Technical Report

In Situ and Dynamic Observation of Reactions by Synchrotron Radiation

Masao KIMURA*

Abstract

Synchrotron Radiation (SR), an X-ray beam which is generated using a high-power accelerator, has excellent characteristics of high brilliance, parallel beam, white beam, and pulse beam. We have utilized SR to investigate various materials and processes since 1987. One of the best advantages is that we can observe changes in structures of materials in real environments ("in situ") and real time-scale ("dynamic"). Furthermore, we can obtain not only the averaged information of the bulk material but also the unique information on (a) surface and/or interface in the depth of a nm-scale, (b) specific element, and (c) crystal information with a high accuracy. We show some of recent researches using developed observation techniques using SR.

1. Introduction

Multifunctional materials and sophisticated industrial processes require increasingly capable observation techniques to support further progress. It is especially important to improve our understanding of how a material may be altered by its processing and how it behaves in the environment in which it is used. One very versatile observation technique uses synchrotron radiation, which is an intense and well-collimated beam of X-ray photons.

The salient features of synchrotron radiation are: (1) outstanding luminance (10^3 to 10^6 times more intense than that from the X-ray equipment used in most laboratories), (2) naturally collimated beams, (3) extremely broad spectral range, from infrared to X-rays, and (4) short, precisely timed pulses (**Fig. 1**). The most striking characteristic of observations that use synchrotron radiation is that a material's structural changes can be observed *in situ* during a specific reaction under conditions closely resembling the actual process or environment of interest, and on a time-scale that can resolve fine details of the process (dynamic observation). To make the most of these advantages, we have developed special X-ray transparent cells capable of reproducing specific reaction conditions. Then we performed *in situ* observations on materials in the cells, using various advanced analytical techniques and synchrotron radiation to clarify the reaction mechanisms of several material systems.

Using the outstanding characteristics of synchrotron radiation makes it possible to obtain not only general information on the structure of bulk materials, but also (a) information on the structure of the material surfaces and interfaces in nm-scale regions, (b) selective information about the structure of specific elements, and (c) accu-
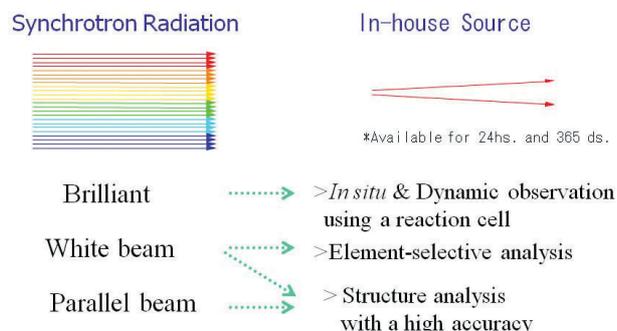

Fig. 1 Characteristics of synchrotron radiation and in-house X-ray source

* Senior Researcher, D.Eng., Materials Charcterization Research Lab., Advanced Technology Research Laboratories
  20-1, Shintomi, Futtsu, Chiba

rate information about the structure of crystals such as strain and/or defects. Dynamic and *in situ* observations of those structures under different reaction conditions have yielded new knowledge that was virtually unobtainable with conventional observation techniques carried out to investigate the characteristics of "quenched" materials.

Due to space limitations, this paper describes only the essence of some representative examples of the research our study group has carried out. For a detailed description of our research, the reader is invited to examine the original publications referred to.

2. Observation of High-Temperature Solid Diffusion —Alloying in Hot-Dip Galvanizing [1, 2]

2.1 Method of *in situ* observation at high temperatures

In order to conduct an "*in situ* and dynamic" observation of changes in crystal structure using the X-ray diffraction method, it is necessary to observe diffracted X-rays, or the Debye-Scherrer ring (D-S ring) over a wide range of scattering angles. Therefore, instead of the conventional method in which a detector scans a wide region of scattering angle, a linear (one-dimensional) or planar (two-dimensional) array of X-ray detectors is used.

We developed a new analytical technique to take advantage of the excellent luminance and energy continuum of synchrotron radiation (**Fig. 2**)[1, 2]. An image plate (IP), which is a two-dimensional detector, is scanned across the back of a slit that is parallel to the diffraction plane formed by the incident X-ray and diffracted X-rays. Scanning the IP continuously records the changes in X-ray diffraction patterns (part of the D-S ring) in different positions in the IP corresponding to different times: t_1, t_2, t_3... (Fig. 2(a)). By controlling the IP scanning speed, it is possible to achieve any time resolution and sensitivity desired (typical time resolution is on the order of several seconds). A specimen in the form of a plate is rapidly heated by an electric heater. Minimizing the effects of thermal expansion of

the specimen on the displacement from the X-ray beam is an important factor in high-temperature X-ray diffraction, so to deal with thermal expansion we developed a strain-relieving mechanism for the heater support electrodes.

