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Characterization Techniques for Development of Products and Processes in the Steel Industry

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1. Introduction

The Materials Characterization Research Laboratory of Nippon Steel Corporation's Advanced Technology Research Laboratories is a prestigious research organization inaugurated in 1963 as the former Analytical Chemistry Laboratory of Yawata Steel Fundamental Research Laboratories. Today it is positioned as the organization that single-handedly shoulders the development of characterization techniques for Nippon Steel (and its affiliated companies). In the past, the predecessor of the organization was renamed several times, from the Analytical Chemistry Laboratory to the Analytical Laboratory (1971), then the Analytical Research Center (1980), the Materials Characterization Research Center (1989), until the present Materials Characterization Research Laboratory in 1991 when the Advanced Technology Research Laboratories was reorganized.

It may be said that the last thirty years were a period in which Nippon Steel took big strides in the administration of multiple businesses, including the steel business. In the course of supporting new businesses, other than steelmaking, we were faced with many new analytical requirements that we had not experienced before. Accordingly, we found it necessary to press ahead with the development of characterization techniques to meet those needs.

Yawata Steel's Fundamental Research Laboratories had a tradition of developing new technologies just for themselves. I remember that such a climate in the laboratories, together with the excitement felt in starting up a new business, fostered a bright atmosphere at the laboratories that attracted many young researchers every year.

The steel industry is now in the midst of global competition. From the standpoint of developing a new steelmaking process to impart denser and more complex structures to steel products, characterization technology that enables us to understand every phenomenon involved in the process on the basis of fundamental principles has become indispensable. The new characterization techniques that have been cultivated in the course of development of new businesses play an important role in clarifying factors in the manifestation of reinforcing mechanisms in high-grade steels and developing next-generation steelmaking processes. I believe that the development of characterization techniques backing Nippon Steel's technological innovativeness will continue to be the driving force for us as a leading player in the world.

In this centennial memorial issue of Shinnittetsu Giho, I shall review the development of characterization techniques at our company over the past thirty years since the publication of the 70th memorial issue.

2. Examples of Technology Development

It may be said that the last three decades of developing characterization techniques were really those of the development of technology to "detect things which have never done yet" and technology for "detecting things the way they are." Some representative examples are introduced below.

2.1 Detecting things which have never done yet

As the first step to clarify a particular basic phenomenon, it is essential first to identify the phenomenon. But what should be done if there is no way of detecting that phenomenon? The Materials Characterization Research Laboratory has been active in developing techniques to answer precisely such analytical problems.

2.1.1 Grain boundary segregation

Nippon Steel has been energetically pressing ahead with the development of techniques to observe the structures of steel materials with the aid of a 1 MeV ultrahigh-voltage TEM (transmission electron microscope) and an energy-filtered TEM together with the most advanced electron microscope technology.

Recently, an aberration-corrected scanning transmission electron microscope (STEM) was developed. This new STEM permits focusing the electron beam on the object of observation even more than does the conventional STEM since the spherical aberration of its magnetic lens used to control the track of the electron beam has been completely eliminated. On the other hand, if the STEM is installed under conditions subject to floor vibration, room temperature-dependent vibration, voltage fluctuation, magnetic field fluctuation, noise, etc., they all cause the lateral resolution of the observed images to deteriorate. Therefore, in introducing an aberration-corrected STEM, we decided to provide an installation environment completely free from those external disturbances and operate the STEM under that environment. As a result, we could dramatically improve the spatial resolution in composition analyses from about 1.0 nm to 0.1 nm or less, allowing for atomic-level composition analyses. The STEM was also applied to study the behavior of grain boundary segregation of trace amounts of boron, which is important from the standpoint of understanding the mechanism of improving the hardenability of high-strength steels used for ocean structures, etc. Using electron energy loss spectroscopy (EELS), we have succeeded in a quantitative analysis of the concentration profile of boron which concentrates in a prior γ-grain boundary at intervals of 1 nm (see **Fig. 1**).[1, 2]

