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Technical Review

Approaches for Fundamental Principles 4: *In situ* Observation of Processes and Reactions by Synchrotron Radiation

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1. Introduction

In the steel manufacturing process, the desired properties are imparted to the steel basically by means of: (a) material design using alloying elements, and (b) various types of thermomechanical treatment utilizing phase transformations. There, such reactions as the transformation and grain growth are, in many cases, controlled by changing process conditions such as temperature, gas atmosphere, and mechanical deformation. It is expected that the knowledge obtained by *in situ* observations of those reactions under actual process conditions will help to optimize the manufacturing conditions and develop new processes.

On the other hand, the steel material manufactured is required to show various properties such as strength, workability, corrosion resistance, magnetic property in various environmental conditions. In order to make the best of them, it is important to clarify the mechanisms of how these properties are performed by implementing *in situ* observations of these phenomena and reactions in its actual environments.

As a means of *in situ* observation of various processes/reactions, we have been focusing on an analytical and scientific approach utilizing a very powerful, high-grade X-ray source called synchrotron radiation. In 1982, when the former Ministry of Education brought into operation the photon factory (PF)—Japan's first full-scale synchrotron radiation facility—at the High Energy Accelerator Research Organization (KEK), Nippon Steel Corporation focused on the possibility of applying synchrotron radiation in research and development on steel materials. Several years later, the company launched exploratory research with KEK/PF.

In those days, the application of synchrotron radiation was found mostly in the fields of fundamental physics and semiconductors. Thus, it was rather challenging to utilize synchrotron radiation in scientific materials research on steel and other metals and inorganic substances. In view of the absence of precedents round the world, Nippon Steel

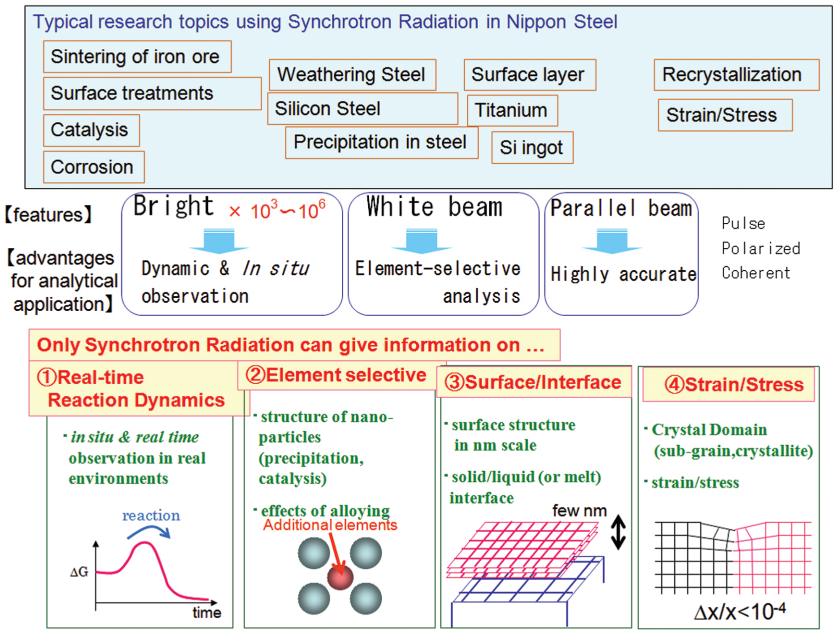

Fig. 1 Characteristics of synchrotron radiation and its application in Nippon Steel

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began by accumulating the technology to make most effective use of synchrotron radiation. Then, the company proceeded, on a step-by-step basis, with the development of technology for *in situ* observation of phenomena characteristic of steel materials and the elucidation of nano-level phenomena. In this manner, the company has conducted its research for almost a quarter of a century. As a result, Nippon Steel has come up with unique new techniques for *in situ* observation that help clarify various phenomena affecting steels and other metallic materials. In addition, the company has applied those *in situ* observation techniques to design various new materials and develop new processes (**Fig. 1**). We are proud that the company's abovementioned achievements have come to attract growing attention from academic societies, etc. at home and abroad.

