Metal surface control technology

Metal Surface Control Technology Contributing to Safe and Secure Society through the Creation of Highly Functional Surfaces

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Abstract

In order to achieve a safe and secure society, various challenges exist, such as extending the lifespan of infrastructure, environmental & energy facilities that use metallic materials, and achieving both reduced environmental impact and enhanced safety of automobiles. Addressing these challenges requires overcoming corrosion and hydrogen-embrittlement occurring on material surfaces, and metallic materials with excellent corrosion and hydrogen-embrittlement resistance are highly sought after. Meanwhile, surface treatment technologies that provide functions such as corrosion resistance, wear resistance, and antibacterial properties to material surfaces play a crucial role in responding to diversified and sophisticated needs for metallic materials. This paper introduces the "Metal Surface Control Technology," which creates highly functional surfaces through the control of metal surface reactions; and discusses examples of initiatives utilizing this technology to ensure a safe and secure society.

Introduction

Metal materials such as steel, aluminum, copper, and titanium are subject to environment-based phenomena that reduce product quality, service life, and reliability. Among these are corrosion (rust forming on the surface) and hydrogen embrittlement (hydrogen penetrating the material and causing it to become brittle). Metal materials with excellent corrosion resistance and hydrogen embrittlement resistance are therefore needed. Such materials extend the service life of infrastructure such as bridges, roads, and tunnels as well as environment- and energy-related equipment. They also reduce the environmental burden of vehicles by reducing weight while improving safety. And finally, these materials will help make the hydrogen society a reality. There is also a growing need for antibacterial and antiviral surface treatments to foster a safe and secure living environment and reduce anxiety related to bacterial and viral infections. This also necessitates wear- and heat-resistant coatings to preserve and improve the service life and reliability of metal materials and components used in vehicles and machinery products. Surface treatments that exhibit properties such as high conductivity and strong bonding properties are needed as well.

To meet such varied and advanced needs and provide materials that ensure a safe and secure society, Kobe Steel is developing the following types of metal surface control technology:

(1) Corrosion and hydrogen embrittlement control technology to improve the service life and reliability of metals and reduce their surface reactivity
(2) High-function coating technology to improve the properties of metal materials by using surface treatments to create high-function surfaces

This paper introduces the current developments and future prospects related to corrosion and hydrogen embrittlement control technology and surface treatments for high-function coating technology.

1. Corrosion and hydrogen embrittlement control technology

1.1 Corrosion-resistant material design and corrosion prediction technology for a safe and secure society

A boom in the construction of societal infrastructure such as bridges, roads, and tunnels occurred in conjunction with a period of strong economic growth in Japan's history. These structures are now beginning to deteriorate, which entails major maintenance and restoration costs. As such, the demand for highly corrosion-resistant steels that can extend the service life of infrastructure and reduce its life cycle cost is expected to rise. Furthermore, the need to reduce the weight of vehicles and other transportation equipment to reduce CO_2 emissions is driving a trend toward stronger steel products. This entails unprecedented susceptibility to environmental embrittlement, corrosion fatigue, and delayed fracture, heightening the need to develop steels with exceptional resistance to corrosion and environmental embrittlement.

Kobe Steel has commercialized many highly corrosion-resistant steels to meet various environmental embrittlement needs, such as weathering steels for bridges,[1] corrosion-resistant steels for shipbuilding,[2] and high-strength suspension spring steels for vehicles.[3] Developing highly corrosion-resistant steel requires accurate evaluation and control of the corrosion phenomena governed by the composition, microstructure, and formation process of rust, a product of reactions occurring at the surface of a material. One approach Kobe Steel is taking delves into the mechanism of rust formation. High-strength suspension spring steel for vehicles constitutes one such example, wherein corrosion fatigue originating from localized corrosion was a major challenge. We developed a technique to suppress localized corrosion by adding alloying elements to the steel to transform the rust into highly corrosion-resistant, amorphous rust. In doing so, Kobe Steel developed high-strength suspension springs.[3] Notably, weathering steels have been put to practical use in bridges.[1), 4] These steels have been made rust resistant through the addition of small amounts of corrosion-resistant elements such as Cr, Cu, Ni, and Ti.