In the future, we intend to improve the quantitativeness of boron concentrations so as to clarify the mechanisms of the grain boundary segregation in the γ temperature region by boron addition and the

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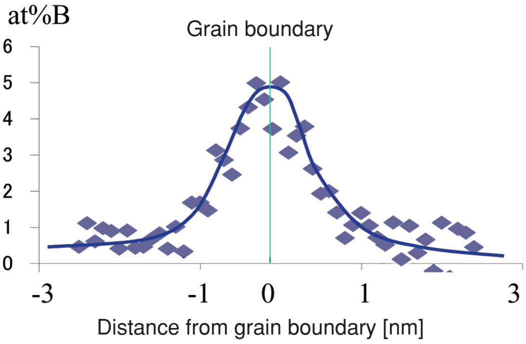

Fig. 1 Boron concentration profile around a prior γ grain boundary measured by Cs-STEM-EELS

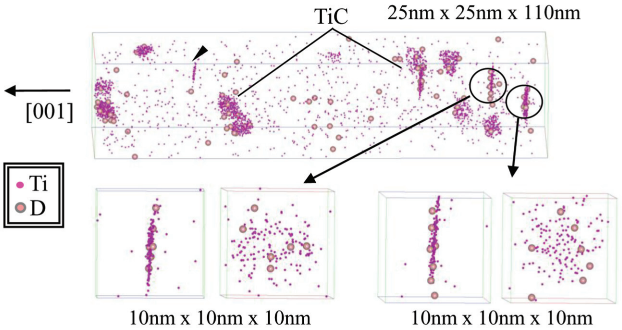

Fig. 2 3D Ti- and D-elemental maps of deuterium-charged specimens of the TiC steel with annealing

subsequent restraining of α transformation.

2.1.2 Hydrogen

The behavior of hydrogen in steel, represented by the hydrogen-induced delayed fracture of high-strength steel, has not been completely clarified because of a total absence of any method to detect hydrogen in steel. Concerning delayed fractures, a researcher has proposed a mechanism whereby a trace amount of hydrogen in the steel embrittles the prior γ-grain boundaries and thereby causes the steel to fracture while in use. On the basis of the above mechanism, two techniques to render the hydrogen in steel harmless have been proposed. One is using nano precipitates as sites to trap the hydrogen, and the other is to control the steel's microstructure.

In the technique using nano precipitates, the ability of the precipitates to trap hydrogen is important. However, the sites where hydrogen should be trapped are unclear and the concept of optimum hydrogen trapping is difficult to define. In the past, secondary ion mass spectroscopy (SIMS) has been studied as a technique to detect hydrogen in steel. However, this technique is insufficient since specifying the hydrogen-trapping positions requires specifying the relevant atoms at an atomic-level resolution. Nippon Steel attempted to detect hydrogen in steel using a three-dimensional atom probe (3DAP). The 3DAP is a kind of mass spectroscopy in which a high voltage is applied to the specimen in the form of a needle to field-evaporate the atoms at the surface of the specimen and detect those ionized atoms. It permits determining the types and spatial arrangement of the atoms that exist in the tip of the specimen, and its lateral resolution is 0.2 nm or less. In the steel industry, our company was one of the first to introduce atom probes, and has since used them to press ahead with the development of atomic-level characterization techniques.[3-9)]

On the other hand, hydrogen is an element which resides in a vacuum and detecting only the hydrogen that exists in steel is extremely difficult. Therefore, in a specimen pretreatment chamber we especially fabricated for ourselves, we first introduced deuterium to a heated needle-shaped specimen for 3DAP in a vacuum and then cooled the specimen rapidly. By so doing, we could successfully introduce hydrogen into the steel. Using the specimen, we confirmed the presence of preferential hydrogen-trapping sites at the surface of a plate-shaped, nano-sized precipitate of TiC (see **Fig. 2**)[10)].

