NIPPON STEEL TECHNICAL REPORT No. 91 January 2005

UDC 620 . 187

Pinpoint Microstructure Characterization Technique by Transmission Electron Microscopy

Masaaki SUGIYAMA*1 Genichi SHIGESATO*1
Yoichi IKEMATSU*1

Abstract

The advancement of transmission electron microscopy has made it possible to analyze the metallographic structure of steel products on a nanoscopic scale, which leads to the detail understanding of microstructures such as fine precipitates and grain boundaries. The application of the characteristic technology to commercial steel products requires consistency in the structural analysis of steel from a macroscopic to a nanoscopic scale. As a solution, a technique for pinpoint analysis of ultra-fine structures of steel has been established through the combination of the focused ion beam technique with a manipulator that can work in a focused ion beam device. Microstructural analyses of a galvannealed coating surface and an intragranular precipitate that triggers phase transformation are described herein as examples of the application of the established technique to commercial steel products. These examples show the effectiveness of the developed technique in solving problems of coating surface quality and refining the metallographic structure of welded joints through a nanoscopic material design approach.

1. Introduction

Steel products are produced through sophisticated and delicate control of rolling and heat treatment processes, and exhibit excellent mechanical properties in large structures several meters or more in size. From a metallographic viewpoint, however, a steel product having a macroscopically homogeneous structure is often composed of complex, localized microstructures. The reason is that even when a steel slab is water cooled after hot-rolling, for example, cooling rates differ between a surface area and a middle part of the slab. As a consequence, the localized structures obtained are not the same. It is not difficult to imagine that such minute microstructural differences are likely to have a significant influence on the strength deterioration characteristics of the steel material and the properties related to those phenomena, the occurrences of which are governed by the local inhomogeneity, such as corrosion and fatigue properties.

Steels used as the materials for a wide variety of infrastructures are designed to obtain a metallographic structure having high potential in a macroscopic scale, while the local metallographic in homogeneity admittedly is inevitable. Transmission electron microscopy that has been brought to the present level of advancement is widely employed as a tool for metallographic analysis in aspects such as clarifying the basic principles of the phenomena that determine the strength properties, fatigue and corrosion resistance and other properties of steel as well as in the quality assurance of steel products. Transmission electron microscopy has come to be employed for various purposes, especially due to its capability of structural character-

*1 Advanced Technology Research Laboratories

ization and elementary analysis by focusing an electron beam on an area of a nanometer size[1]; thus it has contributed to clarifying the essential properties of steel materials.

On the other hand, as atomic-scale analysis techniques such as the above are more widely employed, it is important that the area of an object or the phenomenon observed is really related to the macroscopic properties of the whole material. One nanometer is one millionth of a millimeter, and a commercial steel product cannot be correctly evaluated or characterized unless it is ensured that a phenomenon observed under an electron microscope is consistent with a phenomenon millions of times larger.

As transmission electron microscopy has advanced, the above issue, which is called scaling, has become increasingly important in the study of commercial steel products. In view of this, the authors have concentrated efforts over the last years on the development of a technique for selecting portions to be observed by transmission electron microscopy and as a result, established a new method for fabricating samples for electron microscopy using an ion beam and another for preparing samples using a micro manipulator. The basic principles of the analytical devices for the developed techniques are the same as those of the ultra-fine fabrication techniques in the field of semiconductor production. Taking account for the difference between the semiconductor material and steel, a multi-purpose, pinpoint microstructure characterization technique has been established. This paper describes the essential points in the development of the pinpoint microstructure characterization technique for steel materials.

