NIPPON STEEL TECHNICAL REPORT No. 100 JULY 2011

Technical Report

UDC 543 . 51 : 628 . 44 : 546 : 27

# Development of FIB-TOF-SIMS Apparatus to Evaluate Suspended Particulate Matters

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## Abstract

***FIB-TOF-SIMS apparatus to evaluate a suspended particulate matter has been developed at JST Development of System and Technology for Advanced Measurement and Analysis "Apparatus for evaluating formation and dispersion history of single particle by focused ion beam and laser ionization techniques". A lateral revolution for scanning ion microscope observation is achieved about 10nm, and one for SIMS imaging is about 40nm. This technique is applied to evaluate the chemical states of boron whose leaching is strictly controlled by the regulation from the coal fly ashes, which have different elution characteristics. Boron exists at the top surfaces of fly ash particles which have higher leaching characteristic, and concentrates in the inner part of CaO-MgO particle, especially CaO, which have lower leaching characteristics. This technique can become very useful analytical technique for development of environmentally-friendly steel making process for sustainable development.***

## 1. Introduction

Suspended particulate matter (SPM) is an extremely complex compound that originates from various sources and is subject to change through a complex chemical reaction that takes place under the influence of the environment in which it exists. Therefore, as measures to grasp the actual condition of pollution by SPM and to control such pollution, improvement in the accuracy of dynamic analysis of SPM in terms of both time and space and analysis of historical information about individual SPM particles are strongly called for. In inductively coupled plasma mass spectrometry (ICP-MS) and gas chromatographic mass spectrometry (GC-MS), which predominate in environmental analyses today, pre-treating the specimen is essential since ionization has no material selectivity. This requires prolonged sampling to collect huge specimen volumes, so that it is virtually impossible to carry out elaborate dynamic analysis. We decided to seek, as part of a national project, a new technique that offers high lateral resolution sufficient for analyzing individual minute particles while allowing for nondestructive measurement of organic molecules that can adversely affect the human body.[1)] We made the above decision thinking that if we could develop such a technique, it would make it possible to clarify the causal relationship between a specific suspended particle and an organic molecule found on the surface of that suspended particle having a strong environmental impact and to shed light upon the history of the scattering of suspended particles.

## 2. Content of Technological Developments

Generally speaking, the average particle size of SPM is in the sub-micron to several microns range. Therefore, in order to clarify

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the composition of SPM and the distribution of each of the constituents of SPM, a high in-plane resolution of sub-microns is required. With secondary ion mass spectrometry (SIMS), it is only possible to obtain information on the surface layer (several atoms' thickness) of SPM.[2-5)]

On the other hand, by sectioning a particle in special equipment and analyzing the cross section by SIMS using the shave-off method developed by Sakamoto et al., it is possible to extract information on the particle interior as well.[6)] Thus, information about the source of SPM and historical information about SPM can be obtained at the same time.

It is considered that organic molecules that have a considerable environmental impact concentrate on the surface of SPM. Therefore, it is necessary to first make a nondestructive examination of the surface of the SPM, select particles of it, and then extract information about the organic molecules on the SPM particles.

So we planned to develop time-of-flight-type secondary ion mass spectrometer (TOF-SIMS) provided, as its probe, with a focused ion beam (FIB) that, in principle, permits detection of even extremely small amounts of organic matter with high sensitivity and with higher lateral resolution. In making a search of SPM particles, it is possible to irradiate an FIB onto the specimen and observe scanning ion microscope (SIM) images thereof. In this case, however, the organic matter on the particle surface would be destroyed by FIB irradiation. Therefore, we considered developing FIB-EB-TOF-SIMS apparatus provided not only with an FIB source but also an electron beam (EB) source that would permit observation of the same point on the specimen surface as the FIB.[7-9)]

In the present study, on the basis of our new idea of combining FIB and SIMS, we aimed to come up with a single-particle history analyzer that permits analysis of the chemical composition of SPM particles and the organic molecules on the surfaces of SPM particles that are unique to a specific environment and a specific place.

