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Developments in Steel Characterization Techniques

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Abstract:

The history of development of ferrous materials is characterized by the technological challenge of producing desired bulk structures as represented by control of phase transformation and precipitation. Techniques for analyzing ferrous materials in an integrated manner from macroscopic to microscopic levels have been studied, and many state-of-the-art analytical techniques, especially on microscopy and spectroscopy, have been introduced and used. In the field of surface analytical techniques, previously unobservable structures and physical quantities have been rendered observable by atomic force microscopy and cross-section electron microscopy, in addition to conventional spectroscopy and X-ray diffraction. Atomic force microscopy and electron microscopy are also enabling the development of techniques for controlling the surface as well as bulk structures of ferrous materials. We have now reached the time when we must control the surface structure of ferrous materials more than ever in relation to oxides, such as scale and corrosion films, that exist in various forms on the surface of ferrous materials. This paper describes the way analytical techniques have been used in the past and the way they will be used in the future.

1. Introduction

The *sine qua non* of steel manufacturing is quality and efficient production. Technology development and production departments must work together toward this goal. Sharp quantitative and analytical capabilities have always been required to establish technology developed through experience or with the support of scientific facts. In this course, optimum analytical techniques have been nurtured in all departments and on all occasions, from production factories to research laboratories. To develop products with material properties properly controlled, and to establish processes with phenomena properly understood and controlled, we must use the latest analytical techniques. This is one role of the Materials Characterization Lab., where I work.

The viewpoint is that of material science. The perspective of analytical chemistry is not in the scope of this article. It also covers recent technical trends and future technical outlooks, focusing on the techniques studied by the Materials Characterization Lab. for analyzing microscopic regions in the bulk of materials and analyzing the surface of materials, including various types of coatings and corrosion films.

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2. Analytical Techniques for Local Regions

Many ferrous materials are polycrystalline, with grain sizes ranging from a few micrometers to a few hundred micrometers. It is common practice to examine the surface structure of ferrous

materials by optical microscopy, to investigate their grain-boundary properties by scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) in combination with sample fracturing methods, and to analyze their bulk structure and finer transgranular structure by transmission electron microscopy (TEM). The magnifications employed for the analysis of iron and steel samples are about 10 to 1,000× for optical microscopy, 500 to 10,000× for scanning electron microscopy, 8,000 to 100,000× for transmission electron microscopy, and 100,000 to 1,000,000× for recent high-resolution electron microscopy. These analytical techniques are used to perform systematic characterization on macroscopic metallographic structure to microscopic atomic-level structure. Analytical objects and analytical techniques are schematically illustrated in **Fig. 1** by focusing attention on bulk structures of materials. Most of the important factors in the development of new ferrous materials relate to improvements in strength and toughness. Thus, new products to meet market needs have been developed by controlling macroscopic bulk structures, such as textures, grain size and phase transformation, and by analyzing finer structures such as precipitates and dislocations.

The development of analytical techniques is in large part due to improvements in the spatial resolution of analytical instruments. Consequently, it is becoming possible to study grain-boundary phenomena, based on the results of analysis of grain-boundary segregation and atomic arrangement, and to analyze precipitates and atomic clusters of a few nanometers in size. Static bulk analysis has made remarkable progress. These changes in analytical techniques in recent years will be concretely described later with respect to electron microscopy, atom probe-field ion microscopy (AP-FIM), and synchrotron radiation X-ray diffraction. Some of these analytical techniques are discussed in greater detail in other articles in this issue.

Recently, the market has been demanding materials with better fatigue, fracture and rapid-deformation properties. Therefore, techniques of analyzing dynamic phenomena in materials will become more important, in the same manner witnessed in analytical techniques connected to spatial resolution. One must understand the movement of a dislocation on interface, as well as point defects on the atomic level. Several phenomena will be studied using *in situ* observation.

