NIPPON STEEL TECHNICAL REPORT No. 91 January 2005

UDC 543 . 5

Advances in Nano-Level Materials Characterization Technology

Misao HASHIMOTO*[1]

Abstract

The recent development of nano-level materials analyses technologies such as three-dimensional atom probing was reviewed. The importance of the techniques that enable dynamical observations was also described, combined with a view to the future in nano-level characterization.

1. Introduction

Our generation is witnessing rapid changes being made to our environment. As the things that our society values evolve, it is growing ever more important that we understand the nature of the materials we use. It is essential in order to firmly grasp the elements that control a material's properties, and to utilize those properties to the utmost so that we can continue to provide the basic elements that will meet modern needs. Therefore, as long as material sciences are based on physics and chemistry of matter, the understanding of matter in its unadulterated form will be an important technical base. To attain that understanding, nano-level material analytical technologies promise to be extremely important elements to infrastructural technology in the way we observe the world around us.

The first, fundamental step in recognition, hence the understanding of the nature of matter is to observe the object. This applies to whatever is subject for observation. Even in our daily lives, to understand living things, first we observe them objectively. Then, we view them in greater detail under a magnifying glass. Still further, we can also learn from the way living things respond to external stimuli in its environment. We must also try a variety of methods to view matter, in order to gain a more thorough understanding obtained from having different vantage points. Specifically, it is essential to view material with regard to its characteristics and functions. Therefore, the discussion below focuses on the recent advancements made in nano-level analytical technologies, and provides a view toward their future applications because these dynamic observation and nano-level analytical technologies are thought to be highly significant.

2. Viewpoint from Material Developments and Analysis Technologies

Much of the material found in steel is multi-crystal grains on the order of several tens of μm in size. To grasp the structure of steel, and to understand the relationships of each characteristic of all types of steel material, it is necessary to ascertain its internal structures. There are various levels in the structural factors that are keys to the characteristic of the material. The following list is an example of these levels[1)].

Key Factors in Material Characteristics[1)]
(1) Macro internal structure
  - Texture
  - Transformational morphology
  - Crystal grain diameter
  - Secondary phase, Inclusion etc.
(2) Fine structures inside of grains
  - Dislocation
  - Precipitation
  - Stacking faults
  - Twinning
(3) Structures of grain boundaries
  - Element segregation
  - Grain boundary precipitation
  - Atom array at interface
(4) Fine structures at the atomic level
  - nm size precipitation
  - Local strain
  - Compound point defects (such as clustering)

The characteristic of a material depends upon what level of matter in which it is manifested. Furthermore, while viewed size factors can differ, there are cases in which the combining of different factors is a key to grasping those characteristics. Therefore, it is very important to also have a firm understanding of their mutual relationships.

On the one hand, analytical methodologies are required for use in a variety of angles to handle these key factors. The following summarizes various factors from the viewpoint of specimen size using

---

[1] Advanced Technology Research Laboratories

microscopes as examples.

Example of levels of size factors in analytical technology
- Physical structure (such as phase, crystal structure, structure, heterotopic facies, precipitation)
- Chemical status (such as chemical bonding and segregation)

Analytical size factors (Examples microscopes)
- Optical microscope: From mm in size
- Electron microscope (scanning electron microscope, transmission electron microscope): μm to nm
- Field ion microscope, atom probe: From nm in size

For example, in the macro sense, it is possible to describe deformation in terms of a type of elastoplasticity deformation of a continuum, when considering plastic deformation of steel. However, it is essential to understand the phenomena that occur at the atomic level, such as the mutual affect of a third element and dislocation in order to understand the metallurgical phenomena that occur such as the great variations of mechanical characteristics that can exist with even the slightest difference in structure. The amount of carbon and differences in heat treatment are examples. In conventional textbooks on metallurgy and physics, a philosophy of deformation behavior from the viewpoint of dislocation is propagated. However, while dislocation has been observed using electron microscopes, until recently it was quite rare to be able to actually directly observe how dislocation and carbon mutually affect each other. For that reason, the theories described in textbooks are generally considered to be important signposts that describe such phenomena, albeit they do not lead to the designing of materials through their actual observation.