2.2 Alloying observed during hot-dip galvanizing

Alloyed, hot-dip galvanized steel sheet is used in many applications, such as in the auto industry. A steel sheet is dipped into a hot zinc bath, the zinc is wiped off to achieve the prescribed coating weight, and the steel sheet is heated in an alloying furnace in which a Fe-Zn alloying reaction takes place. This Fe-Zn alloying reaction plays an important role in securing the quality and performance required of the steel sheet, so we attempted to observe it in a hot, open-air atmosphere simulating the actual processing conditions.

To measure the influence of the additional element: phosphorus (P) in the steel on the alloying reaction, we studied the difference between pure iron (specimen name: FE) and pure iron with a very small amount of phosphorus added (specimen name: FEP, P = 0.09 wt%). In the experiment, specimens with a measured amount of Zn deposited were heated up to $T = 733$ K, and we dynamically observed the change in X-ray diffraction patterns during the alloying reaction. By quantitatively analyzing the changes in diffraction intensity as recorded on the IP, we could clarify the progressive change in the proportion of different phases on the surface of each specimen (**Fig. 3** (a)). The following alloying reaction (Fig. 3 (b)) that takes place in the surface layer depends strongly on the addition of a very small amount of P.

η (Zn) → Melting → Solidification → ζ → δ → $\Gamma 1$
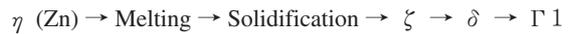
It was clearly confirmed that (1) the addition of a very small amount of P increases the incubation time, or the time from the melting of the Zn to the onset of the alloying reaction (the formation of the ζ phase), and that (2) the timing of the formation of the δ phase—an intermetallic compound of high Fe concentration—re-
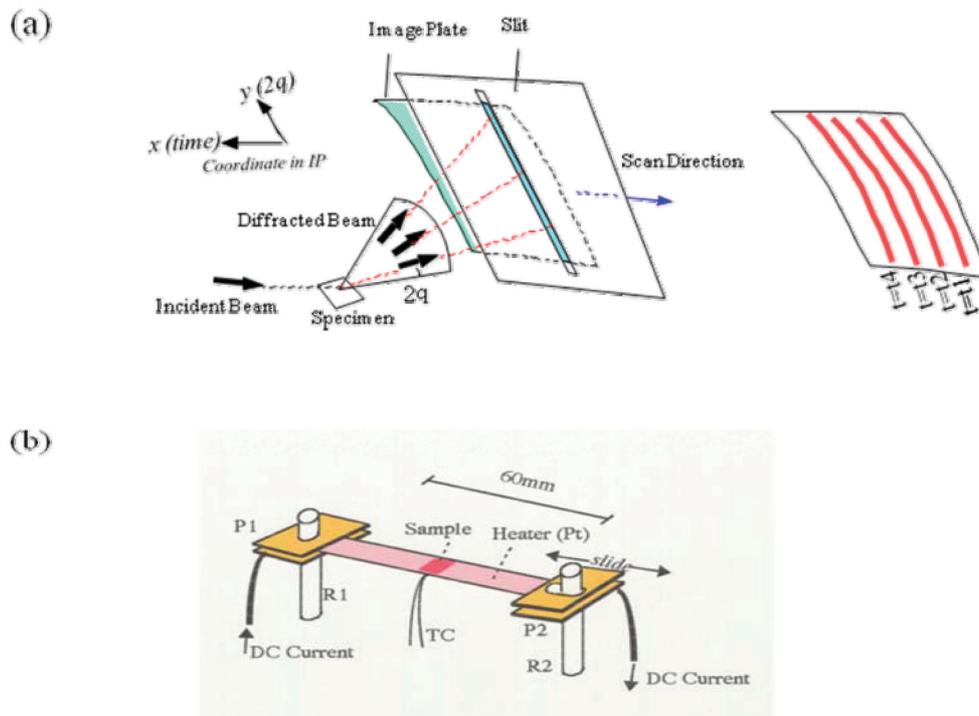
Fig. 2 Schematic diagram of the developed system
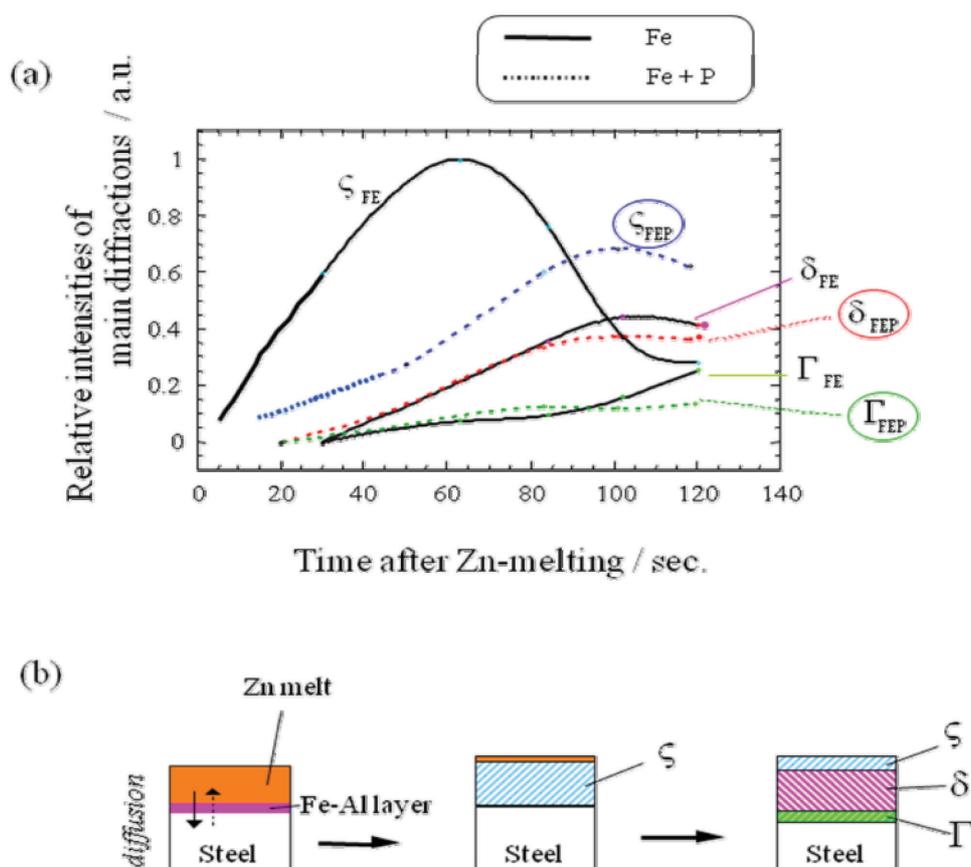**(a) X-ray measurements geometry and (b) the heating system[1, 2]**