It is expected that our research activities, like the one described above, will help to clarify the influence of trapped hydrogen on hydrogen embrittlement and deepen our understanding of hydrogen embrittlement.

2.1.3 Crystal defects

As the fundamental factors in imperfection of crystals, there are atomic vacancies and their clusters. Today, clarifying the mechanisms whereby crystal defects and fracturing of steel sheet occur has become one of the most important research themes in the development of high-tensile steel sheet. As a technique to detect atomic vacancies, Nippon Steel originally developed positron annihilation spectroscopy apparatus.[11-15)] A positron is the antiparticle of an electron. It is the same in mass and spin as the electron, but is opposite in electric charge to the electron. When a positron enters a solid, it loses energy, and is then diffused and annihilated with an electron in 0.1 to 0.2 ns. In many cases, the annihilated positron gives off a couple of 511keV γ-rays in an antiparallel direction. Then, if there is a lattice defect due to atomic vacancies, a potential trough occurs and the positron is captured by the lattice defect. Since the positron captured by the defect goes through a different process from the annihilation between lattices, it is possible to measure the type and concentration of the defect.

When atomic vacancies in a crystal cluster into a void, they can be observed under an electron microscope. Until recently, however, there was no way of directly observing atomic vacancies. In the early 1990s, during the development of positron annihilation spectroscopy, we found that the technique cast a new light on the formation of an ion injection defect introduced into single-crystal silicon and the behavior of recovery thereof after the subsequent heat treatment. Namely, for 2-nm and smaller defects which could not be observed under an electron microscope, we clarified the mechanism of formation of vacancy clusters and the thermal behavior of oxygen-vacancy composite defects. On the other hand, the application of positron annihilation spectroscopy was limited to single-crystal materials for some time. Thanks to positron microscopy developed recently, however, the application of the technique is expanding, as in the observation of plastic deformation-induced defects in iron-copper alloys. It is expected that our technique will make it possible to obtain information about the distribution and density, etc. of dislocations and precipitates.

2.2 Detecting things as they are

If we can establish a technology for observing ultimate reaction fields in a specific manufacturing process—what reactions are taking place there and what is happening in a high-temperature atmosphere, we should be able to quantitatively optimize the manufacturing process. Nippon Steel has been energetically propelling development of *in situ* observation techniques, high-temperature reaction observation techniques, and on-site observation techniques.

2.2.1 Technology for *in situ* observation using synchrotron radiation

As a source of radiation, synchrotron radiation has these characteristics: (1) high brightness, (2) parallel beams, and (3) white light.

A powerful X-ray source not only helps the measuring time shorten but also permits efficiently implementing *in situ* observation of reaction processes and observation of dynamic changes in those processes. Taking advantage of those characteristics, Nippon Steel has been developing technology for *in situ* observation of various processes with the aid of state-of-the-art reaction cells.[16, 17] For example, by introducing parallel beams obliquely to reaction cells, we applied our *in situ* observation technology to study the alloying reaction in the hot-dip galvanizing process and clarify the relationship between surface structure and color fastness of the oxide film on the surface of titanium. In addition, on the basis of the results of an *in situ*, real-time observation of X-ray absorption fine structure (XAFS) spectra utilizing the white light of synchrotron radiation, we clarified the mechanisms of the oxidation-reduction reactions of exhaust catalysts and the formation of oxide film on weatherproof steel. Described below are the observation results for the alloying reaction in the hot-dip galvanizing process.

Hot-dip galvanized alloy steel sheet is widely used, mainly for automobiles. In its manufacturing process, steel sheet annealed in a reducing atmosphere is first dipped in a molten zinc bath to deposit the prescribed amount of molten zinc on the surface. It is then heated in an alloying furnace, in which the Fe-Zn alloying reaction takes place. This Fe-Zn alloying reaction is important from the standpoint of securing the desired qualities of the steel sheet. Therefore, we applied the alloying reaction to observe the influence of added element P under the same high-temperature atmospheric conditions as in the actual process.

