Advanced Techniques for Analyzing Corrosion Resistance of Steels for Infrastructure

Dr. Takenori NAKAYAMA*[1]

*[1] Materials Research Laboratory, Technical Development Group

This paper reviews methods for quantitatively measuring the composition of steel rust by X-ray diffraction using internal standards. Also introduced is a method for evaluating the size of rust particles on the basis of molecular adsorption. Experiments with artificially synthesized rust described here suggest new approaches to improve the corrosion resistance of steels. The atmospheric corrosion phenomena of steels used for infrastructures have been analyzed using the ultra-bright synchrotron radiation generated by SPring-8 and the neutron beam generated by a compact neutron source by RIKEN.

Introduction

Modern steel infrastructures are required to have decreased life-cycle costs and increased lives. Thus, steels with high corrosion resistance, as typified by weathering steels, are gaining more importance.[1] The corrosion resistance of steel is heavily dependent on the structure and characteristics of the rust formed on the steel surface. Hence, Kobe Steel has long established its own technologies for controlling steel rust as a means for improving the corrosion resistance. As a result, the company has newly developed and implemented two types of unique steels for infrastructure. One is for unpainted applications and has higher atmospheric corrosion resistance in chloride environments than conventional weathering steel. The other is for painted bridges, which can prolong the cycle of repainting.[2] Kobe Steel has conducted various activities in parallel, such as joint studies with government and academia, as well as participation in academic societies, to establish new and unique analysis technologies to support studies on corrosion and the prevention of corrosion in steel for infrastructure. These technologies include rust evaluation using, for example, X-ray diffraction, molecular adsorption and highly brilliant synchrotron radiation. They also include a new approach based on experiments using artificially synthesized rust and neutron radiation to visualize the under-film corrosion of painted steel. They have been serving to substantiate the onset mechanism of corrosion resistance and as guidelines for material development. The following introduces the outline and application examples of these technologies.

1. Rust evaluation technologies for weathering steel

1.1 Quantitative analysis of rust composition based on X-ray diffraction using internal standards

Weathering steel is often regarded as "steel using rust to prevent rusting." It is considered that certain alloying elements serve to form a dense, protective rust layer in the air, exerting excellent atmospheric-corrosion resistance. This implies that the first step in understanding its corrosion resistance mechanism is to know which substances constitute the rust layers. The rust formed on steel is generally recognized to consist of crystalline components, such as α-FeOOH, β-FeOOH, γ-FeOOH and Fe_3O_4, as well as other components regarded as X-ray amorphous. X-ray diffraction (hereinafter "XRD") is an analytical method commonly used for discriminating these substances. In XRD, the subject rust sample may be mixed with a certain amount of known substance, called "internal standard substance", to determine the intensity ratios of the diffraction lines for said substance and the individual rust component, such that each intensity ratio can be collated to its respective calibration curve (prepared in advance) to enable quantification. This technique, however, has not been reported in detail so far. It was against this background that Kobe Steel, collaborating with Kobelco Research Institute, Inc., conducted basic studies including the methods of preparing internal standard substances and rust samples, the conditions of XRD measurement and the method for analyzing data; this, in particular, led to the development of a quantitative XRD for rust using ZnO as the internal standard substance.[3] It has turned out that ZnO is preferable because its grains are finer and more homogeneous than those of other conventionally used substances, such as CaF_2, and readily mixes with rust samples. **Fig. 1** outlines the experimental procedure. This quantitative method was further submitted to the *SABI*-chemistry study group, Japan Society of Corrosion Engineering, where its accuracy was verified in a round robin test, and its application technology was improved. This method is being used as a de-facto standard.[4]