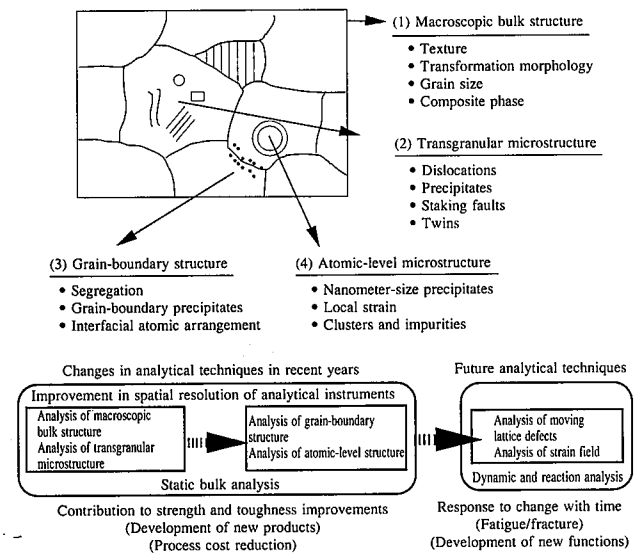

Fig. 1 Present and future analytical techniques for bulk of ferrous materials

2.1 Electron microscopy

Techniques for analyzing the composition and structure of fine precipitates made great progress with the appearance, three years ago, of a 200-kV electron microscope with a field-emission electron gun. Before that, the field emisson electron gun was used only for 100-kV transmission electron microscops. The 200-kV conventional field-emission transmission electron microscope had a great impact on the analysis of ferrous materials. An electron beam that provides nearly 1,000 times higher brightness than that possible with a conventional high-brightness lanthanum hexoboride (LaB_6) filament can be focused to 1 nm with good beam parallelism. As a result, the elemental analysis of 1-nm material areas and the formation of electron diffraction images from few-nanometer material areas is possible, as is high-resolution electron microscope observation.

What does a 1-nm analytical region signify ? One of the important issues with the analysis of ferrous materials is the quantitative analysis of the effective precipitates affecting their strength. Past studies suggested that when the interaction of precipitates with dislocations is taken into account, the most effective precipitate size is a few nanometers, the same as the size of dislocations. Since the highest resolution with which the structures and elements of practical materials could be analyzed by conventional electron microscopy was about 0.01 μm (or 10 nm), conventional electron microscopy could investigate only precipitates of a size slightly larger than that of precipitates for which it was expected to be effective. These issues were not fully solved. The appearance of the 200-kV field-emission analytical electron microscope has made it possible to analyze precipitates of the critical size and to obtain quantitative analytical data on the composition and structure of fine precipitates, such as transgranular niobium carbides, niobium nitrides and vanadium-bearing precipitates.

With quantitative analysis from 1-nm local regions, elemental distributions near the interface between fine precipitates and the matrix, as well as near the grain boundaries, can be measured. The conventional method of measuring the amount of grain-boundary segregation required a fractured sample along the grain boundary, and the amount of grain-boundary segregation was measured by Auger electron spectroscopy (AES) or secondary ion mass spectroscopy (SIMS). Thus, the ability to measure the amount of grain-boundary segregation directly without fracturing the specimen marks a technical breakthrough. The field-emission analytical electron microscope is described in detail in another article in this issue.

As a result of the progress in electron microscopy discussed above, the high-resolution imaging technique[1] has come to be used for practical materials on a routine basis. With high-resolution imaging, an electron beam is transmitted through a sample measuring a few tens of nanometers in thickness. Transmitted waves and diffracted waves interfere with each other, and the periodicity of the crystal lattice array in the region of interest is obtained as an atomic-scale image. High-resolution imaging is a technique for investigating actual atomic arrangement. The atomic arrangement within precipitates and at the interface between the precipitate and matrix, and crystal lattice coherency at the grain

boundaries, among other phenomena, can be examined. When the high-resolution imaging technique is applied to practical materials, computer simulation is especially important in interpreting the high-resolution images. The multi-slice method is a representative image calculation method. An actual sample is assumed to be a stack of very thin slices (measuring a few Angstroms each). The phase change of the electron beam as it passes through the specific thin slices is sequentially taken into account, and the final image contrast is calculated. At present, the multi-slice method has been perfected to a high degree and is under round-robin test to minimize discrepencies in calculation results between different research institutes. Nippon Steel is planning to use the multi-slice method.