Fig. 3 Results of in situ observation
(a) Change of relative intensities of diffractions for phases in the specimens FE and FEP, which was obtained by in situ X-ray diffraction, and (b) the schematic diagram of the reaction

mains unchanged.

2.3 Summary

The technique that we developed for *in situ* and dynamic observation under high temperatures is applicable to various kinds of materials. For example, it can be used to directly obtain kinetic information on reactions taking place at high temperatures or to observe changes in crystalline texture. Following our research, studies using similar techniques have been carried out by other research organizations. In the future, the applicability our technique, which takes advantage of the precise choice of wavelength that synchrotron radiation makes possible, will be expanded to cover a depth-sensitive analysis that includes information on X-ray penetration depth, and an element-sensitive analysis that uses abnormal X-ray scattering. At present, on the basis of the above technique, we are developing a new "*in situ* and dynamic" observation technique that employs a real-time, two-dimensional detector replacing an IP.[3]

3. Atomic Structure of nm-scale Layers on a Metal Surface—Evaluation of an Oxide Film on Titanium Surface [4]

3.1 Observing the structure of a nm-scale layer on a metal surface

The surface layer on metal within several (up to tens of) nanometers in depth and/or the interface of the layer and metal frequently differs in atomic state and structure from the bulk. An X-ray diffrac-

tion method of high precision has been widely used in the analysis of bulk structures. However, since X-rays penetrate deeper into a material (on the μ m order) than beams of electrons or ions, that method has been limited to analyzing the bulk material, when a conventional X-ray source is used. Synchrotron irradiation using evanescent waves can solve this problem and produce a precise analysis of the surface structure on the nm order in depth.