On the other hand, particularly with the recent advances made in nano-technology, atom probing technology has lead to a breakthrough in its practical applications in the study of materials. These technologies enable scientists and engineers to directly observe structures at the atomic level in three-dimensional views. Thus, while it conventionally has only been the realm of discussion in textbooks, we are now entering an age when materials can be directly viewed at the atomic level. This means that it is now possible to correctly verify theoretical hypotheses through real demonstration. Until now, designs and developed materials were based upon theoretical backgrounds.

3. Efficacy of Nano-level Analytical Technologies in Steel Materials

3.1 Development of high strength steel wire: A case study

The following describes a case in which nano-level technology was used in analyses for high strength steel wire which was actually used on the Akashi Kaikyou bridge in Kobe, Japan. This is an example of how the advancements in nano-level technology have made great and real-life contributions to the development of steel. It would be insufficient to employ one strand of conventional 1,600 MPa class wire to support a bridge that has a nearly 2 kilometer span between trestles, as is the case with the Akashi Kaikyou (a bridge in Kobe, Japan). Therefore, higher classes of steel wire, namely 1,800 to 2,000 MPa class wire was required. While it is necessary to create even finer lamella structure for pearlite as the metallurgical controlling factory which is the key, it is also necessary to maintain the structure of pearlite in its heat history when plating.

The lamella structure is partially destroyed according to the heat history of plating treatment on conventional steels. However, the steel that was developed specifically for use in the Akashi Kaikyou bridge correctly maintains its lamella structure in the same heat history, and maintains the high strength of 1,800 to 2,000 MPa under actual use conditions (See **Fig. 1**[2]). The keys to the development of this new steel type were in the increase of the amount of Si additive over conventional steels, and in the controlling of base element distribution behavior of Cr and Mn.

At the time, there were a variety of theories regarding the role of the Si additives, but using analytical technologies at the nano-level, the role of the Si additive became clear for the first time.

Fig. 1 shows the distribution of elements at the interface between cementite and ferrite. Here, it can be seen that the Si element has a high concentration at an interface of several nm in width. In other words, there was the effect of suppression caused by the drag effect of the interface movement according to the Si concentration toward the lamella interface. This resulted in maintaining the lamella structure, and attaining high strength levels. Thus, it was possible to clarify that mechanism using nano-level analytical technologies. That technology is capable of detecting concentrations of elements on the scale of several nm.

Steel has built-in structural defects in the form of grains, stacking faults and precipitates that generally appear at boundary or interface structures, like a boundary (or interface) between the defects and the matrix. In some cases, the thicknesses of the interface structure can differ, but in the case of the grain boundary, it maintains a structure of a scale of several nm. To understand this phenomenon at the interface, it is necessary to describe the observation technology