2. Focused Ion Beam Fabrication Technique and Applications of Scanning Ion Microscopy

Conventionally, samples for transmission electron microscopy were prepared mainly by methods such as electropolishing, microtome and argon ion milling[2]. In preparing samples for observing the structure of a surface treatment film, a corrosion product layer, or the like from a sectional direction, it was necessary to prepare samples using a cross section method wherein two specimen sheets were laminated with the object surfaces against each other and sectional thin-film samples were cut out by argon ion milling. In the previous special edition of Nippon Steel Technical Report for analysis technologies, the authors pointed out that sectional structural analysis and dynamic structural observation would become essential as the next-generation technologies for structural characterization of steel products[3]. In the course of technical progress thereafter, an innovative sample preparation technique, called the focused ion beam (hereinafter referred to as FIB) method, came to be widely employed in the field of semiconductor production[4], and the development of the application of the method to commercial steel products had began.

Firstly, attention was focused especially on the advantage of the FIB method that thin-film samples of either oxide or organic matter could be prepared together with base material steel sheets. An aim was to develop an analytical technique for the sectional structure of the coating layer of surface-treated steel sheets and the complicated surface layers of steel products covered with high-temperature oxides, such as scale, and/or corrosion products. **Fig. 1** schematically shows a trench-shape machining method using a Ga ion beam to fabricate a sample for observing a cross sectional microstructure. Irradiating a Ga ion beam normally to a surface of a sample sputters iron atoms according to the principle of sputtering and causes collision cascades within the sample and as a result, the sample is machined on an atomic scale. The rate of grinding of iron is approximately 0.2 μm^3/s. Since neutral atoms and secondary electrons are emitted from the sample surface during the working, one can obtain a scanning ion micrograph by detecting mainly those electrons having energy equivalent to that of the secondary electrons and having them synchronize with a scanning ion beam.

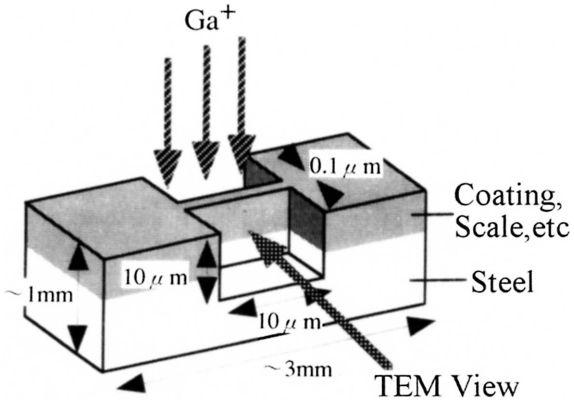

Fig. 1 Schematic diagram of focused ion beam fabrication

This method permits structural observation in the same manner as with a conventional scanning electron microscope (SEM). Since the ions irradiated are Ga ions, which are heavier than electrons, their penetration depth is small, that is about 3nm. As the result, the contrast obtained is mainly channeling contrast, which is sensitive to a change of slight crystal orientation. Thus, the method has an advantage of easily identifying objects such as crystal grains of polycrystalline iron, which do not show clear contrast under a SEM.

Photo 1 shows an example of three-dimensional structural analysis using scanning ion microscopy. In the steel making processes, internal oxidation often occurs to steel materials with a high content of Si during the hot rolling and its coiling at intermediate temperature. It is important for process control to know what kind of internal oxidation layers form in a steel material. Photo 1 is a series of

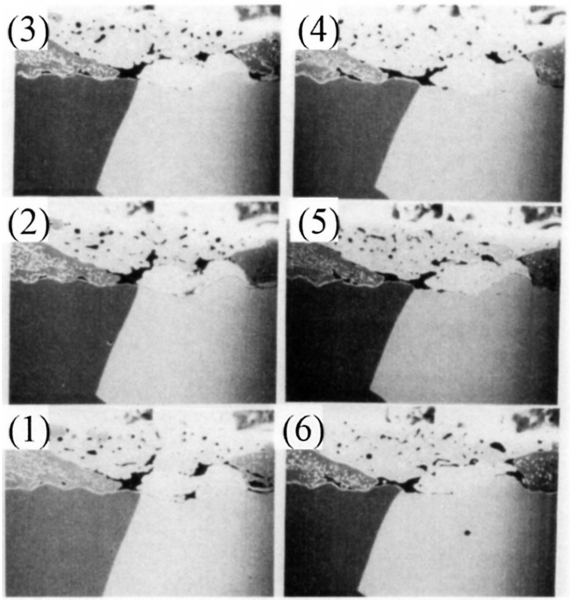

Photo 1 Continuous scanning ion micrographs showing the microstructure of internal oxidation near a steel surface. Cross sections from (1) to (6) are fabricated by a width of 1μm.