The refractive index of X-rays in general solid substances is slightly smaller than 1, so when an X-ray encounters a smooth solid surface at an extremely small angle, it is totally reflected at the surface. When that happens, only a very small proportion of the X-ray enters the solid interior (**Fig. 4**). The X-ray that enters the solid interior is called an "evanescent wave". Its maximum intensity is at the surface of the specimen, and it 'evanesces' (i.e., is attenuated) exponentially as it penetrates more deeply into the specimen. The typical penetration depth, where the intensity decays by a factor of 1/e, is *ca.* 10 atomic layers. Thus the evanescent wave is an X-ray wave that only exists locally near the specimen surface, and can act as a selective probe for the surface region on the nm order in depth. By observing its diffraction, fluorescence and X-ray absorption fine structure (XAFS)[5] caused by an evanescent wave, it is possible to obtain information at various depths in the near-surface region: from the top few, up to 10 atomic layers deep.[6] The diffraction technique that uses an evanescent wave is called grazing incidence X-ray scattering (GIXS).[7]
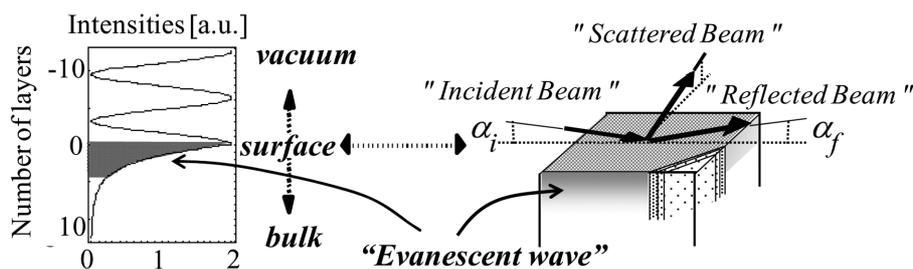
Fig. 4 When a specimen is irradiated by an X-ray beam with a grazing-incidence angle (α_i) as small as the critical angle (α_c) of the surface (right), the X-ray beam was located only near the surface (left), which is called "evanescent wave". The scattered and reflected beams contain information on the surface as small as a few atomic layers.

3.2 Anti-discoloration treatment and surface structure of titanium [4]

With its light weight and excellent corrosion resistance, titanium is widely used as a structural material for aircraft, chemical plants, etc. and as a building material that can display varied and decorative surface colors. The corrosion resistance and decorative coloration of titanium are attributable to the natural formation of a surface layer of titanium oxide (passive-state film) several nm thick (up to tens of nm), which can be artificially formed by anodic oxidation of a titanium surface.

When titanium with an anodic-oxidized surface is exposed to a severe environment for a prolonged period, its surface color may change. This discoloration is due to interference effects when the surface layer increases slightly in thickness. Titanium as an exterior material has sufficient corrosion resistance. However, since surface discoloration can impair its decorative effect, we investigated the cause of discoloration and studied ways to prevent it.

First, we analyzed the change in chemical composition with depth, using conventional surface techniques such as Glow Discharge Spectroscopy (GDS) and Auger Electron Spectroscopy (AES). It was found that TiC within the titanium substrate had an adverse effect on resistance to discoloration. However, it also turned out that titanium sheets having the same low TiC concentration displayed different discoloration resistance depending on the conditions used for anodic oxidation, suggesting that the structure of the surface layer would also significantly influence its resistance to discoloration. With conventional X-ray diffraction it is difficult to evaluate the structure of a film with low crystallinity that is tens of nm in thickness. Therefore, we attempted to evaluate it using the GIXS method explained above.

Two titanium specimens were prepared using different anodic oxidation voltages (V) —12.5 V for one specimen (S_{low}) and 22.0 V for the other specimen (S_{high}). The specimens acquired a similar color tone (gold) but differed in film thickness (26 nm vs. 296 nm). Considering that it was the topmost region of the oxide film that would influence the resistance to discoloration most, we measured the diffraction intensity of the X-ray evanescent wave in each specimen by precisely controlling the X-ray angle of incidence (α_i) on the specimen surface, retaining α_i close to the angle of total reflection and controlling the X-ray penetration depth at 10 nm. Initially, the X-ray reflectivity was measured. Next, the intensity of the scattered X-ray was measured with α_i kept near the angle of total reflection and with the 2θ scanning plane kept within a plane perpendicular to the specimen surface. In order to cope with the deterioration in 2θ angular resolution caused by the widening of the irradiation area on the specimen surface, we used a solar slit to limit the angle of divergence.