## 3. Performance of Experimental Apparatus

The experimental apparatus consists mainly of an FIB source, EB source, specimen manipulator, secondary electron detector, time-of-flight-type mass spectrometer (TOF-MS), and ultrahigh vacuum chamber. Before all these components were assembled into the apparatus, the performance of each of them was verified and improved as required in the process of fabrication. **Photo 1** shows the appearance of the FIB-EB-TOF-SIMS apparatus, and **Fig. 1** is a schematic diagram of the apparatus.

The TOF-MS is installed right above the specimen stage, and the EB and FIB are each positioned on either side at an inclination of 45° so that both the EB and FIB are focused on the same spot on the specimen.

### 3.1 Observation of EB- and FIB-excited secondary electron images

Observing secondary electron images is the most basic function in evaluating the beam diameter—the basic performance of the EB and FIB—and the vibration-proof capability of the entire apparatus. For the experimental apparatus, which was designed for local analysis of SPM in the environment, we strove to enhance the resolution of secondary electron images to the extent possible.

In addition to elaborate measures to prevent vibration of the apparatus, we took measures to reduce noise, such as covering the entire specimen stage inside the chamber with SUS sheet, since the noise from the noble pump to the secondary electron detector was very large.


**Photo 1 Photograph of FIB-EB-TOF-SIMS apparatus**

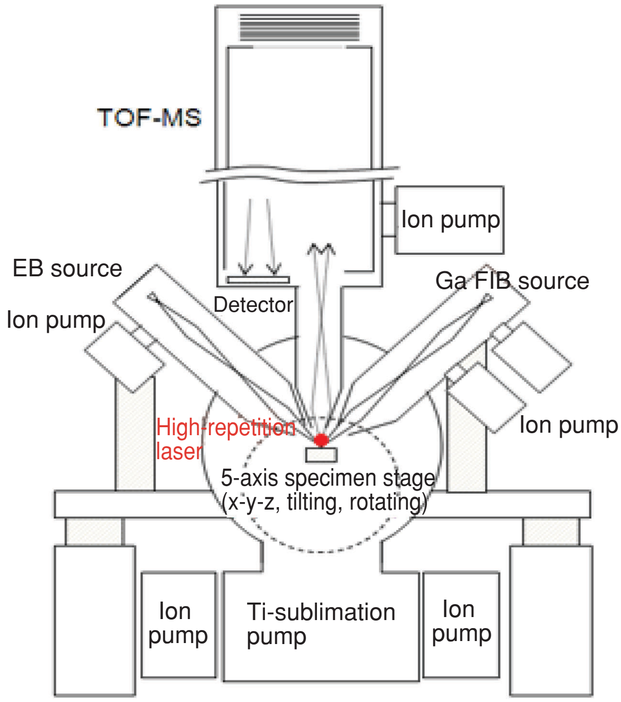
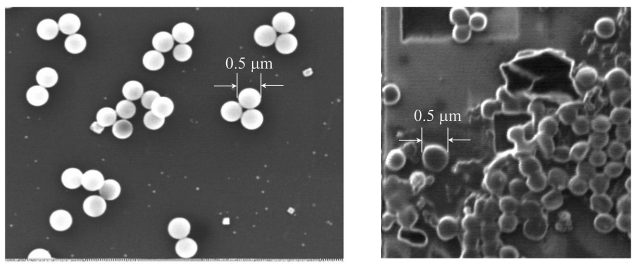



**Fig. 1 Schematic diagram of FIB-EB-TOF-SIMS apparatus**




EB-excited secondary electron image FIB-excited secondary electron image

**Photo 2 SEM image of standard micro-particles with 0.5 mm in diameter taken by electron beam and FIB**

After calibrating the magnification through observation of model particles, we measured the lateral resolution of the EB using a specimen prepared by vacuum evaporation of gold. The lateral resolution obtained was 13 nm. A comparison between an FIB-excited secondary electron image and an EB-excited secondary electron image shows that the lateral resolution of the FIB is nearly equal to that of the EB. Therefore, it may be said that the designed lateral resolution of 10 nm for the FIB was nearly attained. In order to verify the lateral resolution of the EB and FIB, respectively, we obtained EB- and FIB-excited secondary electron images of model particles having a diameter of 0.5 $\mu$m. As shown in **Photo 2**, both the EB and FIB gave clear images