In this technical review, we present an outline of the research fields utilizing synchrotron radiation, and introduce three topics selected from our research aimed at clarifying various phenomena through *in situ* observation of processes and reactions. For details, the reader is requested to refer to the appropriate Shinnittetsu Giho,[1,2] as well as other articles in scientific journals.[3,4]

2. *In situ* Observation using Synchrotron Radiation across Multiple Fields

The major characteristics of synchrotron radiation, which is an excellent X-ray source, are: (a) high luminance (10^3 ~ 10^6 times that of ordinary X-ray sources used in laboratories), (b) parallel beams, (c) white beams, and (d) pulsed light (Fig. 1).[2]

Taking advantage of those characteristics of synchrotron radiation, Nippon Steel has been tackling research and development on *in situ* observation technology for studying materials and processes. There are two points in the above R&D effort. They are: (1) finding a level in the hierarchical structure whose information is to be used as the key for manifestation of material functions (**Fig. 2**) and (2) developing a new method of structural analysis for *in situ* observation of the changes in structure at that hierarchical level in the actual environment.

Therefore, with the cooperation of experts in materials and processes, the company has developed special reaction cell systems to reproduce various processes/reactions and has conducted pioneering analytical research with the aid of advanced methods of structural analysis.

As a result: (1) It has become possible to implement, on a real-time basis, *in situ* observation of various processes/reactions in an environment close to the actual one, and (2) The company has succeeded in obtaining such information that could not be obtained with conventional analytical techniques, like the structure/state of a specific element in a material, the structures of material surface and interface (~ nm region), and precise strain distribution (Fig. 1).

Examples of our *in situ* observation of manufacturing processes include: observation of the secondary recrystallization process of electrical steel,[5] observation of a galvanized sheet manufacturing process,[6] and clarification of the mechanism of anti-discoloration treatment of titanium,[7] etc. As examples of *in situ* observation of reactions in the actual working environment, there are: clarification of the mechanism of atmospheric corrosion resistance of weathering steel,[4, 8-10] observation of pitting reactions in stainless steel,[11] evaluation of stresses in steel materials,[12] etc. In recent years, in the face of various environmental problems, the company has also been implementing *in situ* observation of catalytic reactions,[13] and tackling issues relating to raw materials/fuels and ironmaking.

3. Study of Materials/Processes based on Clarification of Phenomena

In this section, we introduce only a few representative examples in which knowledge obtained from *in situ* observations has been used in the study of materials and processes.

3.1 Electrical steel[5]

The magnetization of iron depends on its crystal orientation (magnetic anisotropy). Electrical steel is a material whose magnetic property is dramatically improved by controlling the orientation of iron grains in the steel. In its manufacturing process, the process in which grains exceeding 10 mm in size are formed from grains tens of microns in size (secondary recrystallization) is especially important. In this particular process, arrangements are made so that a specific crystal orientation (Goss orientation {110} <001>) is preferentially formed

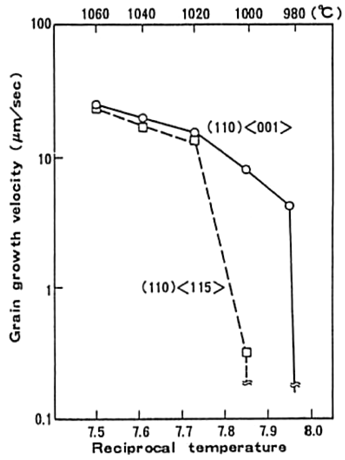

Fig.3 Effect of temperature onthe grain growth velocity[5]