Fig. 5 shows examples of diffraction patterns obtained by the GIXS method. Despite the fact that the angle α_i was kept smaller than the critical angle (α_c) for titanium/titanium oxide ($\alpha_i < \alpha_c$), intense peaks of diffraction from the titanium substrate were observed in the diffraction patterns. In the diffraction patterns, a broad peak, though low in intensity, could be clearly observed at an angle near 2θ = 10 - 25 degrees. This broad peak was considered to have come from the top of the titanium oxide layer, so we attempted to evaluate its structure by Fourier transform to obtain the atomic correlation in the film.[8] The results suggested that both specimens, S_{low} and S_{high}, had a structure resembling that of anatase (**Fig. 6**).

The two specimens were widely different in crystallinity and the crystal domain size of specimen S_{low} was about twice that of specimen S_{high}. The crystal domains in the thicker film, formed using a higher voltage for anodic oxidation, were smaller in size. This is likely because the oxide film formed during anodic oxidation is chemically metastable as compared with thermally formed oxide film, and the domain size and defect structure of the resulting crystals depend largely on the applied voltage.

3.3 Summary

The newly developed technique has been widely used to evaluate not only titanium but also the surface structures of various types of metals, including the passive film on iron,[8] and the stress at the interface of films. The technique has revealed important information
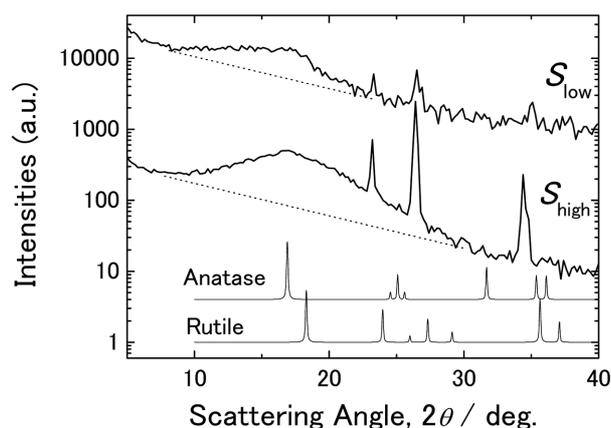

Fig. 5 Diffraction patterns of specimens by retaining α_i = 0.18deg., which corresponds to keeping the penetration depth around 10 nm. Dotted lines show backgrounds. Solid lines below show calculated X-ray diffraction patterns for anatase- and rutile-type of TiO_2 for the same X-ray energy as used for measurements.
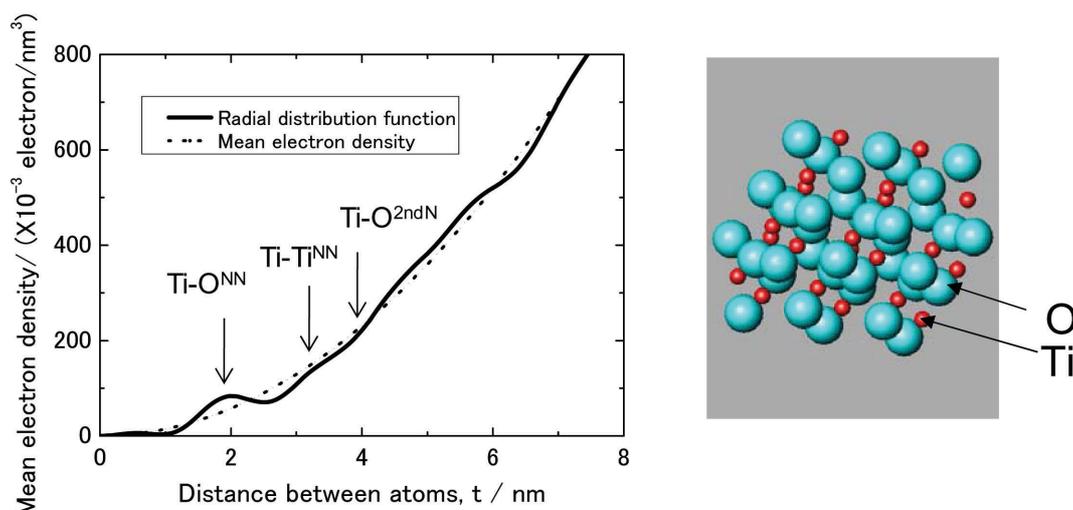
Fig. 6 Radial distribution function of specimen: S_{low} (left), and a structure model of anatase-type of TiO_2 phase (right)

about the changes in surface conditions (discoloration, corrosion, etc.) of materials in the environment in which they are used, and about the relationship between the surface structure and the manufacturing process. In addition, the technique has played a vital role in clarifying fundamental physical phenomena, such as the surface phase transition in intermetallic compounds,[9, 10] the surface melting of Si,[11] and the evaluation of nano-particle/Si substrate stress.[12]