### 3.2 Observation of the same particle by the EB and FIB

The EB and FIB sources are installed so that the EB and FIB irradiate the same spot on the specimen surface at an angle of 45° from opposite directions. Therefore, as long as the EB and FIB irradiate exactly the same spot on a flat specimen, it is possible to observe almost identical images (though they are mirror images) and directly observe the cross section of an FIB-prepared particle by the EB (see **Fig. 2**).

By improving the hardware to measure particles as described above, we established a new particle analysis technology. The process of particle analysis using the new technology is shown in **Fig. 3**. First, a particle is nondestructively sought using a secondary electron image (SEM). Then, the element distribution at the particle surface can be observed using the TOF-SIMS mass spectrum and imaging by a pulsed FIB. After that, the particle is sectioned by a DC FIB and the sectioned particle is eucentrically rotated 180° to obtain a

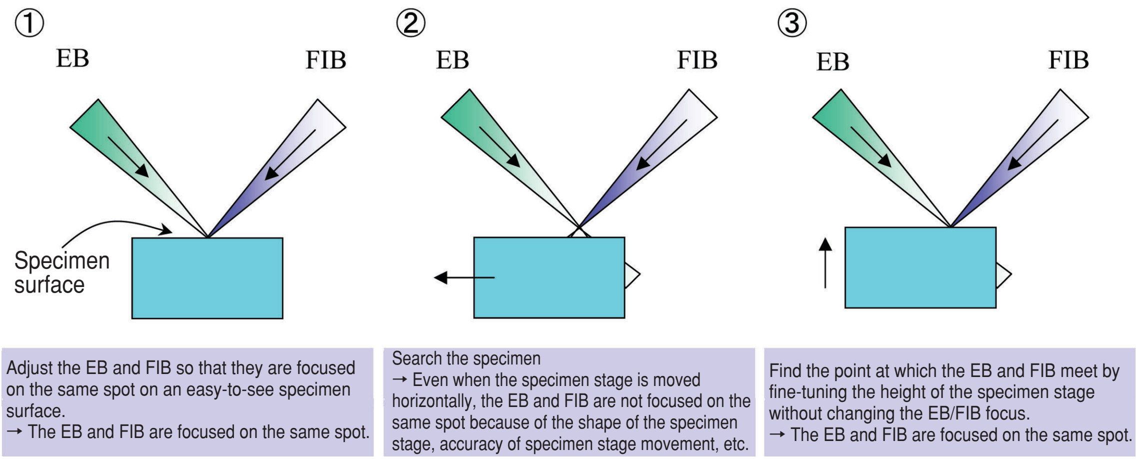



**Fig. 2 Observation procedure of specific area by both electron beam and FIB**

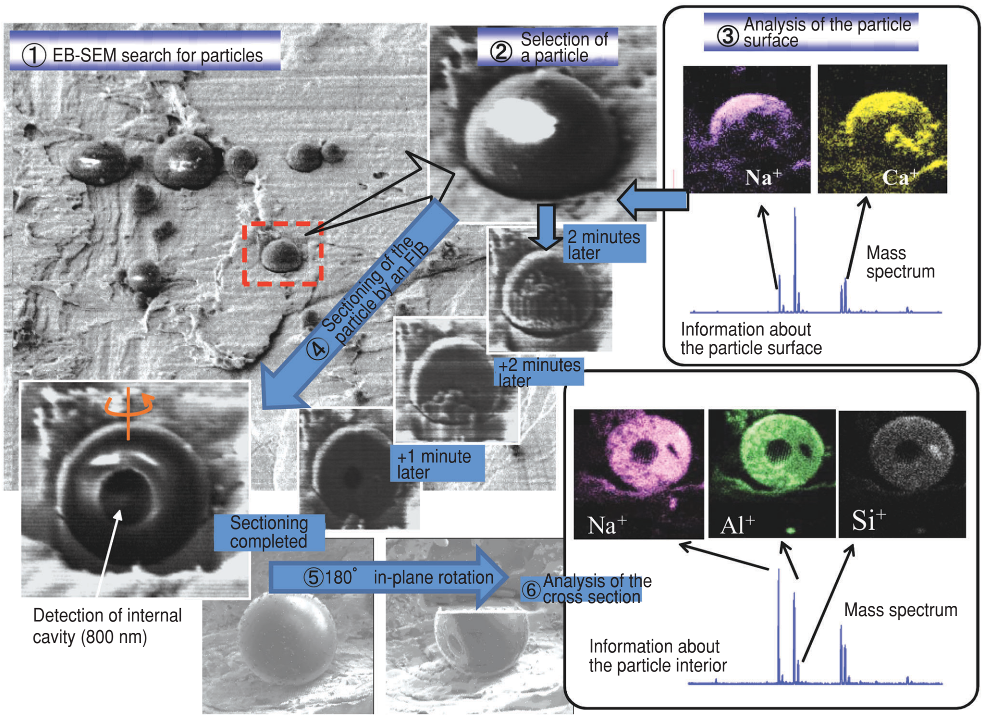



**Fig. 3 Analytical procedure of surface and inner part of a particle**

mass spectrum and a cross-sectional image of the particle using a pulsed FIB. It took about five minutes to cut the 2.5 $\mu$m particle in half. The lateral resolution of elemental imaging by SIMS that has been obtained so far is 40 nm.

By performing the above operation, it is possible to extract information about the distribution of elements in the surface and interior of the target particle.

## 4. Analysis of Coal Fly Ash[10, 11]

An example in which the newly developed apparatus was used to analyze an actual specimen is given below. The use of coal fly ash as a filling material, concrete admixture, pavement material, etc. has been steadily increasing. On the other hand, as a major factor that has impeded