By heating steel sheet specimens deposited with a certain amount of Zn to a high temperature, we made a dynamic observation of the change in diffraction pattern in the alloying process. **Fig. 3** shows the time-serial change in proportion of phases obtained by an analysis of the diffraction patterns. As shown, it can be seen that the following alloying reaction that takes place in the surface layer of steel differs markedly according to whether a micro amount of P is added (specimen FEP) or not added (specimen FE).

η (Zn) ⇒ Melting ⇒ Solidification ⇒ ξ ⇒ δ ⇒ Γ

Namely, we could clearly confirm that as a result of addition of a micro amount of P: (1) the time in which the alloying reaction starts (the formation of ξ phase starts) after the melting of Zn increases, but (2) the time of formation of δ phase, which is an intermetallic compound of high Fe concentration, remains the same (see **Fig. 4**).[18-20]

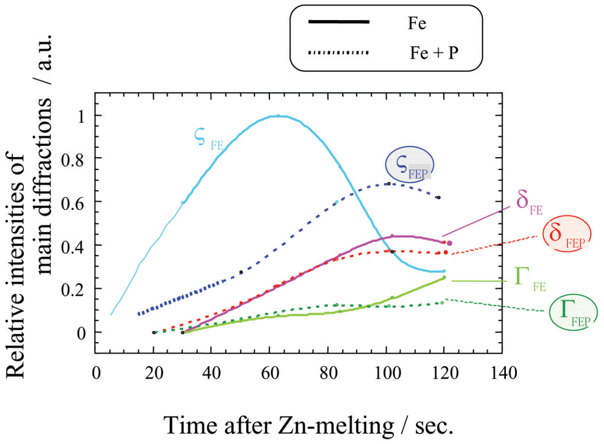

Fig. 3 Change of relative intensities of diffractions for phases in the specimens FE and FEP, which were obtained by *in situ* X-ray diffraction

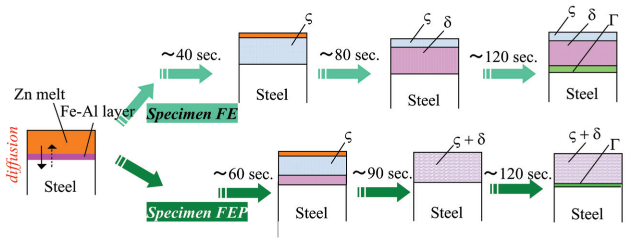

Fig. 4 Schematic diagram of the Zn-Fe reactions revealed by *in situ* observation

The above findings underlie our proposal for the optimum plating and alloying process by steel type and composition.

The application of such research utilizing large-scale public research facilities (so-called “Big Science”) is not limited to synchrotron radiation. Research using the neutron ray sources of the Japan Atomic Energy Agency and J-PARC has also been conducted to promote the development of technology to measure residual stresses in steel materials.[21]

2.2.2 NMR imaging and high-temperature NMR technology

Concerning solid nuclear magnetic resonance (NMR) technology, Nippon Steel is among the five leading research institutes in Japan. This is attributable not to the number of solid NMR systems we own, but to the fact that ahead of many other research institutes, we have been developing new solid NMR techniques to meet our needs.

In order to study a method for direct observation of the coal softening and melting process, Nippon Steel developed the single-point-imaging technique that permits applying NMR to obtain images of the process only with phase encoding using a larger magnetic field gradient. The images obtained by this method are completely free from those adverse effects that afflicted conventional methods, such as the effect of substances which are contained in coal in large proportions and which differ in magnetic susceptibility or the influence of distortion of images caused by a difference in chemical shift. With the technique mentioned above, we succeeded in *in situ* observation of the coal softening and melting process and clarified the difference in the coal softening and melting process by coal type.[22-24]