Kobe Steel is developing materials with more than twice the corrosion resistance of conventional materials in support of infrastructure with an ultra-long service life for a safe, secure, and sustainable society. The company is also developing rust microstructure analysis technology that uses high-brilliance synchrotron radiation (SPring-8) and machine learning, as detailed in Section 1.1.1.

Furthermore, in order to achieve carbon neutrality by 2050, we will work to reduce CO_2 emissions from the coal-fired power plant with a total power generation scale of 2.7 million kW that we operate in Kobe City, by cofiring coal with low-carbon fuels such as biomass and ammonia. Section 1.1.2 covers Kobe Steel's efforts into advancing corrosion control and corrosion diagnostics technologies for use with low-carbon fuels to safeguard the stability of the power supply.

1.1.1 Development of rust microstructure analysis and rust formation prediction technologies in support of highly corrosion-resistant materials

Developing corrosion-resistant steels that have a long service life and contribute to a safe, secure, and sustainable society requires visualization of the microstructure of rust, which had never before been achieved. Necessary as well is to clarify the formation process of rust to precisely control rust composition and improve corrosion resistance. However, determining corrosion resistance lifespan necessitates extensive data regarding the microstructure of rust following decades of exposure to actual conditions, which is extremely difficult to accumulate.

Kobe Steel has therefore centered efforts around high-brilliance synchrotron radiation measurement, with characteristics such as high resolution, high throughput, and the ability to simultaneously use methodologies such as XRD (X-ray diffraction) and XAFS (X-ray absorption fine structure). We are using the large synchrotron radiation facility SPring-8 to build a database on the microstructure and formation process of rust and to study techniques to predict corrosion resistance lifespan. This section introduces some of our latest efforts.

Various models have been proposed to define the formation of rust,[5), 6] including amorphous rust, which is an intermediate stage before the crystallization of rust, including rust that forms under certain atmospheric conditions such as red rust (e.g., α-, β-, and γ-FeOOH) and black rust (Fe_3O_4). Most such models, including **Fig. 1**(a) of rust formation on carbon steel and Fig. 1(b) of rust formation on corrosion-resistant steel,[6), 7] are based on analyses of sections of rust formed by years or decades of atmospheric corrosion or by rigorous accelerated corrosion tests. There are very few examples of direct observation of the two-dimensional structure of rust, in particular of the formation process of amorphous rust, which yields high corrosion resistance.[8] Therefore, Kobe Steel used SPring-8 to develop synchrotron radiation measurement imaging technology capable of two-dimensional measurement and applied machine learning to hundreds of thousands of data points to visualize the detailed distribution within rust, including amorphous rust, for the first time ever.[7] **Fig. 2**(a) shows the crystalline distribution of each rust via XRD imaging, and Fig. 2(b) shows both the crystalline and amorphous distribution of each rust via XAFS imaging. These results shed light on the distribution of crystalline red rust and amorphous

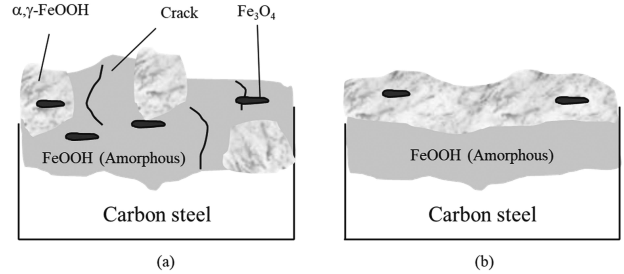

Fig. 1 Schematic representations of rust layer models on (a) plain carbon steel (b) corrosion-resistant steel

black rust and thus the formation of amorphous rust. Furthermore, we used machine learning to correlate the rust microstructure and formation process determined via synchrotron radiation measurement with data regarding the microstructure of the steel to predict the parameters of rust formation. The predicted results were verified to be in strong accord with the actual measurements (**Fig. 3**).[9)]

The use of high-strength materials and highly corrosion-resistant steels in critical infrastructure and equipment necessitates safe and secure corrosion diagnostics technology. Applicable infrastructure includes bridges, transportation equipment including vehicles, and equipment for the production, storage, and transportation of the alternative energy sources of hydrogen and ammonia. We will continue advancing rust analysis technology using synchrotron radiation and machine learning to develop predictive maintenance technology through corrosion diagnostics data.