sequential photographs of cross sectional microstructures of a steel material that has undergone internal oxidation near a grain boundary at a subsurface layer. Oxide, which is lighter than steel, emits less secondary electrons because of the deep entrance of Ga ion, and it appears dark in the photographs; the black spots in the photographs are internal oxidation layers. Each photograph was taken as layers, each approximately 1 μm thick, were sliced perpendicular to the observed surface using a Ga ion beam.

Parts (1) to (6) of Photo 1 clearly show an oxide layer having an ameba-like shape that has developed at a triple boundary point. These are continuous sectional photographs, and when the images are reconstructed on a computer, the shape of the oxide layer can be visualized three-dimensionally. The same method can be applied not only to internal oxidation layers but also to precipitates inside steel, cracks near a surface and so forth in a similar manner. Thus, the application of FIB technology is making it possible to investigate the structures of specific portions of a steel material three-dimensionally, if locally.

3. Establishing Micro-sampling Technique Suitable for Magnetic Materials

In addition to being effective in observing the microstructure of steel materials three-dimensionally, the FIB technology has another advantage in that it makes it possible to cut out thin samples, of substantially even thickness, of composite materials such as steel containing intermetallic compounds or other inorganic material without any significant difference in sputtering efficiency. However, it was found that while the application of the technique as it was to steel materials was highly effective in observing the microstructure of steel at specific portions, the technique was subject to some restrictions in relation to analytical electron microscopy.

One of the restrictions was due to the magnetism of steel materials. Since the correction of astigmatism of an electron microscope became very difficult because of the strong magnetism of steel, the electron beam could not be focused on an area 1 nm in diameter and as a consequence, the capacity of the analytical electron microscope could not be fully realized. What is more, it was known that in elementary analysis by energy dispersive X-ray spectroscopy (hereinafter referred to as EDS), the emission of characteristic X-rays from thick portions other than the thin sample portion could not be prevented and thus, the quantitative accuracy of the analysis became questionable[5]. In view of the above, as a technique making the most of the advantages of the FIB technology, the authors focused attention on a new method of sample preparation using a manipulator inside a FIB device[6]. This method is generally known as the micro-sampling method.

Photo 2 shows the procedures for cutting out a sample using a manipulator. Parts (a) and (b) of Photo 2 show the steps to form a protective film of tungsten (W) on a prescribed area approximately 4 μm wide and 10 μm long for the purpose of examining the microstructure of a surface layer of a steel material that has a variety of structures microscopically. Because one can select a desired area while observing the structure, microscopic analysis can be interrelated with a macroscopic phenomenon (structural anomaly) at this stage. After the W film is formed, trenches are cut around it.

Part (a) of **Photo 3** is a scanning ion micrograph of the specimen seen obliquely at this stage. The sectional structure of the sample, the grain boundary shapes in this case, can be clearly seen and the change of material structure can be examined in detail in a micrometer scale already at this stage of rough machining. After that, the

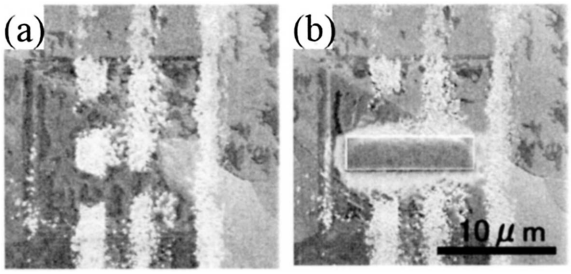

Photo 2 Scanning ion micrographs indicating the W protective layer deposition process
(a) Interesting surface morphology of steel and (b) A W protective layer deposited on the surface by the FIB method