The above technology for NMR observation under high temperatures has evolved into high-temperature *in situ* NMR technology that allows for *in situ* observation under high temperatures up to 1,500℃. Formerly, to study the high-temperature properties of calcium aluminosilicate (CAS) glass, for example, specimens obtained by rapidly cooling a hot melt were used. However, it is rare that a material retains its high-temperature structure after it is cooled rapidly. In this respect, the above new technology that allows for direct evaluation of the network structure and motion of CAS glass at a high temperature helps select suitable elements to be added to the glass chemical composition.[25, 26]

In addition, in Japan, Nippon Steel was quick to tackle the establishment of multiple-quantum magic-angle-spinning (MQMAS) to obtain high-resolution solid NMR spectra of quadrupole nuclei. In recent years, the magnetic field for NMR has been increasingly intensified. By using an intense magnetic field and MQMAS in combination, we have also succeeded in accurately specifying the chemical structures of coal ash and slag.[27, 28]

Furthermore, we co-developed a new probe to measure satellite-transition magic-angle-spinning (STMAS) spectra with an NMR instrument provider and thereby improved the measurement sensitivity by about five times compared with MQMAS. As a result, we

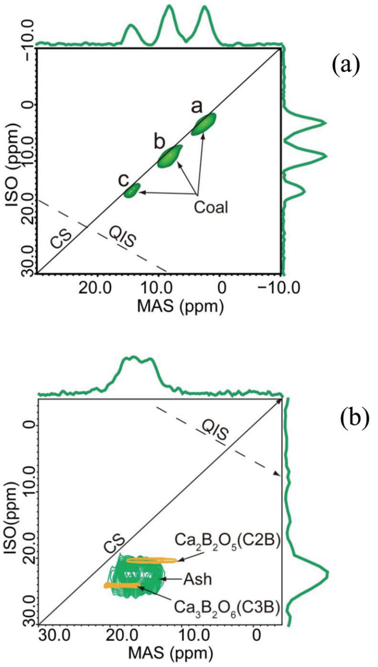

Fig. 5 **^{11}B STMAS NMR spectra: (a) coal and (b) coal ash**
Boron concentrations in coal and coal ash are 0.008 mass% and 0.24 mass%, respectively.

could analyze the chemical structure of a micro-amount of boron (hundreds of ppm) contained in coal ash.28)

Fig. 5 shows the ^{11}B-MAS spectrum of raw coal and coal ash, respectively. For the raw coal, three boron sites can be confirmed. From the interaction values of the quadrupole nuclei, it is judged that they belong to tetracoordinate organic boron. On the other hand, after the coal was reduced to ash at 1,500℃, all of the boron became tricoordinate boron. From its chemical shift, it is considered very likely that the boron exists in the form of a mixture of $Ca_2B_2O_5$ and $Ca_2B_2O_6$.29) In fact, elemental mapping of the same specimen by focused ion beam-time of flight-secondary ion mass spectrometry (FIB-TOF-SIMS) revealed the coexistence of boron and calcium in particles of coal ash, positively indicating that the amount of boron eluted from coal ash having boron concentrated in CaO is smaller than that from coal ash having boron concentrated selectively in the surface layer.30)

Solid NMR that focuses on quadrupole nuclei could hardly be applied to structural analysis of trace elements because of its sensitivity. Thanks to the establishment of the above technique, however, it is expected that solid NMR will become applicable even to low-sensitivity, low-concentration nuclides which were formerly left out of the scope of measurement by solid NMR.

2.2.3 Jet-REMPI technique

Supersonic jet-resonance enhanced multi-photon ionization (Jet-REMPI) is a kind of mass spectrometry. First, a specific trace organic compound in the atmosphere is injected into a vacuum, together with the air, and subjected to adiabatic expansion and cooling to freeze the thermal motion of the molecules of the compound. Then, a tunable laser beam of the same energy as the electron excitation level of the molecules is irradiated for resonance excitation of a specific organic molecule. After that, the molecule is ionized by letting it absorb the laser beam again.