the rapid expansion of coal fly ash use, there is the problem of elution of environmental pollutants into the soil. According to the environmental standard, the allowable concentration of boron (B) in drainage in land areas is 10 mg/L. In many cases, however, there is no linear relationship between the concentration of B in coal fly ash and the amount of B elution into drainage. Therefore, finding how to restrain the elution of B is important. The above difference in elution behavior of B was considered due to a difference in how B exists in coal fly ash. We therefore attempted to clarify the mode of existence of B traces in coal fly ash by using the FIB-EB-TOF-SIMS technique in combination with the STMAS-NMR (satellite-transition magic-angle spinning nuclear magnetic resonance) technique.

Using the STMAS probe developed originally by Nippon Steel, we observed the mode of existence of Coal Fly Ash A (boron concentration 1,050 ppm, elution ratio 50%) and Coal Fly Ash B (boron concentration 540 ppm, elution ratio 17%), respectively. As a result, it was found that Coal Fly Ash A contained not only $Ca_3$(or $Mg_3$)$B_2O_6$ or $Ca_2$(or $Mg_2$)$B_2O_5$, but also Ca(or Mg)$B_2O_4$, whereas Coal Fly Ash B contained only $Ca_3$(or $Mg_3$)$B_2O_6$ or $Ca_2$(or $Mg_2$)$B_2O_5$ as the main boron-containing compound. Thus, the difference between the two types of coal fly ash regarding how boron exists was determined. Concerning these two types of coal fly ash, we attempted to clarify the correlation between the mode of existence and the behavior of elution on the basis of elemental images obtained by FIB-EB-TOF-SIMS.

### 4.1 Measurement using FIB-EB-TOF-SIMS

**Fig. 4** shows examples of the secondary ion images obtained by FIB-EB-TOF-SIMS. It can be seen that Coal Fly Ash B is largely divided into $Al_2O_3$-$SiO_2$- and CaO-MgO-based particles. On the other hand, Coal Fly Ash A does not clearly show any marked difference in particle composition.