Along with the technology improvements in electron microscopes themselves, the new technology of storing electron microscopic images using imaging plates has recently gained notice. The imaging plate is beginning to be used in not only the field of electron microscopy but also the field of X-ray diffraction. It has the nature of semi-digital processing and has been substantially improved in dynamic range with respect to strength, making it easier to quantitatively analyze electron diffraction and images. The imaging plate technique has made it possible to quantify electron diffraction spot intensity, diffuse scattering intensity around electron diffraction spots, and to analyze complicated structure change with phase transformation[2].

The sample stage of an electron microscope may be used as a mini-laboratory. The *in situ* observation of the phase transformation process at high temperatures, fatigue testing in the electron microscope, and *in situ* observation of the crystal growth mechanism at the atomic level are adopted again as analytical techniques. Nippon Steel has used these methods for 30 years and investigated the γ-α phase transformation and the movement of dislocations during tension testing under a 1,000-kV ultrahigh-voltage electron microscope capable of observing thick-film samples. The latest in electron microscopy will be developed using the concept of the mini-laboratory.

2.2 Atom probe field ion microscopy (AP-FIM)

The field ion microscope is a microscope complimentary to the electron microscope. Nippon Steel introduced an atom probe field ion microscope 12 years ago to observe the distribution of individual atoms composing a precipitate or cluster, to analyze their composition using a time-of-flight mass spectrometer, and to identify the species of atoms. These findings proved helpful in the development of fire-resistant steels and high-strength wire steels. For the observation, a needlelike sample is prepared from the bulk of the material by chemical polishing or electropolishing. High voltage is applied to the tip of the needlelike sample to obtain atomic-scale information on the material. Atom probe-field ion microscopy (AP-FIM) is an especially effective analytical technique when fine precipitates or clusters are uniformly distributed in the sample. The structures of fine precipitates had been analyzed primarily by the atom probe-field ion microscope, until the appearance of the above-mentioned field-emission transmission electron microscope[3]. Since the details of the atom probe-field ion microscope are reported in another article in this issue, I describe its technical advances briefly here.

An Oxford University research group has recently developed a position-sensitive detection atom probe[4]. Formerly, imaging of the two-dimensional atom distribution and the composition analysis of each atom were obtained separately. The position-sensitive detection atom probe has made it possible to simultaneously measure the composition of each atom species and its imaging as a two-dimensional map at the atomic level. Moreover, atomic arrangement in three-dimensional space can be reproduced by field evaporating atom layers one by one in the surface of the needlelike sample and processing the stored data by computer. The position-sensitive detection atom probe is a truly monumental technique.

At present, the position-sensitive detection atom probe lacks in mass resolution because the flight time of atoms relative to the accuracy of mass analysis is short, and the amount of energy loss caused during field evaporation cannot be compensated for. These shortcomings limit the number of practical materials that can be analyzed by the position-sensitive detection atom probe[5]. Now that technology to improve the shortcomings is functional at the laboratory level, it is considered certain that a three-dimensional atom probe will become a new powerful tool in the field of ferrous materials in the near future. In other words, the time will soon come when the composition and spatial distribution of clusters of a few atoms each can be elucidated, and when the amount of impure elements in solid solution and the three-dimensional abundance distribution of impure elements in crystals can be imaged.

2.3 Analysis of structures by synchrotron radiation

Nippon Steel makes aggressive use of one of the synchrotron radiation beam lines at the National Laboratory for High Energy Physics in Tsukuba. It also investigates ferrous materials through *in situ* observation of recrystallization behavior and other phenomena by using high-brilliance and high-intensity white X-rays, in addition to using the techniques accumulated through the conventional X-ray diffraction method. This research is reported in another article in this issue. The extended X-ray absorption fine structure (EXAFS) contained in fluorescent X-rays from a trace element can be examined to analyze the local structure around the trace element. The EXAFS technique has been applied to the structural analysis of trace precipitates in steel in recent years.