Nippon Steel suggested that the above technique might be applicable to on-line monitoring of dioxins discharged from an incinerator. Eventually, we pressed ahead with development of the relevant technology through a national project (“Development of Technology for High-Sensitivity Online Analysis of Trace Gas Components in High-Temperature Furnaces” subsidized as a fiscal 2002-2004 industrial-academic innovation creation project under the Ministry of Education, Culture, Sports, Science and Technology). In order to enhance its real-time capability, we gave up adopting the pulsed valve that had been used in conventional Jet-REMPI equipment. Instead, we fabricated an experimental apparatus which permits introducing exhaust gas continuously. In addition, we built a system which was able to detect the signals from organic molecules with a delay of about 150 seconds in the Jet-REMPI equipment installed at a point 23 m from the flue of the incinerator.

Thus, we successfully developed a technique to detect extremely low concentrations of organic molecules on an exceptionally real-time basis. Using that new technique, the company succeeded in detecting monochlorobenzene—one of the precursors of dioxin—at intervals of ten seconds. That made it possible to study the correlation between the operation of an incineration furnace and the occurrence of organic molecules.31-35)

At present, we are developing single-photon ionization mass spectrometry (SPI-MS), which is an upgraded version of Jet-REMPI. At the same time, we are discussing the application of our technology to detect and monitor multiple organic molecules simultaneously to environmental problems.36)

2.2.4 Technique to analyze micro amounts of Fe in seawater

In recent years, a phenomenon called sea desertification has occurred in coastal areas of Japan. It has become a problem since in those areas the seabed is covered with calcareous algae, which prevent the growth of kelp and other marine plants. As the major causes of sea desertification, a rise in seawater temperature, pollution of the seawater, and the voracious appetite of sea urchins, etc. for seaweed have been cited most often. However, some researchers believe that the phenomenon is ascribable, at least in part, to a decrease in the concentration of Fe dissolved in seawater. Under such premise, Nippon Steel considered increasing the concentration of dissolved Fe by feeding into the seawater a unitized mixture of steel slag and humic substance containing a considerable proportion of iron.

On the other hand, the concentration of Fe dissolved in seawater is several to tens of ppb. In order to verify the effect of the above unit, therefore, it was important to establish a technique for quantitative analysis of such trace amounts of Fe in seawater with a high salt concentration. Eventually, the company established a technique to analyze Fe in seawater with a minimum limit of determination less than 1 ppb by utilizing a chelate resin which selectively extracts Fe and other heavy metals to separate out the high concentrations of salt, restraining the disturbance of Fe from the measurement atmosphere, and implementing a low-background measurement in a cool plasma condition under which argon and oxygen molecular ions that cause mass interference with Fe hardly occur. The above technique made it possible to observe the concentration of dissolved Fe around the points where the units were embedded (see **Fig. 6**). It can be seen that the Fe concentration of seawater was highest in the sea area in which the units had been embedded and that it gradually decreased with distance from the shoreline. This result suggests the possibility that the Fe eluted from steel slag—a source of iron—diffuses in the sea and promotes the growth of marine plants. Thus, we could confirm that applying a mixture of steel slag and humic substance as a source of iron elution in a marine desertification zone is effective.37-39)