**Fig. 5** shows the boron distribution at the surface of particles of Coal Fly Ash A and Coal Fly Ash B, respectively. In Coal Fly Ash B, boron was concentrated only on the surface of the CaO-MgO-based

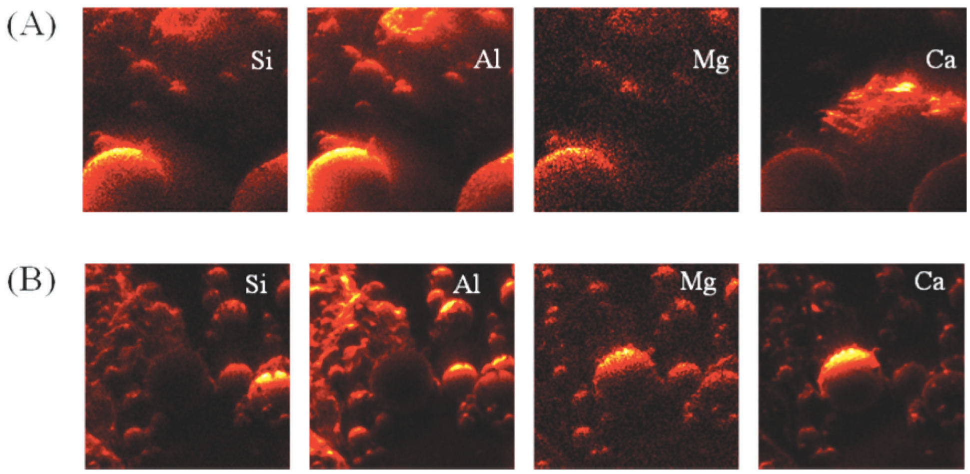



**Fig. 4 Elemental (Si, Al, Mg and Ca) SIMS images of Coal Fly Ash A (A) and Coal Fly Ash B (B)**

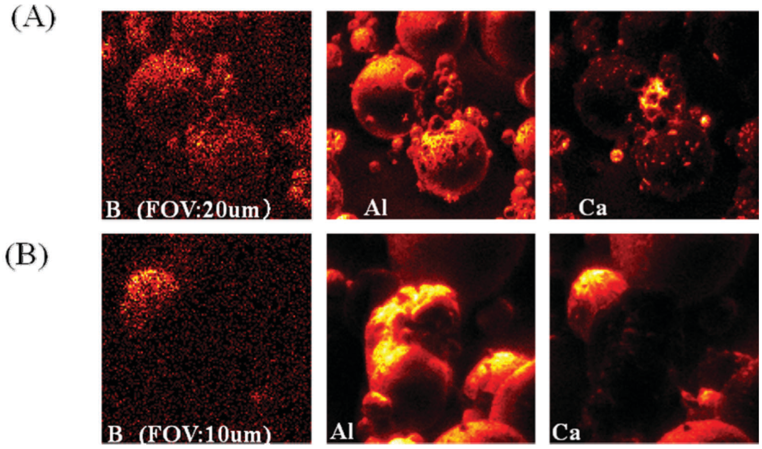



**Fig. 5 B, Al and Ca SIMS images of Coal Fly Ash A (A) and Coal Fly Ash B (B)**

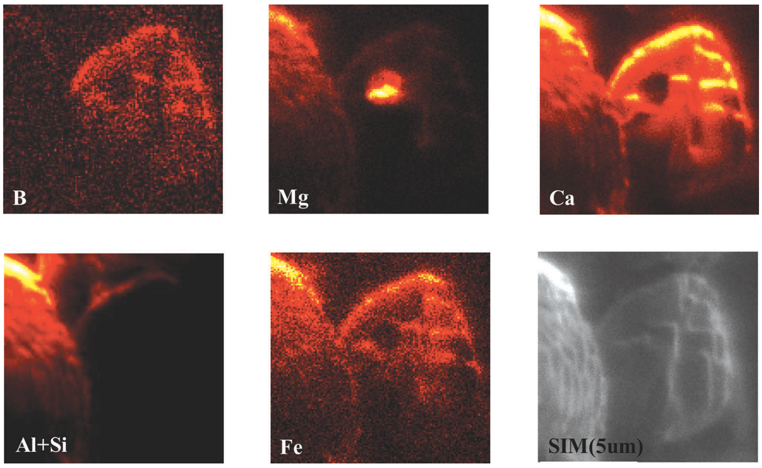



**Fig. 6 Cross sectional elemental SIMS images and SIM (Scanning Ion Microscope) image in Coal Fly Ash B**

particles, whereas in Coal Fly Ash A, boron was concentrated on the surface of every particle.