For example, the initial size of copper precipitates in steel is 1 to 2 nm. These ultrafine copper precipitates have been difficult to analyze structurally. When the fluorescent EXAFS of precipitate copper atoms was analyzed, it was found that copper, which originally has a face-centered cubic structure, has the same body-centered cubic structure as a matrix of steels[6]. The complementary laboratory use of the EXAFS technique, exploiting the characteristics of synchrotron radiation, with the X-ray diffraction technique is expected to lead to new X-ray structural analysis techniques.

3. Analytical Techniques for Surface Layers

Principal requirements for the surface analysis of ferrous materials are related to sheet steel surface layers, such as metal and organic coatings on coated sheet steels; surface films like scale and corrosion films; and surface segregation and precipitates. These analytical objects and techniques are summarized in **Fig. 2**.

The surfaces of ferrous materials have been traditionally analyzed by X-ray diffraction and representative surface analysis techniques like Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and glow discharge spectroscopy (GDS), to analyze the structure and composition of surface coatings, to analyze surface

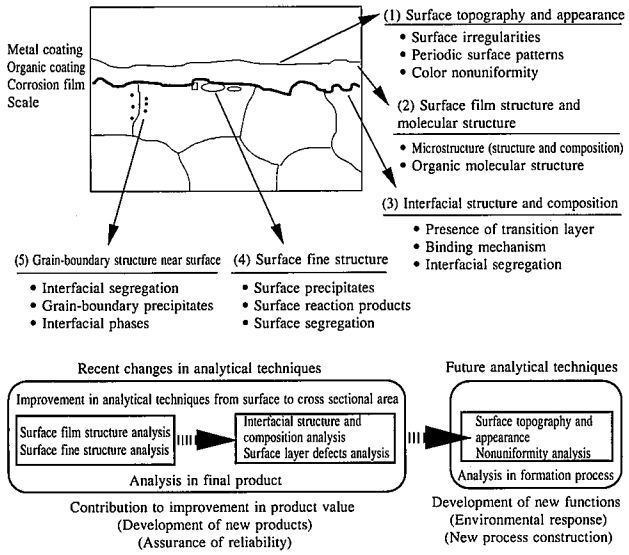

Fig. 2 Present and future analytical techniques for surface of ferrous materials

segregation elements, and to identify surface precipitates. Infrared spectroscopy (IR) and Raman spectroscopy have also been used to identify the phase of crystals and the species of molecules comprising coatings.

Particularly in recent years, techniques to analyze not only from the surface but also in the cross-sectional direction have progressed, with the result that structural and compositional analysis near surfaces is becoming possible. These surface analytical techniques play an important role in substantiating, from the standpoint of analytical science, the excellent functions of ferrous materials as end products. Methods of observing samples in the cross-sectional direction by electron microscopy will be described later.

Progress in cross-sectional analytical techniques for the surface of materials in recent years, along with improvement in the spatial resolution of analytical instruments, has made it possible to analyze the surface structure of materials at the same microscopic level the bulk structure of materials are analyzed at. However, cross-sectional analytical techniques are mainly concerned with the static state of materials surfaces. In the future, we expect advances in techniques for dynamically analyzing the process whereby the surface structure, coating, or film of a material is constructed. If the formation process of a metal coating, oxide film, or corrosion film is analyzed, causes of structural heterogeneity in the metal coating, oxide film, or corrosion film can be clarified. Formation and disappearance of interfacial reaction phases can also be studied microscopically. The present GDS technique will be described later in connection with the rapid analysis of nonuniform element distribution in the surface of materials. These analytical techniques are expected to lead to the development of technology for imparting new environmental response functions to materials required by the times, as well as to highly efficient process technology for controlling heating of, or heat extraction from, the surface of materials.