1.1.2 Corrosion control technology to reduce CO_2 and ensure power supply stability

Equipment such as boilers and heat exchangers in biomass cofiring thermal power plants are exposed to a particularly adverse high-temperature corrosion environment, but the parameters of corrosion behavior in this environment have not been fully defined.[10)] Kobe Steel is developing a technique to predict high-temperature corrosion behavior in a biomass environment. Equipment preservation should preclude damage to ensure power supply stability. In this section, we introduce an example of evaluation of high-temperature corrosion in an environment that emulates biomass co-firing.

Fig. 4 shows a schematic diagram of a thermal power generation system as well as the typical corrosion environment in a boiler. The combustion area of a boiler (lower part of the figure) is a reducing atmosphere. It contains elements such as hydrogen sulfide, which causes hydrogen sulfide corrosion. The downstream side (upper part of the figure) contains an oxidizing atmosphere, in which water and SOx in the gas cause corrosion via oxidation. When the temperature of the gas decreases, the salt in the gas adheres to the surfaces of the heat exchanger and other equipment, causing severe localized molten salt-induced corrosion. Additionally, the chlorine content (which is high in biomass) gasifies and dissolves into the molten salt, generating highly corrosive molten iron chloride and

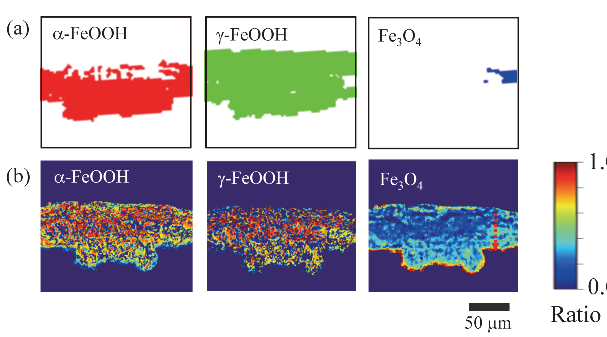

Fig. 2 Comparison of rust maps using synchrotron radiation (a) XRD imaging, (b) XAFS imaging (rust areas are extracted and graphed)

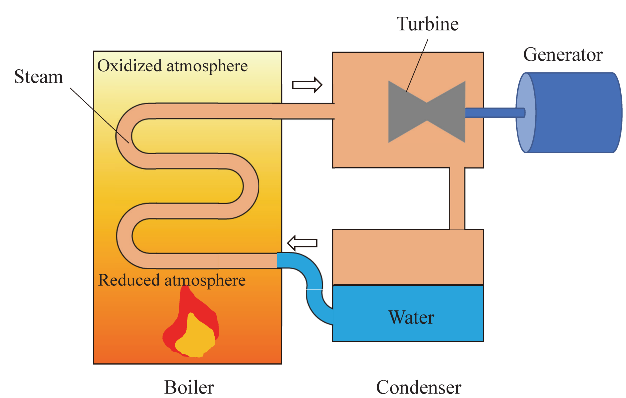

Fig. 4 Schematic diagram of boiler section of thermal power plant and corrosive atmosphere inside the boiler