4. Reaction at a Liquid/Solid Interface—Corrosion of Steel

Many important phenomena occur at the interface between the liquid and solid phases of materials, such as corrosion, battery chemistry and catalytic reactions. It is difficult to quench a reaction at a liquid/solid interface, so clarifying the mechanism of the reaction requires *in situ* and dynamic observation of the reaction as it happens. We have performed atomic-level observation of a reaction between liquid and solid phases using synchrotron radiation to reveal the mechanism of the corrosion of steel, which will be briefly described here, as we have already reported in detail elsewhere[13].

Clarifying the mechanism of corrosion in terms of reactions at a liquid/solid interface requires *in situ* and dynamic observation of the elemental concentrations and atomic structures in the specific solution ("liquid side" of the interface) under the conditions in which the diffusion and electrochemical reactions ordinarily take place. To that end, we developed a new observation method applying the XAFS technique, using synchrotron radiation. The XAFS technique is a structural analysis method based on the principle that a minute change in X-ray absorption near a particular energy reflects the local atomic arrangements around the atom absorbing the X-ray.[5] In XAFS, long-range order is not required for the specimen, and structural information is obtained from a measured spectrum by a simple and direct analysis. For example, in an acid solution near a stainless steel sheet, we could clearly observe differences in the structure of metal ions as a function of the distance from the interface (**Fig. 7**)[14-16].

To understand the mechanism of corrosion, it is essential to observe the changes on the "solid side" as well as on the "liquid side" near the interface of the liquid and solid phases. As mentioned above, synchrotron radiation can provide us with information also about a specific element in the corrosion products formed in the solid, which
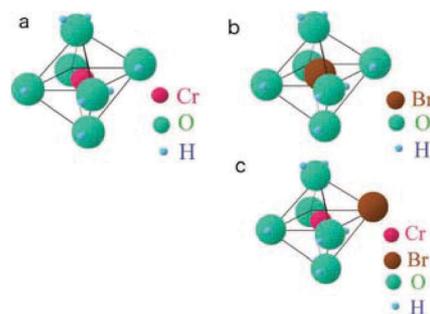

Fig. 7 Atomic configuration of chemical species in the solution of 1M LiBr, which was measured at different distances from the interface of the solution and a sheet of stainless steel.

gives us a fundamental understanding of the effect of alloying elements on corrosion. This approach was applied to the low-alloy corrosion-resistant steel otherwise called weathering steel,[17] in which the addition of 1 mass% or less of Cu/Cr to the steel improves its weathering performance (i.e., its corrosion resistance in open air). Previously, the protective mechanism was widely believed to be the formation of a dense layer of rust on the surface over several years of weather exposure, which limited the penetration of oxygen and water into metal.[18-20]

