Technical Review

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Approaches for Fundamental Principles 3: Basic Research on Corrosion

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1. Introduction

Corrosion is a chemical reaction. In a narrow sense, it is an electrochemical reaction, which is based on electrochemistry. Since the behavior of corrosion of a metal is influenced by the composition and structure of the metal, metallurgy is also a basic field supporting corrosion science. In addition, since corrosion is a chemical reaction that takes place at the interface between the environment and a metallic material, various surface analysis techniques are extremely important in fundamental research into corrosion. In this technical review, the basic corrosion technology that supports the development of corrosion-resistant alloys and techniques to apply them at Nippon Steel Corporation shall be described from a standpoint of engineering research taking corrosion-resistant low-alloy steels, stainless steels and titanium as examples.

2. Key Technology Supporting Development of Corrosion-resistant Low-alloy Steels

In the 1930s, U.S. Steel discovered that by adding an extremely small amount (1wt% or less) of Cu or some other alloying elements to steels, it was possible to obtain weathering steel which corrodes very slowly in the atmosphere. That was really an epoch-making event. At that stage, however, the mechanism of how good corrosion resistance was manifested was unknown. As a matter of fact, the discovery was the result of exposure tests on many steel specimens with various alloying elements added.

With the subsequent progress of surface analysis technology, it was clarified that the rate of corrosion of weathering steel decreases markedly as a highly protective rust layer is formed on the steel surface where the steel is exposed to the atmosphere. Eventually, basic technology for weathering steel was established.

On the other hand, it was found that in areas which are significantly affected by airborne sea-salt particles, the above layer of protective rust is not formed on the surface of ordinary weathering steel because chloride ions (Cl^-) penetrate the layer of rust and thereby reduce the pH value of the steel surface. Nippon Steel developed a new nickel based weathering steel having good corrosion resistance by applying technology to control the ion-exchanging function of the layer of rust to allow Na contained in sea salt to pass through the layer selectively and thereby restrain the decrease in pH value of the steel surface.[1, 2] **Fig. 1** shows the results of a cross-section analysis of the nickel-based weathering steel after an exposure test. It can be seen that Na concentrated in the matrix interface and Cl^- was present on the surface of the rust layer, validating the principle of the above technology. In addition, with the aid of advanced analytical technology for *in situ* observation of corrosion in a wet atmosphere, Nippon Steel succeeded in clarifying the mechanism of manifestation of corrosion resistance.[3]

The main field of application for weathering steel is bridges, since these are public structures which are required to have a service life of at least 100 years. For such long-life structures, minimizing the life cycle cost (LCC) is extremely important. Nippon Steel contributes much to minimization of LCC in the field of bridges through development of the key technology indispensable for bridge engineering, such as techniques to estimate the life of weathering steel, evaluate stable rust quantitatively and repair bridges.

The weathering steel mentioned above is a new and unique corrosion-resistant steel that utilizes rust to reduce the corrosion rate. In the United States, on the other hand, it was found that weathering steel with Cu added is superior to ordinary steel in resistance to the acid dew-point corrosion in the flue-gas systems, etc. of boiler plants.[4] In Japan, on the basis of the above finding, many studies were made to develop new steels having good resistance to acid dew-point corrosion. Through those efforts, Nippon Steel came up with steel with Cu and Sb added that is resistant to sulfuric acid dew-point corrosion (S-TEN1 steel). Recently, the company developed a new S-TEN1 steel that has outstanding resistance to hydrochloric acid, as well as sulfuric acid.[5] The key technologies that supported the development of those acid dew-point corrosion-resistant steels were the surface