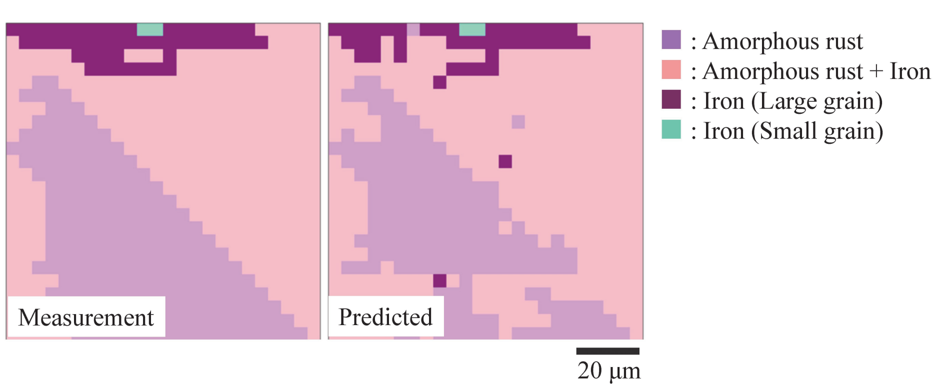

Fig. 3 Comparison of measured and predicted rust morphology after 24 hours (Estimation by machine learning from rust formation process and steel microstructure information)

thereby accelerating corrosion.

As an extreme example of molten salt-induced corrosion, the change in the degree and morphology of corrosion upon a substantial change in salt content are shown graphically and schematically in **Figs. 5** and **6**.[11] The green areas of the images in Fig. 5 are oxides hypothesized to have formed from corrosion. It can be seen that while there is almost no corrosion in the absence of salt, corrosion increases as the salt content increases. An increased salt content causes an oxide film with numerous superficial voids to form. Corrosion within the steel then propagates along the grain boundaries. As shown in Fig. 6, gaseous chlorine dissolves in the molten salt when the chlorine content of the gas increases. This generates iron chloride, which is highly corrosive and volatile. This molten salt quickly volatilizes, forming an oxide film with many voids and thus promoting corrosion within the steel.

Analyzing high-temperature corrosion behavior in an environment designed to emulate that present among biomass reveals the mechanism of corrosion. This in turn enables the development of countermeasures to prevent corrosion, including from corrosive fuel constituents, thereby ensuring power supply stability.

We will advance the high-brilliance synchrotron radiation measurement and machine learning practices described in Section 1.1.1 and develop capabilities for the direct observation of early-stage high-temperature corrosion behavior in the adverse environment of low-carbon fuel. We will also use our comprehensive corrosion database to establish predictive maintenance technology based on high-accuracy prediction of corrosion resistance lifespan, thereby reducing CO_2 and ensuring power supply stability.

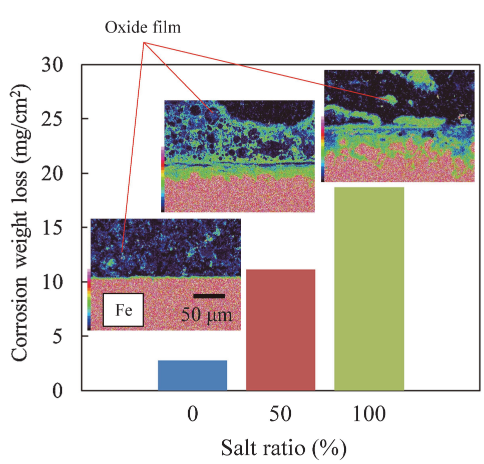

Fig. 5 Corrosion amount and corrosion structure change as ratio of salt content in high-chlorine environment

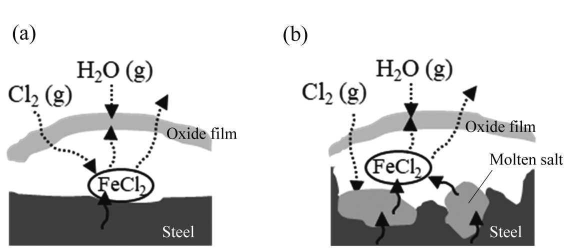

Fig. 6 Schematic diagrams of change in corrosion morphology with increasing salt content in gas
(a) low salt content, (b) high salt content

1.2 Hydrogen embrittlement-resistant materials and hydrogen embrittlement control technology to support high-strength materials and a hydrogen society

Materials with excellent hydrogen embrittlement resistance as well as technologies to control hydrogen embrittlement are necessary to reduce environmental burden. This is because such developments will enable the practical use of high-strength steels and thereby support a hydrogen society and reduce CO_2 emissions and material consumption.