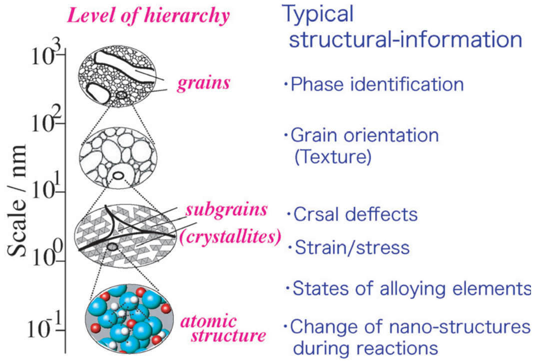

Fig. 2 Hierarchy of materials and typical structural information of each level

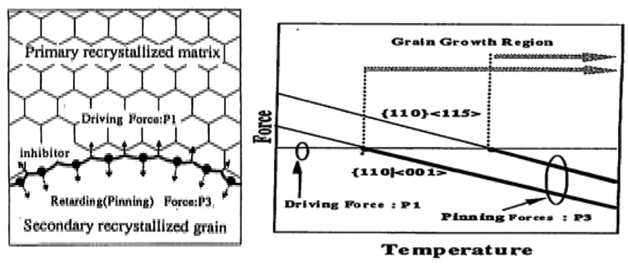

Fig. 4 Schematic diagram of the mechanism of secondary recrystallization[5]

in the steel.

By implementing real-time, *in situ* observation of the process in which secondary recrystallized grains grow by consuming primary recrystallized grains, we found that the velocity of grain growth differed noticeably according to the grain orientation and temperature (**Fig. 3**). As a result, we could propose a reaction model for secondary recrystallization (**Fig. 4**), which helped develop a new manufacturing process with due consideration given to the reaction mechanisms involved.

3.2 Weathering steel[4, 8-10]

Corrosion-resistant, low-alloy steel called weathering steel demonstrates improved weather resistance (i.e. resistance to corrosion in open air) when it has a very small amount (1 mass% or less) of Cu or Cr added. The reason for this is thought to be as follows. On the surface of weathering steel sheet used outdoors, a dense layer of rust is formed over several years, whereby the amounts of oxygen and moisture which enter the matrix decrease and the rate of corrosion declines. However, the reason why the layer of rust formed on the steel surface becomes so dense through the addition of a small amount of a certain element had been unknown for more than thirty years. Therefore, we directly observed the reaction whereby colloidal rust that formed at the early stage of corrosion turned into fine crystalline rust (grain size: several nm) after drying. As a result, from the changes in atomic structure observed, we could clarify the influence of the element added in the above reaction (**Fig. 5**).[4, 8-10]

On the basis of the above reaction mechanisms, we proposed design guidelines for materials with good resistance to atmospheric corrosion as follows: (a) Prevent the decline in pH at the interface between the matrix and corrosion products formed (this is important from the standpoint of colloid science), and (b) Prevent the diffusion of H^+, Cl^- and other ions into the interface (**Fig. 6**).[4)] Those concepts were first realized in the advanced high-Ni weathering steel (NAWTEN®) the company developed subsequently. Together with the later development of a comprehensive application technology, including life prediction techniques and maintenance/repair techniques,[14, 15)] it is now possible for the company to offer technology that supports the social infrastructure through reduced environmental impact.

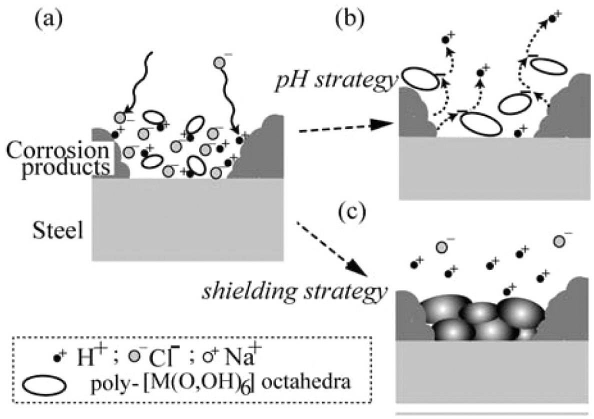

Fig. 6 Schematic illustration of proposed strategies for improvement of atmospheric corrosion

3.3 Catalysts for purifying exhaust fumes[13)]

Efficiently purifying engine exhaust fumes containing NO_x, SO_x, and CO, etc. is an important technology to reduce their environmental impact. To that end, it is important to develop catalysts which meet these conditions: low cost, high efficiency, and long life. On the other hand, implementing an atomic-level observation of the behavior of a catalyst in the actual environment requires a sophisticated observation technique. Therefore, knowledge of catalyst behavior is still insufficient. This has been one of the obstacles to efficient development of catalysts.