3.1 Techniques for observing cross-sectional structure by electron microscopy

If an electron beam is transmitted through a sample, not from the surface but laterally, the structure of a surface layer of a few micrometers in thickness on ferrous materials, such as a metal coating, corrosion film, or oxide film, can be analyzed to a high degree by using conventional transmission electron microscopy (TEM). To this end, the sample must be thinned to about 0.2 μm a thickness through which the electron beam can pass without destroying the surface structure of the sample.

For observation with high resolution or analysis with high accuracy, samples must be thinned to tens of nanometers. In this case, the sample preparation technique employed is a key point. Main sample preparation methods are 1) cutting a thin sample with a microtome, 2) the cross-sectioning method, 3) the micromachining method with a focused ion beam (FIB) thinner.

The cross-sectioning method is schematically illustrated in **Fig. 3**, and a cross-section TEM micrograph of a sample thinned by the cross-sectioning method and near the interface between a corrosion film and steel sheet is shown in **Photo 1**. The cross-sectioning method has progressed as a technique for structural

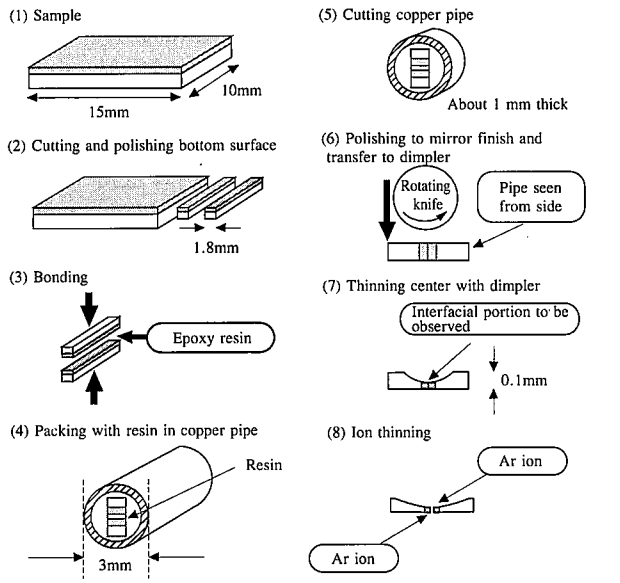

Fig. 3 Electron microscope sample preparation procedure for observing cross-section microstructure

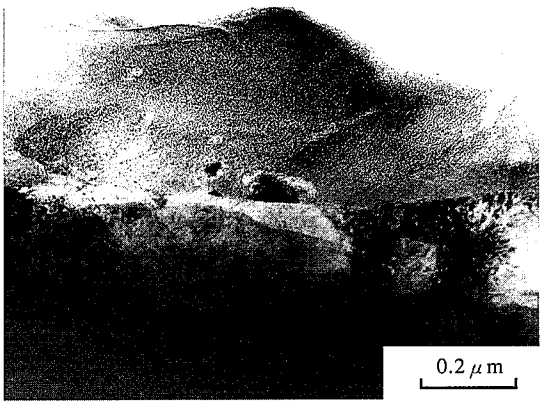

Photo 1 Cross-section TEM micrograph of interface between corrosion film and steel sheet

analysis in the field of large-scale integrated semiconductors. It is routinely used for silicon, but has been rarely applied in the iron and steel field. This fact reveals the difficulty of thinning the area of the interface between an irregular-surfaced metal and a brittle corrosion film to a thickness of a few tens of nanometers. The FIB method is characterized by thinning the sample with a gallium ion beam while observing the thinned area of a sample. Kuroda and Saka have succeeded in simultaneously thinning the interface between the metal coating and the sheet of a coated sheet steel using the FIB method and have reported the high-resolution TEM observation of the interface region[7].

The FIB method semi-directly produces a thinned region in the sample under observation. In the near future, it will be possible to thin a microcrack area of steel and a pitting corrosion region of a surface. More and more such sample preparation techniques will be studied for electron microscopy, and techniques for analyzing the fine surface structure of materials will advance further.