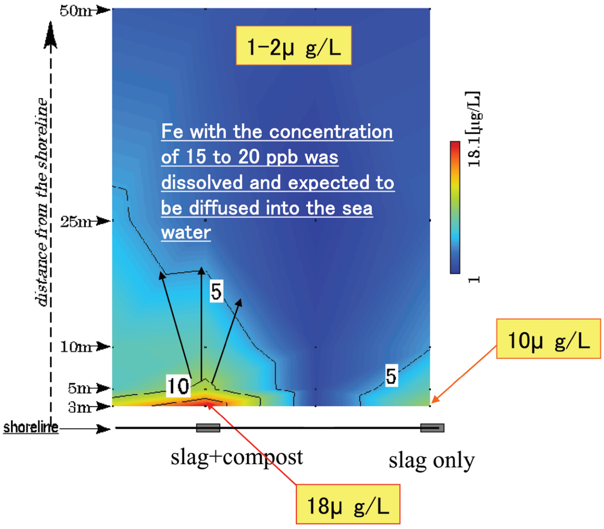

Fig. 6 Distribution of dissolved Fe in the monitored region around the sea shore
Fe with the concentration of 15 to 20 ppb was dissolved and expected to be diffused into the sea water.

3. Tasks to Tackle in the Future

So far, Nippon Steel has focused its efforts on detecting things which have never done yet. In the future, the company will be demanded to determine the factors in manifestation of various functions of steel materials. To that end, we recognize that the following points are important. Thus,

(1) Multi-dimensionalization

Technology for extracting three-dimensional information, especially the hidden points of manifestation of steel functions, from two-dimensional information obtained by SEM, TEM, etc. will become important. Further, we consider it important to evolve this into a four-dimensional one, including kinetics, in the future.

(2) Hybridization

Observing the factors in functional manifestation from various angles is important. We consider that it will become necessary to systematize technologies that allow for a multi-angle analysis of such factors in the reinforcement of steel structures as precipitates, dislocations and crystalline textures using different techniques which are complementary to one another in order to make a comprehensive quantitative evaluation of the mechanisms of functional manifestations.

Nippon Steel is tackling nano- and atomic-level analyses of nano-sized precipitates that play a vital role in precipitation hardening of steel, grain boundary segregations that govern the hardenability of steel, etc. In the future, we will accelerate our activity to clarify new factors that govern material properties by making the most effective use of 3DAP and aberration-corrected STEM—our two powerful tools for advanced atomic-level analyses—and apply the new knowledge to develop next-generation, high-function steel materials.

(3) Multi-scale analysis

By means of atomic- and nano-level observations, the dynamics in manifestation of universal factors, materials, and processes are derived to understand and predict the processes of manifestation of macroscopic physical properties at various levels (magnitude). In the future, it is expected that the role of analytical technology in the development of new, high-value-added products and advanced new processes will become ever more important. Nippon Steel considers that equipping itself with innovative new analytical technology that permits meeting the above expectations as far as possible will become important from the standpoint of securing its technological innovativeness. In the future, we would like to establish multi-scale, multi-dimensional measurement technology incorporating not only 3DAP, but also TEM tomography and 3D-EBSP (Electron Back-Scattering Patterns), etc. and thereby clarify various factors in the manifestation of functions of steel materials.

(4) In-situ observation and observation in extreme atmospheres

Nippon Steel will further speed up the *in situ* observation technology it has developed so far. At the same time, we will make it possible to control the atmosphere of *in situ* observations. By reproducing the actual atmosphere, it should become possible for us to analyze complicated and inhomogeneous phenomena and extract and propose guidelines on the improvement of existing processes.

4. Conclusion

I have so far introduced various topics relating to the development of analytical techniques at Nippon Steel in the past thirty years. The contents introduced herein concern only a part of many outstanding results of the company's R&D activities. In fact, there are quite a few technical achievements that are really worth mentioning but that have not been dealt with in this technical review. In this respect, I, the author, would like to apologize here for a lack of deep insight into the subject.

The steel industry has continued to advance while meeting diverse challenges, such as utilizing raw materials and fuels effectively, developing new steel materials and new processes and responding to environmental problems. Those challenges will become increasingly difficult for us to meet successfully. In the future, whether or not those problems can be solved will depend on the ability to translate new problems into the seeds of analysis and solve pending problems on a timely basis. Implementing research on analytical science in that direction will become important to our company in the future.

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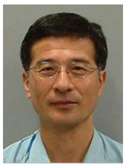

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