The mechanism of hydrogen embrittlement begins with the penetration, accumulation, and dispersion of hydrogen from the environment. These phenomena are affected by the stress and strain distribution and the microstructure of the material, and they lead to crack initiation and propagation that in turn leads to fracture.[12] Deciphering the mechanism of hydrogen embrittlement and developing materials with excellent hydrogen embrittlement resistance require hydrogen evaluation techniques that account for the influencing factors of materials, the environment, and stress/strain. Challenges in understanding hydrogen embrittlement include quantifying trace hydrogen on the order of ppm, which causes hydrogen embrittlement; evaluating the complex changes in hydrogen distribution caused by stress and strain; and understanding how hydrogen diffuses easily even at room temperature, including how diffusion changes over time. Techniques to overcome these challenges must be developed. Kobe Steel has therefore been developing hydrogen evaluation technologies including technology for evaluating trace hydrogen in materials;[13] hydrogen embrittlement evaluation[14] and hydrogen distribution visualization technology[15), 16] to understand the effects of stress and strain; and in-situ hydrogen penetration measurement technology to determine parameters regarding the environment.[17] We are using these technologies to develop and commercialize high-strength steels such as steel for high-strength bolts as well as ultra-high-tensile strength steels, thereby ensuring safety and security in community development and manufacturing. Our company will continue advancing hydrogen embrittlement evaluation technology in support of a hydrogen society. It is essential to prevent hydrogen embrittlement in equipment that contains or uses hydrogen (pressurized hydrogen and liquid hydrogen tanks, hydrogen fuel cells, etc.), from production to transportation, storage, and use.

As described above, corrosion and hydrogen embrittlement control technology is a metal surface control technology that is intertwined with various disciplines such as electrochemistry, materials, and dynamics. Cutting-edge analytical techniques and computational science combine to form this important technology that is used in the KOBELCO Group's wide range of products and processes, including machinery, engineering, electric power, and materials such as steel, aluminum, and titanium. We support a safe and secure society by promoting research and development that meets the changing needs of society.

2. High-function coating technology via surface treatment

Surface treatment technology enhances materials and components via superficial high-function coatings that impart characteristics such as electrical conductivity, lubricity, coating adhesion, and resistance to wear, friction, heat, corrosion, and microbes. Surface treatments include plating, conversion coating, anodizing, thermal spraying, painting, and vapor phase deposition methods such as PVD (physical vapor deposition) and CVD (chemical vapor deposition). Kobe Steel has refined numerous surface treatment technologies, which have recently garnered interest for their ability to add substantial reliability and functionality to products after manufacturing. The KOBELCO Group possesses diverse, advanced material technologies for steel, aluminum, copper, titanium, welding consumables, and more. In conjunction with surface treatment technologies, these technologies solve societal challenges by enhancing the value of materials and machinery products.

Kobe Steel products use surface treatment technologies that combine electrochemistry and thin-film technologies. The resulting coatings exhibit various functions through layering, compounding, and composition control. Examples include the following: chromate-free surface-treated sheet steel with excellent corrosion resistance, coating performance, and workability using organic/inorganic composite coatings; KENIFINE™, a high-function proprietary alloy coating with exceptional antibacterial and antifungal properties; highly hydrophilic, corrosion-resistant, press-formable pre-coated aluminum fin stock via a multilayer coating; and PVD coating equipment and surface treatment technologies that achieve high durability, low wear, and a long service life via atomic/molecular layer deposition. These products create unique, high-function coatings using advanced surface treatment technology for precise control of surface characteristics.