However, the reason why the addition of trace elements makes the rust layer dense was unknown. Using various techniques including synchrotron radiation we could directly observe the reaction in which the colloidal rust that forms in the early stages of corrosion becomes a crystalline rust (crystal size: several nm) after drying. Then, from the change in atomic configuration in the rust, we could reveal the effect of additional elements in detail. **Fig. 8** shows the mechanism of the reaction revealed by our *in situ* and dynamic observations using synchrotron radiation.[21, 22] Based on these observations, we proposed "various scale analyses to create functioning corrosion products." [23]
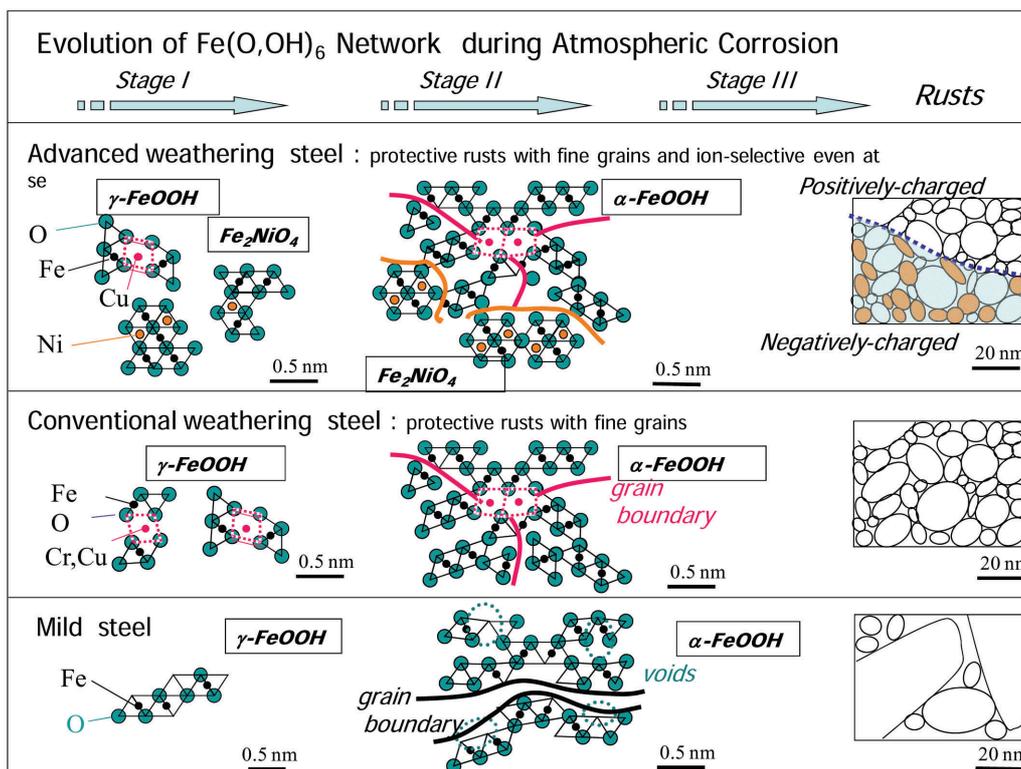
Fig. 8 Schematic diagram of evolution of the Fe(O,OH)$_6$ network in rust formed on the advanced watering (top), conventional weathering (middle), and mild steels (bottom)

5. Reaction Initiated by Change in a Gas Atmosphere —Redox Reactions on an Automotive Emission Control Catalyst [24)]

5.1 *In situ* and dynamic observation of reactions initiated by change in a gas atmosphere

Changes in the structure of a material caused by its reaction with the surrounding gas play important roles in showing catalytic performance. Many catalytic reactions take place quickly, so clarifying their mechanisms requires *in situ* and dynamic observation in the environment in which they actually take place.

In those reaction systems, the size of crystals of the metallic elements that give the material catalytic characteristics are as small as several nm, and in many cases their crystallinity is low. Therefore, we focused our attention on the XAFS technique, which permits analysis of the structure of the targeted metallic element even under these conditions. To obtain an XAFS spectrum in a short time, we used a method called the dispersive XAFS technique (DXAFS)[25, 26]. In this method, "white" X-rays (X-rays with a wide range of energies) irradiate the specimen at a diverged angle that differs as a function of their energy. The intensities of the X-rays that pass through the specimen are simultaneously measured by a linear detector. This has made it possible to obtain an XAFS spectrum in tens of ms without energy scanning.

By analyzing the XAFS spectrum, it is possible to obtain quantitative information about a targeted element, specifically: (a) its valence, and (b) the local atomic arrangement around the neighboring atoms (distance, coordination number, atomic structure).

5.2 Observing redox reactions of the catalyst performing automotive emission control [24)]

From the standpoint of reducing environmental impact, it is es-sential to purify exhaust fumes that contain NO_x, SO_x, CO, etc, and to do so efficiently. This requires the development of inexpensive high-performance catalysts with long service lives. However, atomic-level observation of the behavior of a catalyst in its actual environment has been limited because of experimental difficulties. This has impeded the development of efficient catalysts.

A Pd/Fe-O based catalyst has been developed that can control the undesirable components of automobile exhaust using significantly smaller amounts of precious metals than catalysts currently in use. The air-fuel ratio in the exhaust gas from the engine fluctuates around a theoretical value as engine conditions change, so the gaseous environment of the catalyst alternates between a fuel-rich reducing atmosphere and a fuel-lean oxidizing atmosphere. Using the DXAFS technique, we observed change in palladium states during the reduction-oxidation (redox) cycles.

In the experiment, we set the specimen at the focal point of the wavelength-dispersed X-rays obtained by irradiating a curved crystal surface with wide white X-rays, and simultaneously measured the X-rays passed through the specimen with a linear detector. By using reaction cells to control the gas mixture and temperature, we could measure the XAFS spectrum in a short time (tens of ms) without energy-scanning, which is required in conventional XAFS measurements.