An application example of this quantitative method is demonstrated in **Fig. 2** showing the relationship between the thickness loss (corrosion
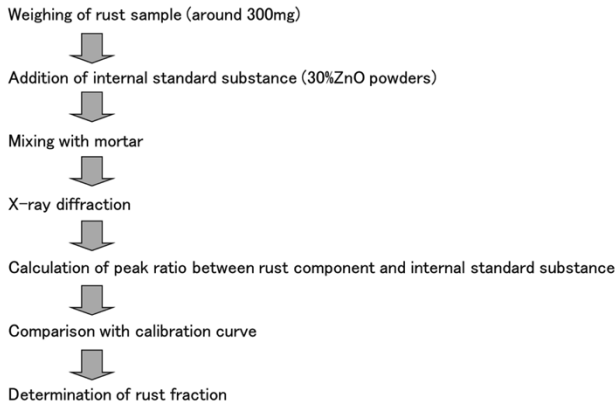
Fig. 1 Experimental procedure of quantitative analysis by XRD of rust composition
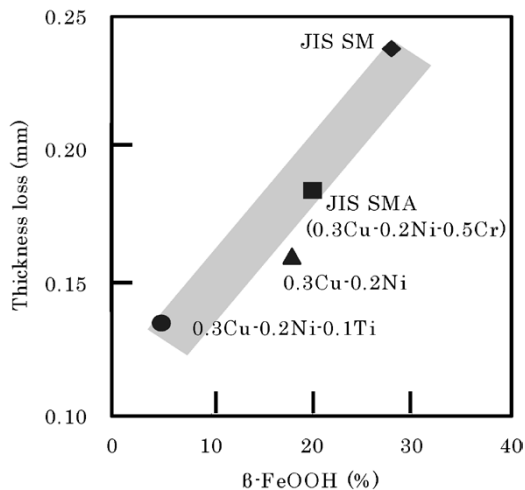

Fig. 2 Relationship between thickness loss and β-FeOOH rust fraction of various steels exposed at Kakogawa Works quay for 1 year

Fig. 3 Plots of specific surface area (SA) of the steel rusts formed by cyclic corrosion test against the decrease in thickness

resistance) and rust components of various steels exposed to a chloride environment.[5] The thickness loss correlates with the amount of β-FeOOH rust. The results indicate that proper amounts of alloying elements such as Cu, Ni and Ti suppress the formation of β-FeOOH, classified as a detrimental rust, and improve the resistance against corrosion in a chloride environment.

1.2 Evaluation of specific surface area of rust based on molecular adsorption

A rust layer on steel can be regarded as a porous aggregate consisting of fine particles of individual rust components. Finer rust particles are considered to form a denser, protective rust layer, exerting corrosion resistance. In reality, however, rust particles have various shapes and strongly aggregate; this makes it difficult to determine their sizes quantitatively by, for example, electron microscopy observation or particle size analyzer measurement. The molecular adsorption, on the
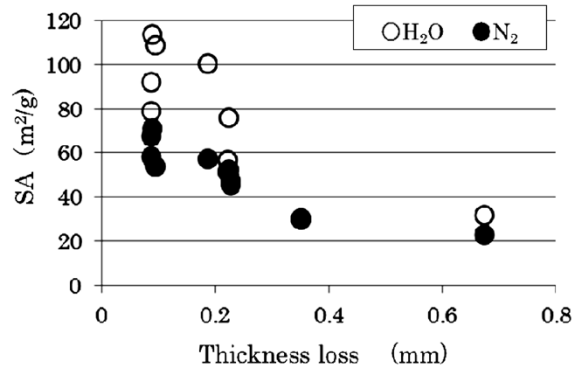
other hand, makes it possible to obtain molecular size information even from aggregated rust because it uses gaseous molecular probes. With this in mind, Kobe Steel has collaborated with Osaka Kyoiku University and Shimane University to conduct adsorption experiments, using the molecules of nitrogen (N_2) and water (H_2O), on various rusts formed by atmospheric corrosion. Specific surface areas (hereinafter "SAs") were measured which were considered to reflect the particle sizes of the rusts. It was found that the SA can be an evaluation index for the corrosion resistance of weathering steels.

Fig. 3 depicts, as an example, the SAs obtained by cyclic corrosion testing (CCT) of various weathering steels, plotted against their corrosion resistances (thickness losses).[6] The results show that the SA increases with decreasing thickness loss, indicating that finer rust particles densify the rust layer, improving the corrosion resistance. The results also indicate that the adsorption of water molecules can reflect the denseness of rust more sensitively than nitrogen.