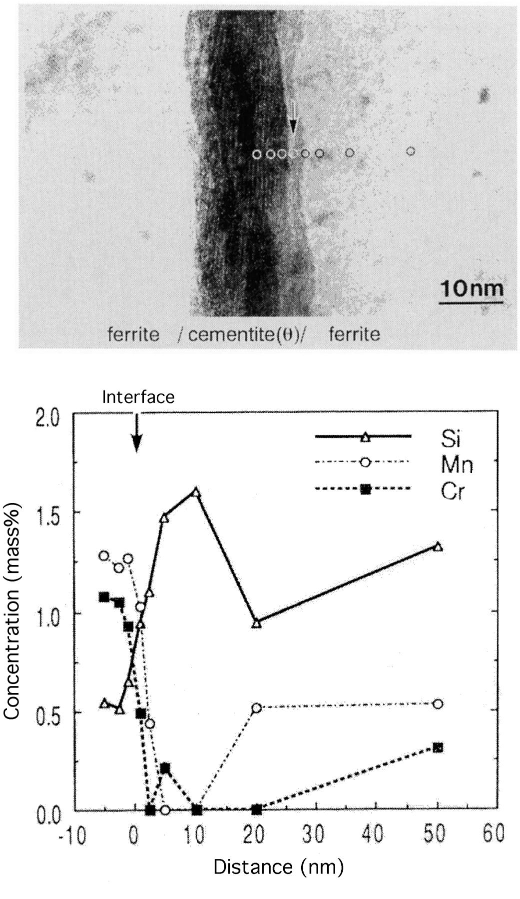

Fig. 1 Segregation of various elements at the interface between cementite and ferrite[2]

and the phenomenon at the nano-level. To express this differently, it was possible to clarify through actual demonstration the phenomena occurring at the interfaces for the first time thanks to the breathtaking advancements made in nano-level observation technology.

The discussion above describes nano-level analysis in relation to base element segregation toward the interface. However, this technology has also played a key role in the strengthening of precipitate for minute precipitation. It has also played an important role at the structural level, such the use as a transformation starting point to make finer structures, and in the pinning effect of interface movement. Recently, precipitation at the nano-level is also an important factor in controlling structures. Furthermore, analytical technologies for that end are becoming ever more important. In this field, there have been much progress made in observation technology which employs EELS (Electron Energy Loss Spectroscopy) for nano-precipitation. A method for analyzing the shapes and distribution of precipitates (such as TiN) of specific base elements such as Ti has been developed which promises to be a powerful tool in the field of electron microscopes3).

3.2 Leading edge of nano-level materials analyses technologies – Three-dimensional atom probing technology –

As discussed above, to understand the phenomena occurring at each interface structure as one of the defects in the subject matter, it is always necessary to understand the behavior of the various base elements at the nano-level. Conventionally, a field ion microscope (FIM) has been used as a means for observing the structure of surface atoms. However, recently there have been developments made in three-dimensional atom probing which can measure three-dimensional position information of atoms as they are. **Fig. 2**4) shows the basic theory of this method.

Among the technical advancements, it is particularly important to be able to detect three-dimensional position information and that an energy compensation mechanism can be applied to steel material. Because there are important additives in steel, such as Cr, Mn and Ni, near the Fe mass number which is a main component in analyses of mass, it is necessary to correctly separate the three-dimensional position information of a small amount of additives from the peripheral noise and to measure this to increase mass resolution.

Fig. 35) shows an example of using a three-dimensional atom probe for observations of the carbon atoms segregating near the interface in steel. It can be understand that the same phenomenon as the interface segregation of the Si element occurs on the Akashi Kaikyou bridge, but it can be observed as three-dimensional position information of the carbon atom. As is described in this special issue5), at present it is possible to quantitatively observe carbon which segregates at the grain boundary. There is much anticipation in the field that this will become a powerful methodology for various analyses on actual materials in the future.

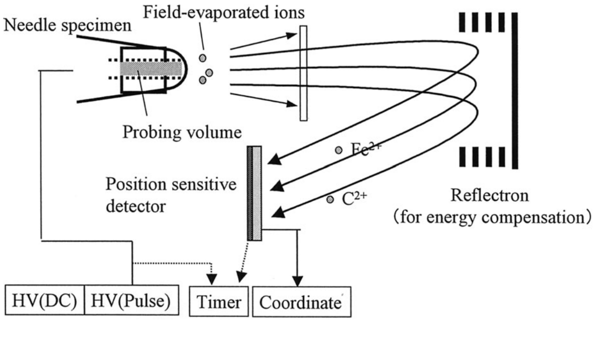

Fig. 2 Schematic illustration of 3D-AP4)