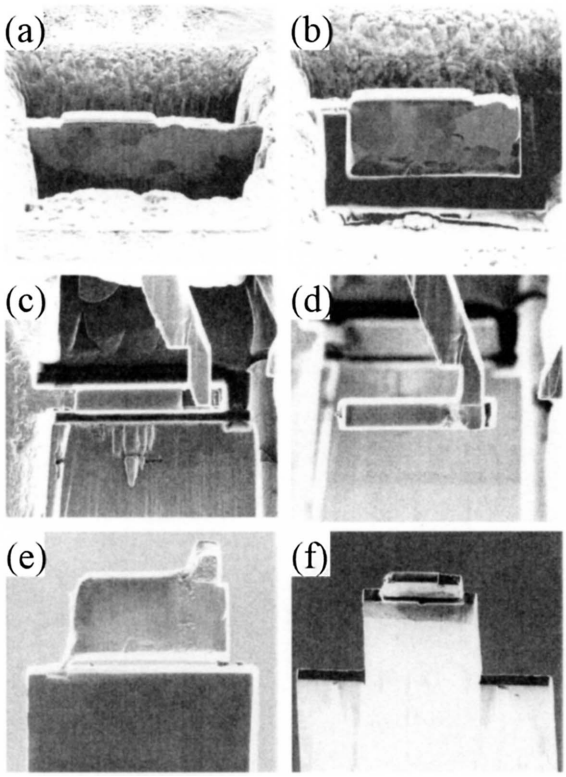

Photo 3 A series of scanning ion micrographs showing the micro-sampling process
(a) First fabrication of surrounding areas of the target, (b) A tiny suspended sample is prepared, (c) Bonding a manipulative needle to the sample, (d) Picking up the sample, (e) Setting the sample onto a TEM sheet, (f) Final fabrication of the extracted sample

ends of the sample to be cut out are machined, its bottom is cut off the base material to form a suspended piece supported by a small bridge at an end as seen in part (b) of Photo 3. Then, a manipulator is attached at a side of the W protective film as seen in part (c). The manipulator is bonded to the sample by sublimating crystalline $W(CO)_6$ at approximately 60˚C, blowing its gas to the bonding position and then scanning the position with a Ga ion beam. A vapor-phase chemical reaction takes place at the position and atomic W deposits there in the form of an amorphous film to exert bonding and protecting effects.

Then, the micro sample extracted from the base material steel sheet is lifted up by the manipulator as seen in part (d), and is set on

a separately prepared support sheet for electron microscope observation as shown in part (e), and its base is bonded to the sheet also with a W layer. Part (f) of Photo 1 is an oblique view of the sample set on the support sheet. There are various types of support sheets according to the object of observation; the sample shown in part (f) is set on a thin sheet in order to suppress the strength of the spurious X-rays that would result from X-ray irradiation to side walls during EDS analysis. Finally, the center portion of the sample is ground by FIB milling into a thickness suitable for transmission electron microscopy. Since the sequence of work steps for sample extraction takes only a few hours and the final finishing is completed within an hour, the micro sampling method is effective also in reducing the heating of a sample by an ion beam and other damages[7].

The application of the above technique to steel materials has made it possible to extract samples for transmission electron microscopy tens of micrometers in size directly from base materials some centimeters large. In addition, since the structure of a sample can be confirmed with a secondary electron image during the extraction work, a macrostructure observed through a light optical microscope or a SEM can be easily correlated with a nanoscopic structure observed through a transmission electron microscope (TEM) in a pinpoint manner. Thus, the consistency of structural analysis in a size range of one to a million is ensured.