2. Approach based on experiments using artificially synthesized rust

Alloying elements such as Cr, Cu, Ni and Ti are known to densify the rust layers of steel and thus improve the corrosion resistance. A rust layer is an aggregate of particles of individual rust components, as described above, and its performance is affected by environmental factors such as chloride ion, dissolved oxygen and pH. Thus, the formation of rust on steel in real conditions is complex, with various factors interacting complexly with each other, making it difficult to clarify which alloying element works on which rust component to densify the rust. The fundamental improvement of corrosion resistance, however, requires clarification of how individual alloying elements affect the formation

and structure of each rust component. As a new approach to achieving this, Kobe Steel, collaborating with Osaka Kyoiku University and Shimane University, has been conducting experiments on artificially synthesized rust and has established a technology for artificially synthesizing an intended rust composition with intended alloying elements under intended environmental conditions. As a result, the effects of alloying elements and environmental factors on the composition of rust layers are being systematized.

Table 1 shows, as an example, the results of a study on the effects of typical metallic ions on the crystallinity and particle size of each rust component formed under typical rusting conditions.[7] The results show that Cu(II) can densify rust components other than β-FeOOH. It is also shown that Cr(III) has small effects on α-FeOOH and β-FeOOH, but refines γ-FeOOH significantly. Divalent nickel, Ni (II), has little effect on the refinement of β-FeOOH, but refines other rusts, in particular, γ-FeOOH. Unlike other metallic ions, Ti (IV) is found to refine β-FeOOH significantly. In order to densify rust layers and improve corrosion resistance, it appears to be more effective to add combined alloying elements, taking into account the effects of alloying elements and the corrosion environment, rather than adding each element singly. Atmospheric rust formed in a chloride-free environment, for example, mainly contains α-FeOOH and γ-FeOOH. Therefore, it stands to reason that the addition of Cr, Cu, and Ni is indispensable to the conventional weathering steels stipulated in the Japan Industrial Standard (JIS). Chloride environments, on the other hand, give rise to the formation of β-FeOOH and Fe_3O_4, which are regarded as detrimental rusts. Thus, Ti is strongly recommended as an element that inhibits the formation of β-FeOOH and improves the

resistance against corrosion in chloride-containing atmospheres. Further addition of Ni and Cu, the elements densifying Fe_3O_4, α-FeOOH and γ-FeOOH, is expected to improve the corrosion resistance even more.

3. Application of ultra-bright synchrotron radiation

Synchrotron radiations, having high brightness and wide wavelength windows, excellent in directionality and stability, are recently gaining attention as new X-ray sources that provide analytical information featuring, for example, high resolution and a high S/N ratio. In particular, the large synchrotron radiation facility, SPring-8 (Super Photon-ring, 8 GeV), in Nishiharima, Hyogo in Japan, achieves the world's highest performance and offers brightness more than one hundred million times higher than do conventional X-ray tubes. Kobe Steel participates in promoting the industrial application of SPring-8, exploiting the facility in elucidating the corrosion processes of steel and the structures of rust formed.

Fig. 4 exemplifies the results obtained by the XRD apparatus of the SPring-8 Hyogo Beamline (BL24XU), in which the corrosion process in iron was traced during the beginning stages of wet/dry cycles.[8] This experiment involved dry-polishing a surface of high-purity iron and dispensing a saturated NaCl solution onto the surface every 60 minutes, while measuring in-situ the XRD intensity at a low incidence angle. Here, Fe_3O_4 and FeOOH (presumed to be α-FeOOH) were detected with a higher ratio of Fe_3O_4 immediately after the salt solution was supplied, and with a decreased ratio of Fe_3O_4 as the solution slowly dried naturally. The NaCl solution was replenished 60 minutes later, which increased the ratio of Fe_3O_4 again, and this behavior was repeated thereafter. These behaviors seem to agree with the electrochemical redox model proposed by U. R. Evans, which states that, in wet processes, FeOOH is reduced into Fe_3O_4 by cathodic reduction, which acts as an oxidant to promote the corrosion of iron, while, in dry processes, Fe_3O_4 is oxidized by air into FeOOH: these processes are repeated, promoting atmospheric corrosion.