**Fig. 6** shows cross-sectional elemental SIMS images and an SIM (scanning ion microscope) image of Coal Fly Ash B. It can be seen that CaO and MgO separately form island structures within the CaO-MgO particles and that boron is selectively concentrated in CaO, together with Fe.

The high lateral resolution of 40 nm of the FIB-EB-TOF-SIMS equipment made it possible for us to obtain the above information for the first time. In addition, the mode of existence of boron, which cannot be determined by STMAS-NMR, was found to be either $Ca_2B_2O_5$ or $Ca_3B_2O_6$ from the fact that B coexisted with Ca. In the measurement using NMR, a very sharp spinning side band (SSB) was observed in Coal Fly Ash B. The SSB was found to have occurred at the site where B and Fe coexist.

As has been described above, we examined the mode of existence of boron in two types of coal fly ash with markedly different boron elution ratios using STMAS-NMR and FIB-EB-TOF-SIMS. In Coal Fly Ash A with a boron elution ratio of 50%, boron was concentrated at the surface of every particle. On the other hand, in Coal Fly Ash B with a boron elution ratio of 17%, boron was concentrated largely in the CaO-MgO-based particles, especially the CaO portion of those particles, in a selective manner. Therefore, we consider that in the boron elution test, the boron elution ratio of Coal Fly Ash A, with a considerable proportion of boron concentrated at the surface, was high, whereas that of Coal Fly Ash B was low, because much of its boron was concentrated in the CaO compound.

## 5. Conclusion

With the aim of extracting information about the history of scattering and the sources of suspended particulate matter, we developed apparatus to analyze the history of single particles using a combination of focused ion beam (FIB) and laser ionization as part of the Advanced Measurement/Analysis Technology and Apparatus Development Project under the Japan Science and Technology Agency (JST). The apparatus we developed is based on the secondary ion mass spectrometer (SIMS), the probe of which is an FIB used to prepare extremely thin specimens for electron microscopy. Thanks to the 40-nm-level lateral resolution attained by the FIB, the apparatus enables elemental mapping. In addition, the apparatus permits observation of the surface and interior of fine particles separately since their cross-sectional images can be obtained by an FIB. The particle interior provides information about the origin of suspended particulate matter (SPM), and the particle exterior provides clues to the history of scattering of SPM.

Through a national project, we have also studied laser post-ionization technology while developing a technology to detect trace amounts of organic molecules contained in gases.[12-17]

We have clarified the possibility of ionizing specific elements that have a large environmental impact and are implementing a highly quantitative, high-sensitivity elemental analysis by irradiating an ultraviolet laser beam on particles sputtered by an FIB.[18-23]

Furthermore, we have clarified the fact that laser ionization permits information to be obtained about the skeletal structure of organic molecules, which cannot be obtained with conventional SIMS.

Thanks to the development of the above technology, it became possible to obtain information about the origins of suspended particulate matter. We consider that by positively pressing ahead with the application of this technology in the future, we will be able to supply information of great importance in developing a new environment-friendly steelmaking process.

## Acknowledgments

We wish to express our heartfelt thanks to Prof. Masaaki Fujii of the Tokyo Institute of Technology, the project team leader, Prof. Tetsuo Sakamoto of Kogakuin University, the main co-developer, Dr. Shunichi Ishiuchi of the Tokyo Institute of Technology, and Prof. Takunori Taira of the Institute for Molecular Science of the Okazaki National Research Institutes for the generous advice and guidance they extended to us during this technological development.

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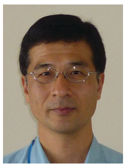


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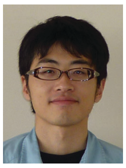


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