Concerning the process in which the state of the active noble metal in the catalyst changes according to the change in composition of engine exhaust fumes, Nippon Steel succeeded in performing *in situ* observation of the process within tens of milliseconds (**Fig. 7**).[13)] As a result, the company could obtain knowledge about the reaction mechanisms from the standpoint of chemical kinetics.

On the basis of those mechanisms, we proposed guidelines for the design of a catalyst capable of efficiently purifying exhaust fumes

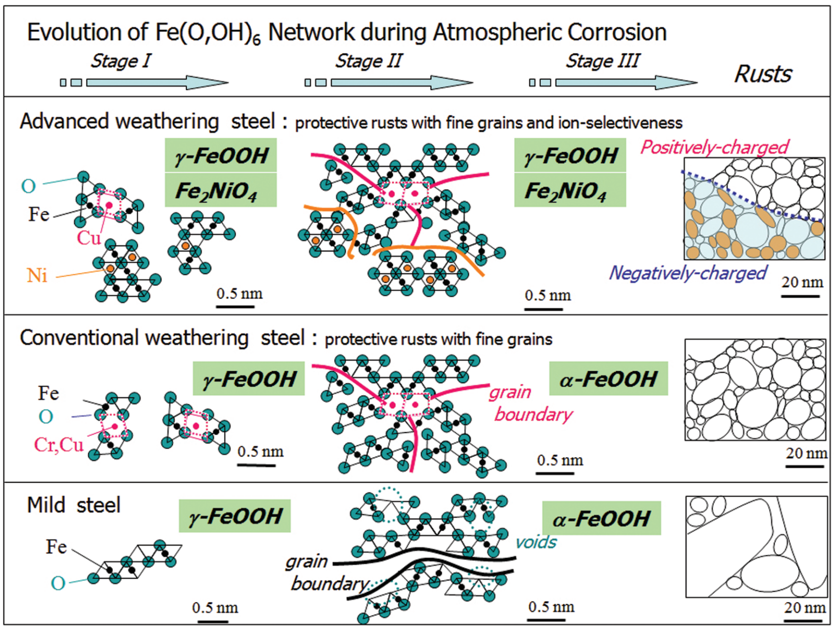

Fig. 5 Schematic diagram of reactions in nano-scale during atmospheric corrosion[10)]

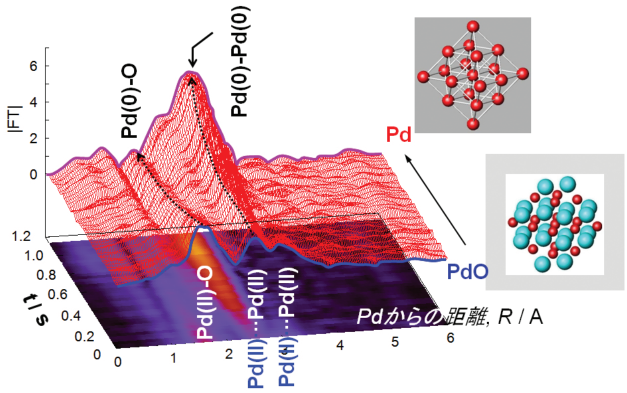

Fig. 7 Change in structures of PdO/Al_2O_3 in a reduction reaction

as follows: (a) a catalyst whose Pd nano-sized particles appear/disappear according to the oxygen potential in the exhaust, and (b) a carrier with a crystalline structure which facilitates the entry/exit of oxygen atoms to allow for the above swift and reversible reaction. Those concepts were validated by a newly developed Fe-based catalyst to purify exhaust fumes.[16] In accordance with the above guidelines, the development of new catalysts and research into their applications have been conducted.