3.2 Glow discharge spectroscopy (GDS)

Glow discharge spectroscopy (GDS) is highly conventional in that the distribution of the composition in the depth direction from the surface of materials can be rapidly obtained. The analytical region is usually about 4 mm in diameter. Since the analytical region is sputtered almost at a time, it is advisable to think that the average composition is measured there. Since the mainstream GDS technique uses direct-current (DC) voltage, its samples generally were conducting solid samples in the past. In recent years, high-frequency discharge GDS has been practically applied. GDS can now be applied to thick insulating coatings and films as well and is finding use in many other applications.

Suzuki and his coworkers[8], for example, showed that GDS can very stably determine the composition of a coating film of about 30 μm thickness on a prepainted sheet steel for refrigerator outer panels. They also reported that a titanium pigment-based organic paint film was applied to a chromate-preplated and zinc-coated sheet steel. Sufficient quantitative determination capability is now confined to the DC voltage GDS technique, but the high-frequency discharge GDS technique is expected to acquire sufficient quantitative determination capability in the near future.

GDS excels in that the elemental distribution of a region of about 4-mm diameter in the depth direction can be determined in a few minutes. Application techniques for GDS are expected to appear as techniques for analyzing the nonuniformity of surface topography. If the discharge phenomenon taking place during measurement is understood more, GDS may evolve as a totally new concept of rapid analytical technique.

3.3 Scanning probe microscopy

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have made rapid progress in recent years. They can measure surface phenomena in atmospheric and aqueous solutions and have been used for the *in situ* observation of initial grain-boundary corrosion in stainless steel, and in the observation of initial pitting corrosion in stainless steel[9]. The local distribution of frictional force, distribution of electrostatic force, distribution of hardness, and distribution of magnetic force can be obtained as mapping images by attaching various probes to the tip of the atomic force microscope. Since it was difficult to determine these distributions from practical materials, this mapping technique is expected to find increasing use in many applications.

Besides the observation of various physical quantities in the surface of materials, nanometer-level physical properties in the surface of materials can be precisely measured to provide a more advanced approach to the clarification of the atomic-level mechanisms of phenomena, or to the presentation of design guidelines for new material functions. For example, adhesion is a basic phenomenon that governs the functions of material surfaces, such as stain resistance, adherence and slipperiness. The technique of measuring the atomic-level adhesive force between the tip and the sample is studied as a special application of the atomic force microscope. Since the adhesion phenomenon between a given material and its substrate can be quantitatively measured by coating the tip with the material, this technique is expected to develop further in the future.

The microscopes described above are covered by the generic term "scanning probe microscopy." Applications for scanning probe microscopy are increasing rapidly. Scanning probe microscopy will prove useful in analyzing the formation processes of various phenomena because it can yield information from macroscopic force distribution to atomic-level surface topography and can observe such phenomena *in situ*.

4. Conclusions

This article has summarized the past trends and future outlooks of analytical techniques for surface and bulk analysis of ferrous materials. Specific examples, centering on electron microscopy, have been briefly described as they relate to the improvement of spatial resolution in conventional analytical techniques and the development of new analytical techniques. There are many similar examples for spectroscopy and X-ray diffraction, but such cases are not discussed in detail here, because I specialize in electron microscopy.

To enhance the competitiveness of products in the steel industry, with its severe present conditions, we must analyze each product down to the physical properties of the material from which it is made. To achieve cost savings in steel production processes, we must quantify phenomena taking place at each step of the production process and make necessary improvements. The latest in analytical techniques are required for these purposes, and I hope that they will be helpful in accomplishing our purposes.

As discussed above, it is especially important to develop analytical techniques that can dynamically observe materials at the microscopic level and follow change over time in the growth and formation processes of materials. As many of the electron microscopes and other surface analysis instruments discussed here advance further with incorporation of the latest electronics technology, the theoretical substantiation of analytical techniques will assume increasing importance. It will be necessary not only to improve the capability of analytical instruments but also to use analytical techniques with the full understating of the materials to be analyzed. These activities will give us the chance to find new phenomena overlooked in the past and develop new ferrous materials to support the next century.

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