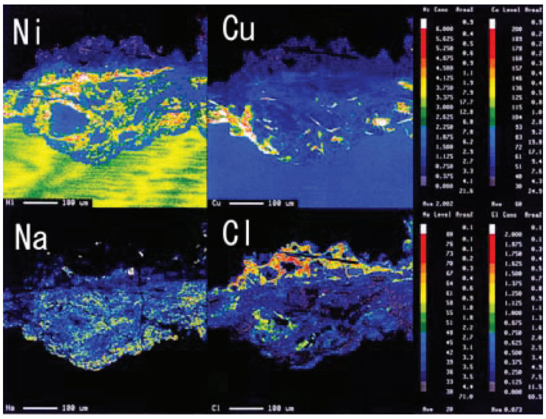

Fig. 1 Results of CMA (computer-controlled X-ray microanalyzer) analysis of cross section of 3%-Ni weathering steel exposed to the atmosphere for nine years

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analysis technology mentioned above and the potentiostat. Potentiostats have made it possible to speedily and quantitatively measure the influences of various alloying elements on the anodic and cathodic reactions that are useful in analyzing corrosion reactions. As a result, remarkable advances have been made in phenomenological understanding and clarification of the mechanisms of improvement in acid dew-point corrosion resistance of steel. Even so, in order to further clarify those mechanisms, we consider it indispensable to clearly understand the composition and structure of the film formed at the interface between the corrosive solution and the steel material, the condition of the state of dissolved ions at the corrosion interface.

As the last example of development of corrosion-resistant low-alloy steel, we describe below the key technology that supported the development of corrosion-resistant steel for bottom plate of cargo oil tank in crude oil tanker mentioned in Chapter 1. In the 1990s, pits up to 10 mm in depth occurred in the bottom plates of many oil tankers due to unknown causes. In the worst case, they numbered much more than 1,000 per tank. Since there were concerns about pollution of the ocean due to crude oil leaking through those pits, the need for inspection and repair of bottom plates increased sharply and suitable corrective measures were called for worldwide.

In Japan, the SR242 Sectional Study Meeting of the Shipbuilding Research Association of Japan carried out a comprehensive investigation into the pitting of crude oil tankers for the first time in the world. The “Study on the Behavior of The New Type of Corrosion of Crude Oil Tankers” (1999-2002) provided us with new findings and extensive knowledge about the subject. However, concerning the pitting mechanism, the above study only presented a number of hypotheses based on the formation of macro cells that were useful in developing new steel materials.6) Under those conditions, Nippon Steel attempted to clarify the mechanism of pitting corrosion for itself. As a result, the company discovered for the first time that when the pit interior locally becomes strongly acidic (pH 0.85) due to the presence of concentrated NaCl, the steel material corrodes exceedingly quickly. Upon discovering the mechanism, the company devised a corrosion test simulating the pit interior and set criteria (target levels of corrosion resistance) to judge whether or not each individual tanker requires repair. From the standpoint of developing key technology, the company eventually came up with NSGP®-1 (Nippon Steel Green Protect-1), a new type of corrosion-resistant steel for crude oil tanker bottom plate.7)

3. Key Technology Supporting Research on Corrosion Resistance of Stainless Steels and Titanium

In this section, we describe the key technology for the corrosion resistance of stainless steels and titanium. It is well known that unlike the corrosion-resistant low-alloy steels mentioned earlier, stainless steels and titanium display superior corrosion resistance thanks to a passive film several nm thick that is formed on the surface. However, even with the most advanced surface analysis equipment, the structure and composition of a passive film formed in a solution have not been completely clarified. This means that the properties required of the passive film from the standpoint of corrosion resistance are not properly understood yet.

In terms of engineering, stainless steels are corrosion-resistant materials having a history of about 100 years. Various types of stainless steels have been developed to suit specific corrosion environments.8) It is well known that in order to improve resistance to local corrosion (pitting and crevice corrosion) of stainless steels in an environment containing Cl^-, it is effective to add Mo and N, together with Cr. Whether the improvement in corrosion resistance by the addition of Mo or N is attributable to the enhancement of corrosion resistance of the passive-state film or the types of ions eluted into the local corrosion solution (e.g., MoO_4^{2-}, NH^{4+}, etc.) is still undetermined.