4. Pinpoint Sample Preparation Technique and Nanoscopic Structural Analysis

The above pinpoint sample preparation technique has greatly advanced the possibility of analyzing various phenomena that influence the quality of a steel material. Some such examples are described hereafter. It is known that a great number of craters form at the surfaces of galvannealed steel sheets widely used for automobiles as a result of the alloying reactions of the zinc coating layers and the steel substrate. The craters are suspected to have many effects, both favorable and unfavorable: they serve as oil deposits and are of advantage in forming work, but when distributed unevenly, they cause surface marking adversely affecting surface quality. In view of this, the authors examined the mechanisms of crater forming using the pinpoint sample preparation technique[8].

Part (a) of **Photo 4** is a photomicrograph showing a general view of craters, and part (b) is a sectional micrograph of the structure at the position marked with X in part (a) taken with a scanning ion microscope. The portion between B_1 and B_2 corresponds to the bottom of a crater; where the small grains as those marked with A are not seen. Through analysis in combination with TEM observation, the small grains marked with A were identified as an Fe-Zn alloy phase (Γ phase), and it was made clear that the Γ phase did not exist at a crater bottom. Secondly, preparing electron microscope samples pinpointing crater bottoms and observing them under a TEM, the interface layer between an alloyed galvanizing layer and a steel substrate is an Fe-Zn alloy phase having stacking faults (δ phase) formed, as shown in **Photo 5**. The finding was the same with many craters. Since the Γ phase is formed at a late stage of alloying reactions, it is concluded that the crater area is made as a result of a delay in the galvanizing reaction.

Further, over a depth of several tens nanometers at the interface between the δ phase and the steel substrate, the authors confirmed the existence of Al atoms, presumably the vestiges of the decomposition of an Fe-Al barrier layer, which had formed at an early stage of galvanizing reactions, as shown in **Fig. 2**. These results also indicate that a delay in galvanizing reactions accounts for the formation of the craters as shown in **Fig. 3**. These findings have been applied to the quality improvement measures in the commercial production of the product.

Another example of the application of the pinpoint sample preparation technique relates to the crystal grain refining of welded joints. Utilizing oxides such as Ti_2O_3[9], Nippon Steel has found that ferritic structure was refined during the γ-to-α transformation, and studied the mechanism of the transformation from various viewpoints[10]. While it was essential to identify the kind of precipitate that served as the starting points of the ferrite transformation, all precipitates did

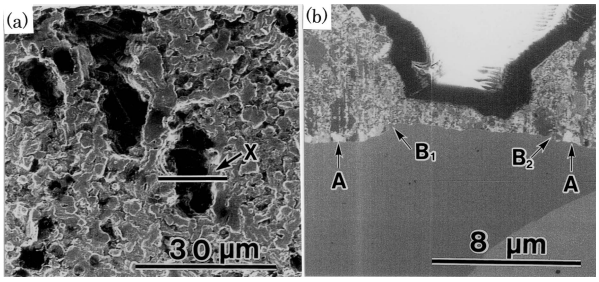

Photo 4 Morphology of craters formed on the galvanized steel observed by a scanning ion microscope
(a) The top view of craters, and (b) The cross-section view of the crater noted by line X in photograph (a)

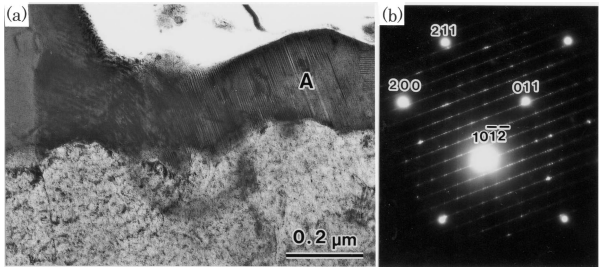

Photo 5 Transmission electron micrograph showing
(a) A bright field image of the cross-sectional microstructure around the bottom of a crater, and (b) The selected area diffraction pattern taken from the crystal noted A in the photograph. The diffraction pattern is identified to be the δ-phase.