Furthermore, we are making advancements in adhesive joining, which is attracting attention as a next-generation joining technology. For example, we are using cutting-edge analytical techniques and computational science to uncover the mechanisms behind adhesive strength at the interfaces of metal materials and to develop surface treatment technology that ensures long-term adhesive strength in metal materials. Specifically, we have discovered the mechanism by which enhanced chemical interaction at the interface between adhesive and metal materials generates adhesive strength[18), 19)] using hard X-ray photoelectron spectroscopy (HAXPES) via synchrotron radiation. We also used a unique hybrid quantum-classical simulation of molecular dynamics and first-principles calculations to reproduce at the molecular and atomic level a phenomenon that has been acknowledged for some time, which is that moisture reduces adhesive strength. This revealed the theoretical mechanism by which the adsorption of water at the adhesive interface inhibits chemical interaction, thereby reducing adhesive strength.[20)] These findings increase confidence in the adhesive joining of metal materials and will lead to the development of better products.

The technological development of fuel cell vehicles (FCVs) is fostering progress toward a carbon-neutral hydrogen society. Polymer electrolyte membrane fuel cells (PEMFC) contain hundreds of metal separators, each of which requires a surface treatment (pre-coat) that combines surface conductivity and corrosion resistance with press-forming capability. Kobe Steel developed a composite coating of nano-sized carbon and titanium oxide, including a roll-to-roll continuous coating process for titanium sheet coils, to create the world's first pre-coated separator material: nano-carbon composite coat (NC) titanium. These developments yield fuel cell separators with both electrical conductivity and corrosion resistance.[21)] NC titanium is detailed next.

Fig. 7 shows the cross-sectional structure of the NC coating. The NC coating has two primary constituents. One is titanium dioxide, which promotes adhesion to the titanium. The other is carbon, which provides a path for current flow to improve the titanium's surface conductivity.

Following is a description of how the NC coating is created. In a high-temperature environment at atmospheric pressure, the inward diffusion of oxygen causes an oxide film to grow from the surface of titanium to the inside of titanium.[22] However, below a certain low partial pressure of oxygen, titanium diffuses outward, and an oxide film grows on the surface.[23] The NC coating capitalizes on this outward oxidation phenomenon of titanium, causing a pre-coat of carbon particles on the surface of titanium to become incorporated into titanium dioxide. The favorable bonding properties of the titanium dioxide enable press forming without peeling of the NC coating. Moreover, the titanium substrate exposed by cracking of the NC coating exhibits the inherent corrosion resistance of titanium. We have thus established a surface treatment (pre-coat) capable of undergoing press forming. Stainless steel can be thought of as a competitor to titanium. However, pre-coating this material presents challenges because of the elution of iron ions[24), 25)] associated with pinholes in the coating and exposed areas of substrate, degrading the properties of the battery. The NC coating also improves productivity in separator manufacturing by eliminating the handling and surface treatment of each sheet after press forming.

NC titanium is the exclusive source of substrate for the separator of Toyota Motor Corporation's Mirai fuel-cell electric vehicle, which was released to market in December 2020. In the future, fuel cells are expected to be used not only in vehicles but also in the rail, shipbuilding, and aircraft sectors.

To achieve the requisite properties for a given application, the surface of a material must be controlled on a microscopic level via surface treatment technology. As such, Kobe Steel incorporates advanced analytical techniques and computational science to reveal pertinent mechanisms and develop technologies for highly reliable high-function coatings. The KOBELCO Group will continue using its distinctive diverse and advanced material technologies and surface treatment technologies to develop high-function materials that support societal needs and a safe and secure society.