Fig. 9 shows the change in XAFS spectrum around the Pd-K absorption edge when the gas atmosphere was changed from 20 vol%O$_2$-He to 4 vol%H$_2$-He at T = 673 K. It was clearly observed that the Pd in the catalyst was in an oxidized state (Pd (II)) close to PdO in the oxidizing atmosphere but that it changed into metallic clusters (Pd (0)) shortly (t = 0 to 2 s) after the reducing gas was introduced. We carried out a similar observation with alternating gas
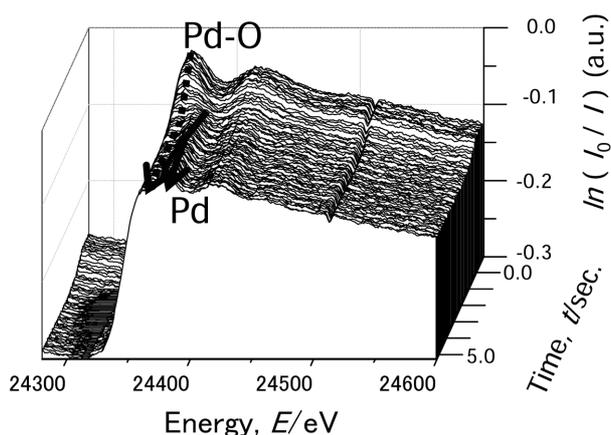
Fig. 9 A part of change of XANES spectra from the state of Pd-O to Pd, when the gas was changed from 20 vol%O_2-He to 4% H_2/He at T = 673 K.[24]
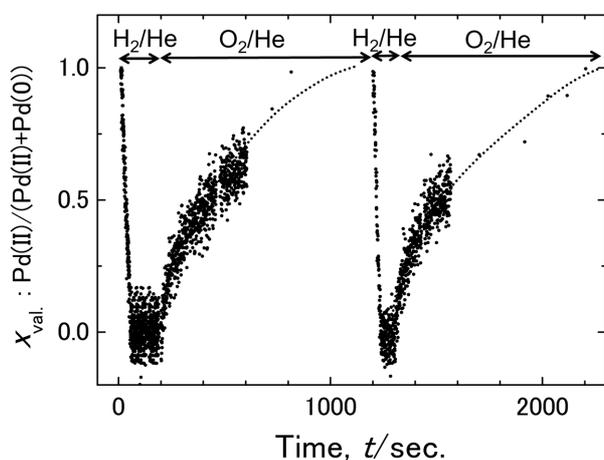

Fig. 10 Time-evolution of the atomic fraction of Pd (II) by *in situ* XAFS measurements during redox reactions.[24]

mixtures to observe the time-scale of the change in the proportion of Pd (II) ($x_{val.}$ = Pd (II)/ (Pd(II) + Pd (0)) (**Fig. 10**). We found that (a) Pd metallic clusters appear and disappear as the gas atmosphere alternates, and (b) oxygen diffusion from and into the oxide support is synchronized with the change of Pd states. Those findings help clarify the mechanisms of how the newly developed Pd/Fe-O based catalyst shows high performance in spite of the reduction of the amounts of precious metals in the catalyst.

5.3 Summary

The "*in situ* and dynamic observation technique" can be applied not only to catalytic reactions but also to various other kinds of reactions. We are applying the method to observe various reaction systems, including the process of Cu precipitation in Cu-added steel and the process of iron ore reduction.[27]

6. Conclusion

We have introduced typical representative applications of the *in situ* and dynamic observation of various reactions using synchrotron radiation, carried out at the Nippon Steel Corporation. As materials and processes have become more diverse and sophisticated, the need has increased for analytical techniques to become correspondingly

diverse and sophisticated. Both at home and abroad, more and more synchrotron radiation facilities have been constructed and the number of users of those facilities is increasing rapidly. Synchrotron radiation is an excellent X-ray source. In order to develop new analytical techniques that make the most effective use of synchrotron radiation, however, it is important to fully appreciate the current need for new materials and processes, and to develop new analytical techniques to observe the key phenomena on which they rely. Taking advantage of the synchrotron radiation technology that Nippon Steel has accumulated over more than 20 years of research and development, we intend to continue studying materials and processes using synchrotron radiation. This will help us to maintain Nippon Steel's leadership in the research and development of cutting-edge processes and materials.

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Masao KIMURA
Senior Researcher, D.Eng.,
Materials Charcterization Research Lab.,
Advanced Technology Research Laboratories
20-1, Shintomi, Futtsu, Chiba