Fig. 5 shows an example in which the state of Ti (the radial distribution function around Ti) in Ti-added, β-FeOOH rust was analyzed using the X-ray absorption fine-structure (hereinafter "XAFS") apparatus of the SPring-8 Industrial Consortium Beamline (BL16B2).[9] Kobe Steel has recently developed an advanced weathering steel containing nickel, in which a minor quantity of Ti is added to suppress the formation of β-FeOOH rust and

Table 1 Comparison of effects of metal ions on crystallinity and particle size of iron rusts

Rusts		Cu(II)	Cr(III)	Ni(II)	Ti(IV)
α-FeOOH	crystallinity	◎	●	○	＊
	particle size	○	○	○	○
β-FeOOH	crystallinity	△	○	○	◎
	particle size	●	○	△	◎
γ-FeOOH	crystallinity	○	○	○	●
	particle size	○	◎	◎	○
Fe₃O₄	crystallinity	○	○	○	○
	Particle size	○	○	○	○
X-ray amorphous	crystallinity	○	○	○	○
	particle size	△	●	△	△

● : rise, △ : unchanged, ○ : fall, ◎ : marked fall
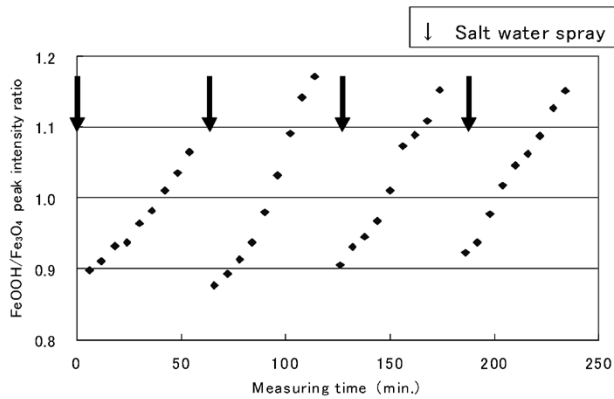＊ : double domain particles consisting of an α-FeOOH core and a poorly crystalline shell

Fig. 4 Time change of $FeOOH/Fe_3O_4$ peak intensity ratio during the iron rust formation process by wet/dry cycle using in-situ SR-XRD observation
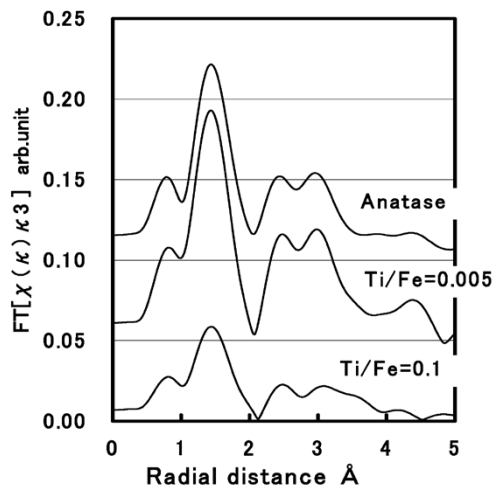

Fig. 5 Radial distribution functions of Ti in Ti-containing β-FeOOH rusts and anatase type TiO_2 obtained from SR-XAFS measurement

thus improve the resistance against corrosion in chloride environments. This development involved the above experiment as well as high-resolution TEM observation. These analyses imply that, in the advanced weathering steel with a minor addition of Ti, nanometer scale particles of anatase-type TiO_2 are formed to promote the refinement of β-FeOOH rust, providing excellent resistance against corrosion in chloride-containing atmospheres. Synchrotron radiation XAFS enables highly sensitive detection of information on local structure and the electronic state around specific elements, regardless of whether the subject is solid or liquid, allowing, for example, studies currently on-going on the action mechanisms of alloying elements in corrosion processes.

4. Application of neutron radiation

Painting is widely used for preventing the corrosion of steel infrastructure; however, with the passage of time, water may penetrate under the coating film through, for example, film defects, which promotes under-film corrosion and eventually causes the coating to blister. Painted steel structures therefore must be repainted periodically, which raises the maintenance cost. Attempts are being made, including the development of heavy duty coating, to prolong the life of coatings. Kobe Steel focused on the densification of rust and pH control at corrosion tips and has developed a unique alloy steel for painted application to deter the progress of under-film corrosion. To further advance this development, the mechanism of under-film corrosion must be elucidated; however, the conventional X-ray analysis tools have insufficient sensitivity to water and low power for penetrating through steel material, limiting the analysis of under-film corrosion. Neutron beams, on the other hand, have penetrating power that is remarkably higher than that of X-rays in principle and has an excellent capability for detecting the water involved in corrosion. Kobe Steel is collaborating with RIKEN, as a part of study-group activities of the Iron and Steel Institute of Japan, to visualize the movement of water inside the blisters of painted steel by a neutron imaging technique using a compact neutron source system, the RIKEN Accelerator-driven Neutron Source (RANS), maintained and upgraded by RIKEN.