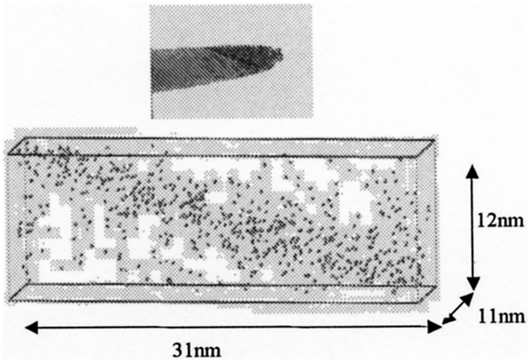

Fig. 3 Carbon segregaion at grain boundary measured by 3D-AP5)

3.3 Peripheral technology supporting nano-level observation technology – Pinpoint observation technology –

Nano-level observation technology is a powerful means for clarifying phenomena and mechanisms. However, a drawback to this technology is that it has an extremely limited scope. If the location to be observed is available substantially uniformly throughout the material, then it is not a problem to provide samples from any location. However, if the portion to be observed is an interface, or a grain boundary (or interface), as in the example relating to the wire analyses conducted in relation to the Akashi Kaikyou bridge, sample preparation technologies for accurately preparing the targeted location as a observation point also become extremely important.

Pinpoint sampling technology is already mainly in use as a failure analysis method in the semiconductor device field, but Nippon Steel Corporation was early to recognize it and to promote its use in steel as a coherent observation technology. **Fig. 4**6) shows the methodology of this technology.

This technology is applied to find the regions to target for sequential observations using an optical microscope, and then observing images using a focused ion beam (also known as FIB). Then, it is applied to form the necessary areas using an ion beam to cut out the necessary minute samples. With this technology, it has become possible to bring grain boundaries into the region of observation in three-

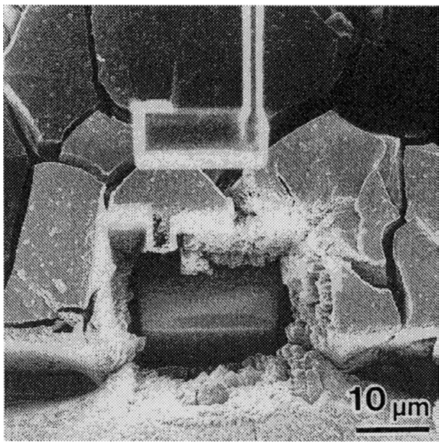

Fig. 4 Development of micro-sampling technique applied for steels6)

dimensional atom probing (at the scale of several 10s of nm).

It is also very important to be able to access problems in actual materials accurately and quickly at an observable range in consideration of the efficiency of the preparing samples. Nevertheless, by using a technology that enables observations with pin-point accuracy, not only is there a quantitative merit in the increased rate of success of sample preparations, but there is also a dramatic increase in the quality of observation data. For those reasons, it is a very important technology. As the frequency of observations at the nano-level increases, it is thought that sampling technology will also become an increasingly important related technology.

4. Analytical Method for Understanding Changes in Materials

It is possible to observe the material characteristics as a response to various types of stress (mechanical displacement such as stress, or chemical displacement such as corrosion) applied thereto by its environment. For that reason, it is important to understand how a material changes in response to external stresses, and to understand the process of those changes to truly understand the characteristic of the material. If it is possible to predict how a material will change, then it is possible to design having a full understanding of its nature. Also, by knowing how a material will change when an object is manufactured, it will be a basis to developments toward better material manufacturing methods and processes.

Mechanical factors, such as stress and strain, and problematic chemical factors, such as corrosion, and still further metallurgical factors that become evident at high temperatures and which are particularly problematic during manufacturing are all forms of ambient stress applied to iron and steel. Materials can change by the intertwining of these factors. Be that as it may, at the observation stage, it is very important to take in as many of these factors that can vary in the external environment as is possible and to understand their changes over time in the material as a result at a real-time level. While the latest sharpening methods, such as three-dimensional atom probing are extremely effective in observations to be made at the atomic level, observations are only possible in an ultra-high vacuum chamber which means that it is also a technology in which it is difficult to load factors that have an affect from the ambient environment. Although there is the possibility of a dynamic observation technology being developed in this field, other methods must be relied upon at the present.