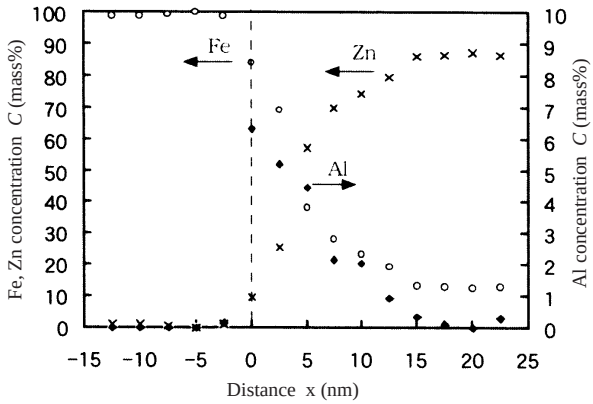

Fig. 2 Change of Fe, Zn and Al concentration along the interface between δ-phase and the steel, measured by EDS analysis. The positive values correspond to the distance from the interface to the galvanizing phase.

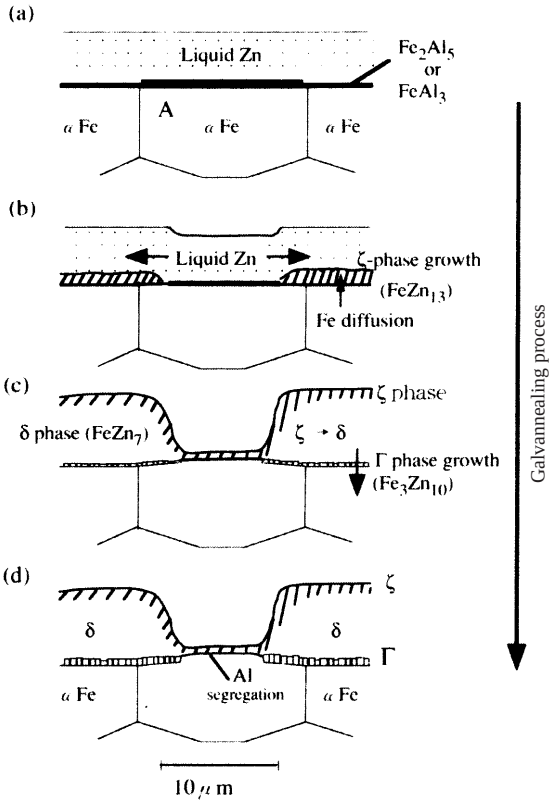

Fig. 3 Schematic diagram indicating the model for the formation of a crater during the galvannealing process

not necessarily serve as the transformation starting points, and it was impossible to randomly analyze a wide variety of precipitates dispersed in steel. The pinpoint analysis technique proved effective in this situation, and an observation technique was developed, whereby a precipitate that served as a transformation starting point was identified beforehand using a SEM and its sectional structure was observed using a TEM.

Photo 6 shows an example of the observation by the developed method. Part (a) of photo 6 is a scanning electron micrograph of a structure in which a crystal grain underwent intra-granular transformation into fine ferrite grains, with a precipitate serving as the starting point. Detail examination of the precipitate with a TEM revealed that it did not consist of a single phase but was a composite precipitate and it had a thin MnS layer. The authors focused attention on the interface between the MnS layer and ferrite, and carried out EDS analysis and as a result, it was found that there were Mn-depleted regions over a range of tens of nanometers in the ferrite grains, as shown in part (c) of Photo 6. The following model is inferred that, since Mn was a γ-forming element, the local decrease in Mn concentration raised the ferrite transformation temperature by tens of degrees Celsius and as a consequence, the transformation began preferentially near the MnS layer. The tests were repeated under different heat treatment conditions, estimated the formation of the Mn-depleted regions using quantitative calculation based on the diffusion behaviors of Mn and S in steel, and as a result, clarified that the Mn depletion was the principal governing factor of the intra-granular α transformation[11].