Fig. 6 shows examples of the results.[10] Specimens of normal steel (SM400) and alloy steel (0.8Cu-0.4Ni-0.05Ti) were compared. They were coated with modified epoxy paint, and artificial defects were induced into the coating. These specimens were subjected to CCT tests to create blisters of under-film corrosion. These specimens were ① stored in a room for one month after the CCT tests, ② immersed in distilled water for 110 min, and ③ dried by blown air for 30 min using a fan after step ②. These 3 states are compared in the figure. In the naturally dried state (①), contrasts (attenuations of neutron transmittance) due to the defects of rust layer or to the residual water in the coating and steel/coating interface were observed in addition to the rust component (FeOOH) formed under the film. For both steels, these contrasts were found to be enhanced when the specimens were immersed in water (②) and, conversely, found to be weakened when they were dried (③). These changes in contrast are considered to reflect the movement of water (changes in moisture) under the films. Compared with the normal steel, the alloy steel has a localized water-containing region, which makes it easier for water to disappear, so it is less likely to be retained. Water being a direct cause of corrosion, this implies
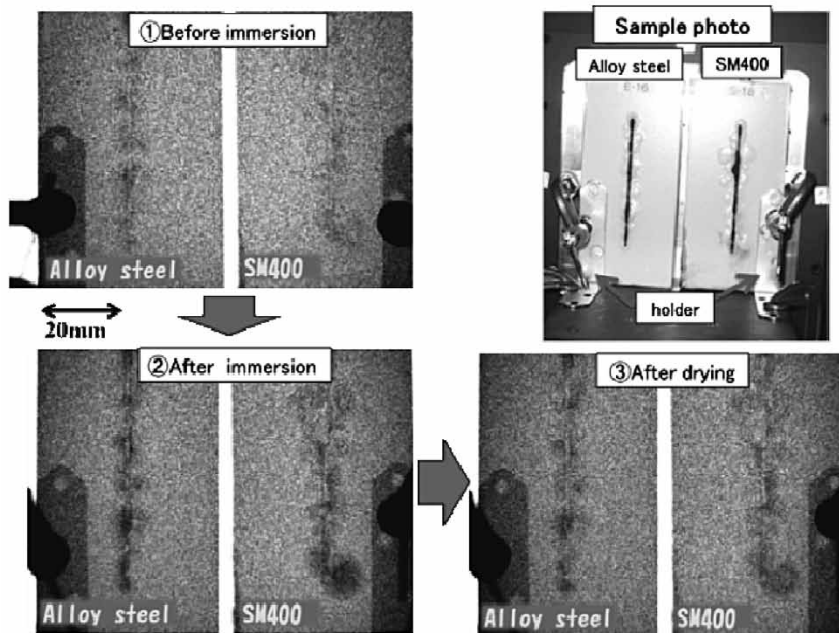
Fig. 6 Neutron images of under-film corroded normal steel (SM400) and alloy steel (0.8Cu-0.4Ni-0.05Ti) during water immersion and drying process

that the alloy steel has excellent resistance against under-film corrosion.

Conclusions

This paper has introduced a few examples of evaluation/analysis technologies that Kobe Steel has worked on to evaluate the corrosion resistance of steel for infrastructure. Neutron beams, in particular, have high penetrating power and excellent capabilities of detecting the water and hydrogen involved in corrosion phenomena and are expected to be used, with synchrotron radiation, for example, in a complementary manner. Infrastructures will be required to have a further decreased life-cycle cost and increased lives, and corrosion-resistant steel is expected to gain more importance. To support this, the technologies for evaluating and analyzing corrosion resistance must be advanced further. We will continue to strive to respond to a variety of sophisticated demands from customers.

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