOH}$  phase, the arrangement of  $\text{Fe}(\text{O}, \text{OH})_6$  octahedron unit nuclei is significantly in disorder. In contrast, the structure of the latter is that of the  $\alpha\text{-FeOOH}$  phase, and there is little disorder in the arrangement of the  $\text{Fe}(\text{O}, \text{OH})_6$  octahedron unit nuclei. This indicates that, whereas the former is a kind of rust that grew rapidly in a short period, the latter is another that grew at a low corrosion rate and ripened into a structure having a small number of defects.

Through detail investigations of the historical change in the arrangement structure as the above, the authors clarified the influences of alloying elements on the mechanism of rust growth as described below (see Fig. 6)<sup>8,9)</sup>. The growth of the  $\text{Fe}(\text{O}, \text{OH})_6$  unit nuclei into the network structure depends on the balance between the nucle-

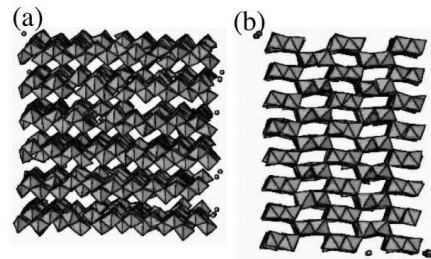


Fig. 5 Network structures of rust<sup>9)</sup>. (a) the colloidal rust formed on Fe immersed in artificial seawater for 2 weeks, and (b) the rust formed on weathering steel exposed to atmosphere in a rural area for 31 years.

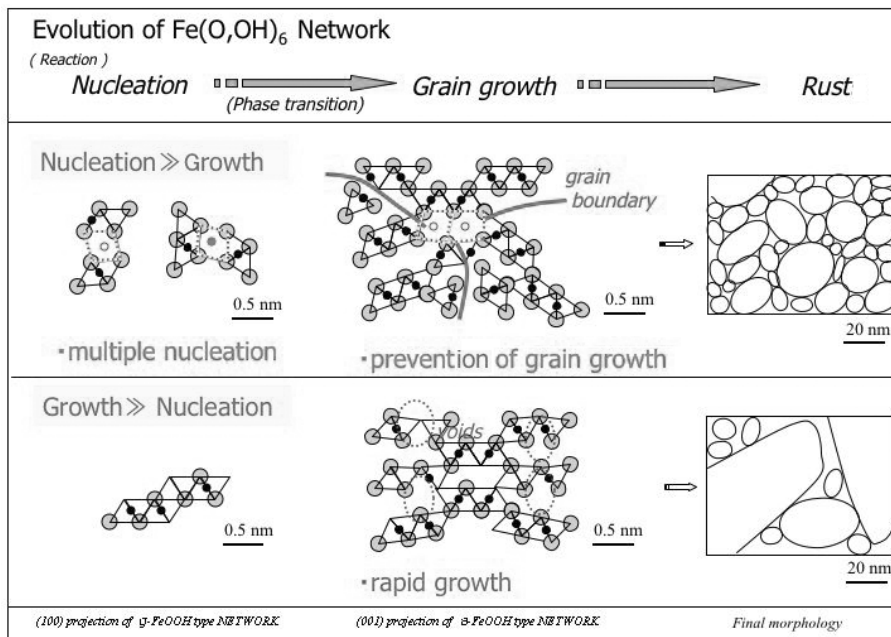


Fig. 6 Process of rust formation on steel surfaces when exposed to atmosphere: for weathering steel (above) and mild steel (below)

ation and grain growth. In the case of the corrosion of conventional ordinary steel, the reaction rate of grain growth is far greater than that of nucleation, and as a result, nuclei, once formed, grow into a large crystal grain. As a result of the high growth rate, the microstructure of such rust contains a great number of defects and its density is low (see the lower part of Fig. 6). In the case of weathering steel, on the other hand, alloying elements serve as the starting points of nucleation, and in contrast to the above, the reaction rate of grain growth is far smaller than that of nucleation. What is more, the alloying elements inhibit the growth of fine nuclei into large crystals, and as a consequence, protective rust having a fine and compact structure forms (see the upper part of Fig. 6).

### 5. Stage III: Formation of Rust Structure

The authors' analyses clarified that alloying elements significantly affected the process of Stage II; this change in the reaction process brings about fundamental difference in the structure of rust that forms during a long-time exposure to environment. The effects of alloying elements on the formation of fine rust structures several nanometers to 100  $\mu\text{m}$  in size are explained below, using the newly developed 3Ni advanced weathering steel<sup>4, 5</sup> as an example.

The amounts of corrosion of the 3Ni advanced weathering steel and a conventional weathering steel were investigated after exposing their specimens in a coastal region for 9 years (see Fig. 7). The corrosion amount of the 3Ni advanced weathering steel (Advanced) was less than 1/20 that of the conventional weathering steel (Conventional), which evidenced the excellent weatherability of the developed steel.

Sectional observation of the specimens of the advanced weathering steel revealed that the rust was composed of an inner layer directly contacting the base steel and an outer layer on the atmosphere side. Compositional mapping demonstrated that, whereas the concentration of Cl was higher in the outer layer, those of Na and Ni were higher in the inner layer (see Fig. 8)<sup>4, 5, 22</sup>. The distributions of Cl and Na in the specimens of the advanced weathering steel were exactly contrary to those in the specimens of the conventional weathering steel, although they were subjected to the corrosion test under the same condition. This means that the Ni addition in the advanced weathering steel brings about a characteristic rust structure wherein Cl is ejected from the portion near the steel substrate.