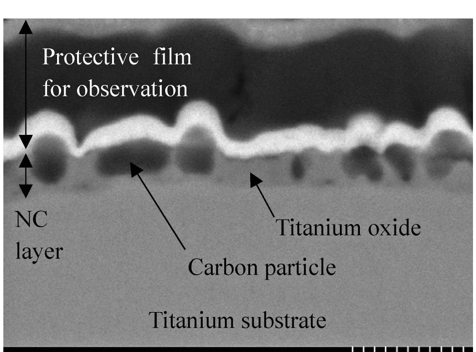

Fig. 7 Cross-sectional SEM image of NC titanium

Conclusions

This paper has outlined the metal surface control technologies that yield high-function surfaces. The longevity and safety of societal infrastructure and transportation equipment require maximum corrosion resistance of metal materials such as steel, aluminum alloys, copper alloys, and titanium. Additionally, highly accurate service life assessment technology is necessary to reduce maintenance costs. These points drive us at Kobe Steel to develop and refine technologies for preventing corrosion and hydrogen embrittlement. Surface treatment technology also plays an important role in the development of functional materials that meet all manner of societal needs. Kobe Steel will create added value by combining this technology with its various advanced material technologies. Our company will continue using metal surface control technology to create high-value-added materials. We will also continue using advanced analytical techniques and computational science based on sophisticated evaluation technologies to determine the reliability and safety of materials. Pursuing these objectives is one of the many ways we are ensuring a safe and secure society.

References

1) F. Yuse et al. R&D Kobe Steel Engineering Reports. 2015, Vol.65, No.1, pp.6-10.
2) S. Sakashita et al. R&D Kobe Steel Engineering Reports. 2008, Vol.58, No.1, pp.32-35.
3) T. Nakayama et al. R&D Kobe Steel Engineering Reports. 1997, Vol.47, No.2, pp.50-53.
4) T. Uno et al. The Japan Institute of Metals and Materials. 1971, Vol.10, No.5, pp.308-315.
5) U. R. Evans. Nature. 1965, Vol.206, pp.980-982.
6) T. Misawa et al. Corrosion Science. 1971, Vol.11, No.1, pp.35-48.
7) T. Ozawa. Denki Kagaku. 2022, Vol.90, No.1, pp.21-25.
8) S. Hara et al. The Journal of The Japan Institute of Metals and Materials. 2007, Vol.71, No.3, pp.346-353.
9) T. Ozawa et al. Proceedings of the 2020 Conference on Materials and Environments, 2020-5-20/22. Japan Society of Corrosion Engineering. 2020, s20c306.

10) H. P. Nielsen et al. Progress in Energy and Combustion Science. 2000, Vol.26, No.3, pp.283-298.
11) Y. Noguchi et al. Materials and Environments - Papers of the 68th Japan Conference on Materials and Environments. 2022, Vol.71, No.6, pp.183-186.
12) M. Nagumo. Fundamentals of Hydrogen Embrittlement. 1st edition. Uchida Rokakuho. 2008, p.219.
13) M. Kawamori et al. ISIJ Int. 2022, Vol.62, No.8, pp.1731-1740.
14) J. Kinugasa et al. ISIJ Int. 2021, Vol.61, No.4, pp.1071-1078.
15) M. Kawamori et al. ISIJ Int. 2021, Vol.61, No.4, pp.1159-1161.
16) J. Kinugasa et al. ISIJ Int. 2021, Vol.61, No.4, pp.1091-1098.
17) M. Kawamori et al. Corrosion Science. 2023, Vol.219, 111212.
18) Y. Takahashi et al. Journal of The Surface Finishing Society of Japan. 2021, Vol.71. No.4, pp.238-241.
19) Y. Takahashi et al. R&D Kobe Steel Engineering Reports. 2023, Vol.72, No.1, pp.130-136.
20) S. Ogata. FOCUS case studies. [Manufacturing] Phenomena Analysis of Adhesive Joining between Metal Materials). April 2022.
21) T. Choda. R&D Kobe Steel Engineering Reports. 2022, Vol.71, No.2, p.78.
22) K. Hauffe. Oxidation of metals. Plenum Press. Springer New York. 1965, p.217.
23) T. Sato et al. Ti-2007 Science & Technology. The Japan Institute of Metals and Materials. 2007, pp.1679-1682.
24) W. Li et al. Diamond Relate. Mate.2021. Vol.118, 108503.
25) Yu. A. Dobrovol'skii et al. Russian Journal of General Chemistry. 2007, Vol.77, pp.752-765.