A method used to understand the changes occurring in matter at high temperatures was established as a dynamic SIM (or Scanning Ion Microscope) observation technology that is used as one FIB technology at Nippon Steel Corporation[6)]. Although discussed in detail in this special issue, it should be noted that there has been success in capturing the circumstances under which the transformation of ferrite from precipitation occurs with priority over transformation from the grain interface which is important in the technology for making crystal grains finer in steel materials. This was achieved by carefully using the dependence on crystal orientationof secondary electrons generated during Ga ion sputtering to allow observation of high contrast images from each crystal grain and combining high temperature stages. See **Fig. 5**[7)] for a representative example of an observation. This is a SIM showing the progression of ferrite deformation (the black part) in priority from the inclusion in the grains. This technology makes it possible for researchers to directly observe the conditions inside the steel while it is undergoing manufacturing at high temperatures or the structural transformations occurring in a material under a high stress environment such as a coagulated structure after welding. This is seen to be a highly significant technology for providing onsite observations through the development to higher levels of accuracy than the conventional pinning theory. It also contributes immeasurably to finer material manufacturing methods.

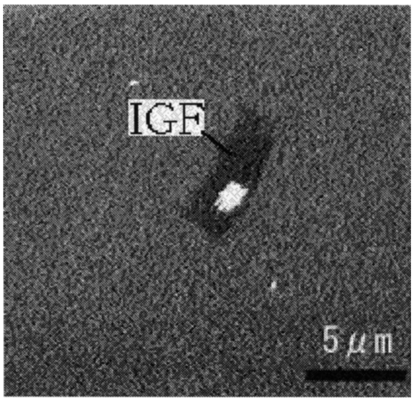

Fig. 5 In situ SIM observation of the phase transformation around an inclusion at high temperature[7)]

The space resolution under these means is on the order of sub μm. However, in recent years there has been research into applications for steel materials using an even higher resolution in LEEM (Low Energy Electron Microscopes). Nippon Steel Corporation has been verified its logical efficacy[8)]. The space resolution of an LEEM image is possible up to approximately several nm. Due to the use of a video mode, the time resolution is extremely high. Therefore, there is much anticipation of the advancements made with this technology as a high-speed imaging observation means for use at the nano-level in high temperature ranges and as a methodology that can be thoroughly used in real applications such as those for steel materials.

Nevertheless, steel material will degrade through corrosion or the like if used in conditions under actual use such as atmospheric environments. Various steel products have been developed that employ plating, painting, or weather-proofing in order to prevent degrading influences from the environment to which it is exposed. However, this is also very valuable analytical technology in the area of material design for maintaining superior usage characteristics under environments of actual use by ascertaining how the surfaces of steel materials change under corrosive environments where moisture is present. The degree to which one can observe these is restricted to the probes used in observation when observing the changes of materials under a humid environment. Often times it is necessary to create a vacuum for generation or detection of the electron beams and/or ion beams. Therefore, observation under humid environments for example is extremely difficult. On the other hand, optical probes have the capacity to permeate moisture under fixed conditions. Therefore, this method makes it possible to understand the changes of materials under humid environments.

As an example, the analysis of rust under a humid environment using X-ray structural analyses can be given. While this is discussed in detail in this special issue, there has been success in directly understanding how fine rust structures of weather proved steel changes in form over time[9)]. Differing from the three-dimensional atom probing method, this method does not directly observed position information in the space. However, it is a valuable methodology in view of enabling predictions of changes over time as a method for dynamically understanding the changes of atoms arrays or cluster sizes.