To clarify the formation mechanisms of this rust structure, the authors investigated the state of Ni in the developed steel by the XAFS analysis using synchrotron radiation and found that an  $\text{Fe}_2\text{NiO}_4$  (see Fig. 9) phase formed in the rust layers<sup>22</sup>.

The authors investigated further the grain size distribution of the phases that composed the rust by the Mössbauer spectrometry. The method was employed because measuring the Mössbauer spectra of rust in a wide temperature range from 15 to 300 K and theoretically analyzing the temperature dependence of the spectra yielded quantification of different states of iron atoms<sup>23</sup>. As a result, they obtained the volume fractions of the  $\alpha$ -,  $\beta$ -,  $\gamma$ - $\text{FeOOH}$  and  $\text{Fe}_2\text{NiO}_4$  phases and the size distributions of the grains that contained these phases<sup>24</sup>. The analysis of the inner rust layer of the 3Ni advanced weathering steel exposed in a coastal region for 9 years revealed that the grain size was continuously distributed in a range from a few nanometers to 10 nm<sup>22</sup>.

These results indicate that the principal factors of the excellent weatherability of the 3Ni advanced weathering steel in a coastal environment are (I) the formation of a tightly packed inner layer composed of nanoscopic fine particles and (II) the prevention of Cl from

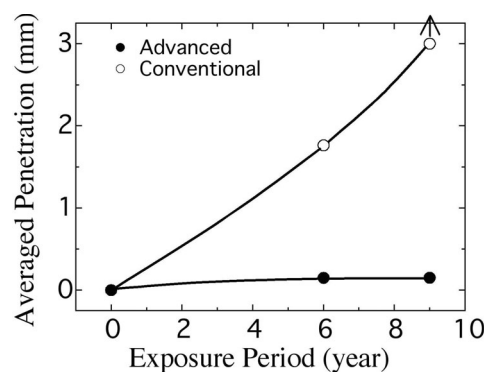


Fig. 7 Penetration curves of the advanced and conventional weathering steels exposed in a coastal area

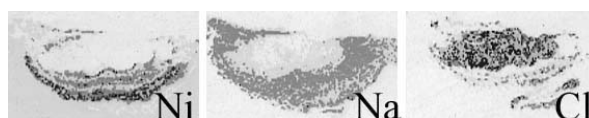


Fig. 8 Cross-sections near the surface of the advanced weathering steel which was exposed in a coastal area for 9 years. Each figure shows concentrations of Ni, Na, and Cl in a gray scale.

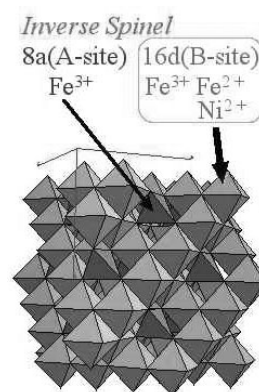


Fig. 9 Atomic structures of  $\text{Fe}_2\text{NiO}_4$  contained in rust forming on the advanced weathering steel exposed in a coastal area for 9 years

coming close to the base steel by changing the surface charge of  $\text{Fe}_2\text{NiO}_4$  in the inner rust layer to the negative side<sup>22</sup>.

Considering the rust formation processes from the colloid chemical viewpoint<sup>13</sup> clarified the mechanisms by which Cl was prevented from coming close to the interface between the base steel and the inner rust layer<sup>4, 5, 22, 25</sup> (see Fig. 1). In a corrosive environment (wet environment) of a coastal region, with conventional weathering steel, the  $\alpha$ - $\text{FeOOH}$  phase that composes rust combines with  $\text{H}^+$  in the solution and becomes positively charged. As a result, a vicious cycle wherein  $\text{Cl}^-$  is taken into the rust, the pH of the rust falls and corrosion advances further repeats with increasing speed. In the case of the 3Ni advanced weathering steel, on the other hand, since rust has a network structure containing  $\text{Fe}_2\text{NiO}_4$ ,  $\text{H}^+$  is discharged from the rust even in a corrosive environment (wet environment) of a coastal region, and the rust is negatively charged. As a consequence, rust combines with  $\text{Na}^+$  in the inner layer, the fall of pH is prevented, and the increase in the corrosion rate is suppressed.



## 6. Closing

The authors examined the formation mechanisms of protective rust of weathering steels by nanoscopic analysis techniques using X-ray beam produced from synchrotron radiation, and obtained findings about the corrosion mechanisms of combined electrochemical and colloid chemical reactions proceeding in multiple steps and the effects of alloying elements on the above mechanisms. These findings are very important for quantifying environmental conditions under which weathering steels are used and estimating long-term service life of structures made of weathering steels<sup>26)</sup>. Based on the knowledge thus acquired, the authors are expanding their study activities towards development of new weathering steels having improved properties.

The approach techniques mentioned herein yield valuable pieces of information that other techniques cannot. These techniques are being applied to the clarification of corrosion reactions occurring in a wide variety of environments other than that of atmospheric corrosion. The nanoscopic analysis, understanding and control of reactions that take place at a liquid/metal interface will become increasingly important not only in the study of corrosion but also in various other fields.

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