5. Closing

The establishment of the FIB sample fabrication technique combined with a manipulator and the scanning ion microscopy has made it possible to correlate the results of structural observation using conventional light optical microscopes or a SEM with the analysis technology using a TEM in a pinpoint manner. As a result, nano-scale material structure analysis technology has become applicable not only to steel material design in laboratories but also to the solution of various problems of commercial steel products, bridging the distance

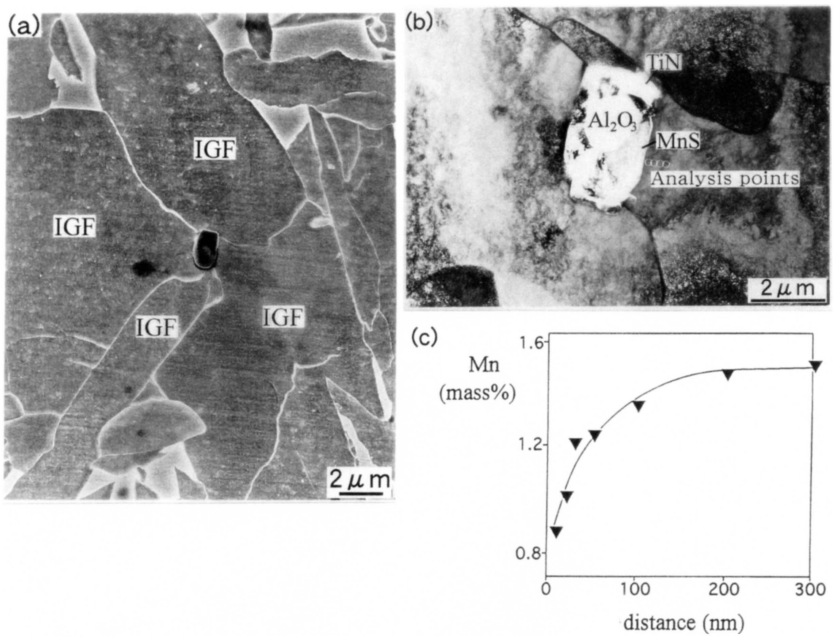

Photo 6 Characterization of the precipitate showing the intra-granular transformation
(a) Scanning electron micrograph of the precipitate and intra-granular transformed ferrites, (b) Cross-sectional transmission electron micrograph of the precipitate, and (c) The change in Mn concentration in a region near interface of MnS measured by EDS analysis

between fundamental research and field application studies.

What is expected now is to closely link field production technologies with fundamental technologies so as to materialize new findings obtained through nanoscopic analysis in new product development as quickly as possible as well as clarify various complicated phenomena that directly influence product quality from the viewpoints of fundamental research.

References

1) Maruyama, N., Uemori, R., Morikawa, H.: Shinnittetsu Giho. (359), 6(1996)
2) Nakai, K. et al.: Practical Electron Microscopy and Its Application to Materials. Maruzen, Tokyo, 2002, p.12
3) Sugiyama, M.: Shinnittetsu Giho. (359), 1(1996)
4) Ishitani, T.: Electron Microscopy. 32(1), 28(1997)
5) Saito, M. et al.: Jpn. J. Appl. Phys. 37, 335(1998)
6) Onishi, T. et al.: Proc. 25th Int. Symp. Testing and Failure Analysis. Santa Clara, 1999, p.449
7) Sugiyama, M.: Electron Microscopy. 37(3), 167(2002)
8) Sugiyama, M., Okada, M., Takada, Y., Suehiro, M.: Journal of Japan Institute of Metals. 65(5), 397(2001)
9) Ohkita, S., Wakabayashi, M., Homma, H., Yamamoto, H., Matsuda, S.: Seitetsu Kenkyu. (327), 9(1987)
10) Ogibayashi, S.: Shinnittetsu Giho. (351), 64(1993)
11) Shigesato, G., Sugiyama, M., Aihara, S., Uemori, R., Tomita, Y.: Tetsu-to-Hagané. 87(2), 23(2001)