5. Conclusion – Future Expectations of Nano-level Observation Technologies in Steel Materials –

A discussion was provided on the recent advancements of dynamic observation technologies under high temperatures and humid environments as a means for understanding the changes that occur in steel materials. As an example 3-dimensional atom probe technology was used as an example of one of the extremes in nano-level observation or analytical technologies. The flow is summarized in **Fig. 6**.

The recent advancements attained in nano-level technology are making it possible for higher analytical methods that will enable discussions that focused directly on elucidating phenomena that occur at the atomic level even for steel materials. Furthermore, these dynamic observation technologies are taken to be an access for understanding changes that occur materials in their environment of use and under the manufacturing conditions, to maintain superior characteristics in their actual usage environments, and as a way to create direction for creation of even the more superior material characteristics.

Nano- level analytical technologies raise the theoretical dimension to materials to provide an effective viewpoint for the correct understanding of phenomena and direction for the design of materials. On the other hand, as long as the final product has a functional expression at the macro level, the structure of the elemental technologies from the nano-level to the macro-level as well as the overall combining of a variety of the available methodologies will become very important. For that reason, while making efforts to the development of materials in nano-level observation technologies, it is important to apply even more efforts into the development of understanding of phenomena that occur at the nano-level at the macro level.

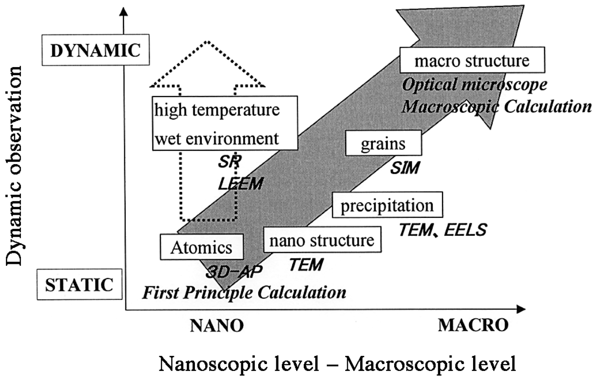

Fig. 6 Future trend of nano-level materials characterization techniques

Although not covered in this special issue, the computational material sciences are also an important field of nano-level analytical means as a means for filling in gaps between the results of experiments and phenomena that actually occur. According to the first principle calculation, it is possible to obtain the final analysis without having to use parameters that are free. For that reason, nano-level can take us up to where it is limited number of atoms that can be handled, but now, where experimentation is already at the nano-level, it is believed that the hurdle is being lowered by combining the first principle calculating method with actual testing data. There are also direct calculation models for properties and characteristics such as point defects, dislocation, diffusion, grain movement, transformation, structural change, strain states, deformation, and forming. Thus, it is thought that there will be advancements to the understanding of materials that incorporate unified and dynamic changes from the nano-level to the macro level.

References

1) Sugiyama, M.: Shinnittetsu Giho. (359), 1 (1996)
2) Maruyama, N., Uemori, R., Morikawa, H.: Shinnittetsu Giho. (359), 6 (1996)
3) Ikematsu, Y., Shigesato, G., Sugiyama, M.: Shinnittetsu Giho. (381), 16 (2004)
4) Takahashi, J., Kawasaki, K., Kawakami, K., Sugiyama, M.: Shinnittetsu Giho. (381), 22 (2004)
5) Takahashi, J., Sugiyama, M., Maruyama, N.: Shinnittetsu Giho. (381), 26 (2004)
6) Sugiyama, M.: Electron Microscopy. 37(3), 167 (2002)
7) Shigesato, G., Sugiyama, M.: J. Electron Microscopy. 51(6), 359 (2002)
8) Hayashi, S., Fujioka, M., Yasue, T., Koshikawa, T., Bauer, E.: Application of PEEM/LEEM and Synchrotron Radiation to Nano Technology Research. 3rd Workshop of Nano Technology Support, 2003-8-8, Japan Synchrotron Radiation Research Institute (JASRI)
9) Kimura, M., Kihira, H.: Shinnittetsu Giho. (381), 77 (2004)