4. Conclusion

Implementing *in situ* observation of various processes/reactions helps not only to optimize materials and process conditions, but also to obtain knowledge that might lead to the development of innovative new materials and processes. Recently, the conditions surrounding raw materials/fuels and the environment have been changing dramatically. Accordingly, securing our technological innovativeness calls for unconventional new ideas based on fundamental principles. In this respect, clarifying the mechanisms of processes/reactions is indispensable. As one approach to the knowledge required for that purpose, *in situ* observation will steadily increase in importance in the future.

On the other hand, research that utilizes synchrotron radiation as an X-ray source has become increasingly active at home and abroad. While the development of next-generation radiation sources, such as the X-ray free electron laser (XFEL), is forging ahead as one of the national key technologies, more and more small-scale rings, etc. have been constructed and synchrotron radiation as a general X-ray source has become available to many materials researchers. In addition, efforts have been made to make neutron sources more sophisticated and expand the application thereof J-PARC, etc. It is expected that analytical technology taking advantage of large research facilities will further advance in the future.

In view of the company's needs and the technical trends at home and abroad, we have conducted research utilizing various facilities to apply synchrotron or neutron radiation in accordance with the specific research purpose. Concerning synchrotron radiation, we have conducted joint research with KEK/PF and research utilizing the SPring-8 and other facilities, such as the NSLS of the United States and the SSRL of Stanford University. With respect to neutron radiation, we utilize the Japanese Research Reactors (JRR) at the Japan Atomic Energy Research Institute and the J-PARC facilities.

In the future, we would like to conduct research and development with the major emphasis on: (a) the best combination of various advanced beams, such as synchrotron (X-ray) and neutron beams, in accordance with specific purposes, and (b) combination of analytical techniques of *in situ* observations with computational sciences in order to reveal and design reaction schemes.

References

1) Kimura, M., Kihira, H.: Shinnittetsu Giho. (381), 77 (2004)
2) Kimura, M.: Shinnittetsu Giho. (390), 41 (2010)
3) Kimura, M.: Mater. Sci. Res. Int., Special Tech. Pub.-1, 394 (2001)
4) Kimura, M., Mizoguchi, T., Kihira, H., Kaneko, M.: Characterization of Corrosion Products on Steel Surfaces. Chapter 11, Springer, 2006
5) Ushigami, Y., Kawasaki, K., Nakayama, T., Suga, Y., Harase, J., Takahashi, T.: Mat. Sci. Forum. 157-162, 1081 (1994)
6) Kimura, M., Imafuku, M., Kurosaki, M., Fujii, S.: J. Synchrotron Rad. 5, 983 (1998)
7) Kaneko, M., Kimura, M., Tokuno, K.: Corr. Sci. 52, 1889 (2010)
8) Kimura, M., Suzuki, T., Shigesato, G., Saito, M., Suzuki, S., Kihira, H., Tanabe, K., Waseda, Y.: J. Japan Inst. Metals. 66, 166 (2002)
9) Kimura, M., Suzuki, T., Shigesato, H., Kihira, H., Suzuki, S.: ISIJ International. 42, 1534 (2002)
10) Kimura, M., Kihira, H., Ohta, N., Hashimoto, M., Senuma, T.: Corros. Sci. 47, 2499 (2005)
11) Kimura, M., Kaneko, M., Ohta, N.: ISIJ International. 42, 1398 (2002)
12) Suzuki, H., Akita, K., Misawa, K., Imafuku, M.: Materials (J. Soc. Mat. Sci., Japan). 51, 730 (2002)
13) Kimura, M., Uemura, K., Nagai, T., Niwa, Y., Inada, Y., Nomura, M.: J. Phys. Conference Series. Vol. 190, 012163, 2009
14) Kihira, H., Senuma, T., Tanaka, M., Nishioka, K., Fujii, Y., Sakata, Y.: Corros. Sci. 47, 2377 (2005)
15) Kihira, H., Kimura, M.: Corros. Sci. in print (2011)
16) Uemura, K., Nagai, T., Kimura, M., Ito, W., Kasuya, M., Okazaki, Y.: Society of Automotive Engineers of Japan, Collection of Preprints of Academic Lectures. 2008

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