Through its research employing synchrotron radiation, which is an advanced X-ray source, in combination with a new-type of electrochemical reaction cell, Nippon Steel succeeded for the first time in the world in detecting the presence of Mo in local corrosion,3) and proposed a new mechanism to improve corrosion resistance using polymerized molybdate. In designing a corrosion-resistant alloy of stainless steel, it is very important from an engineering standpoint to develop a technique to estimate the life of stainless steel against pitting and crevice corrosion. Pitting/crevice corrosion refers to the condition of the anodic part where local corrosion develops with the surrounding cathodic part existing separately at the stainless steel surface. Since the rate of localaized corrosion is influenced by various factors, estimating the service life of stainless steel is an extremely difficult technical problem. Nevertheless, Nippon Steel, on the basis of the results of a long-term exposure test it continued for 10 years, obtained a growth law for maximum pit depth of various types of stainless steel by means of a statistical analysis of extreme values. In addition, on the basis of the results of the above statistical analysis, the company developed a laboratory test method for accelerated pitting corrosion. Eventually, it devised a technique to estimate the service life of stainless steel to the maximum pit depth in a corrosive atmosphere.9)

The above technique has made it possible to select the optimum stainless steel material according to the amount of airborne sea salt that is the governing factor in the corrosion of stainless steel in the atmosphere. On the other hand, concerning prediction of the service life of stainless steel against crevice corrosion, Nippon Steel, with the aid of an electrochemical measurement method, built a base of technology to estimate service life paying attention to the corrosion latency stage and the corrosion growth stage separately.10, 11) Namely, the company developed a method of estimating the time that crevice corrosion occurred based on the principle of crevice corrosion occurrence, clarified the growth potential of crevice corrosion, and systematized the technology for estimating the service life of stainless steel in the presence of crevice corrosion. On the basis of this technology, the company has proposed optimum stainless steels mainly for food processing plants and seawater desalination plants which are required to have excellent long-term resistance to pitting and crevice corrosion.

It is well known that titanium shows far superior resistance to Cl^- compared to stainless steels. Titanium is also a metal whose specific gravity is comparatively small. Because of those advantages, commercially pure titanium sheet began to be widely used in the 1990s as a maintenance-free material for roofs, walls, etc. At first, titanium as a building material was considered to be completely free from corrosion. However, in the late 1990s, the change in color of the titanium surface into the color of iron rust became a problem. This change in color, or discoloration, is due to the interference action of light induced by growth of an oxide film (a few tens of nm in thickness) on the titanium surface. It poses no problem to the corrosion resistance of titanium as a roofing material. Even so, since titanium as a building material is required to offer not only good corrosion resistance but also aesthetic appeal, the above discoloration of the titanium surface significantly lowered the commercial value of titanium. Accordingly, Nippon Steel clarified for the first time that the discoloration of titanium occurred as the surface layer of TiC was changed into a layer of titanium oxide by acid rain. Eventually, the company came up with a new titanium-based building material that hardly discolored.[12] The key technologies that supported the development of this new titanium material were the most advanced surface analysis technology and the method of accelerated discoloration that was developed based on the mechanism of discoloration the company had clarified and that permitted reproducing in only one week the surface discoloration that would occur on titanium after ten years of exposure to the atmosphere.

4. Conclusion

The key technologies supporting our R&D on corrosion that have been described so far are indispensable elements for systematizing, handing down, and evolving the huge volumes of extensive knowledge and technology relating to corrosion that the company has accumulated in the past. From the standpoint of building a recycling-type society and protecting the global environment, in particular, future corrosion-resistant materials are required to have much higher durability and include less alloying elements. In order to develop such materials, it is indispensable to clarify the mechanisms of corrosion through an analysis of the phenomenon of corrosion and the mechanisms to improve corrosion resistance with the addition of alloying elements. Thus, further seeking key technologies in the field of corrosion resistance is extremely important.

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