3D surface analysis using a synchrotron Mössbauer source

Understanding the chemical states of iron compounds and their three-dimensional (3D) distributions near the surface is crucial for advancing steel science. One of the most effective tools for chemical analysis of iron is ^{57}Fe Mössbauer spectroscopy, which extracts hyperfine parameters from spectra to provide valuable insights into the electronic environment surrounding the nucleus. The isomer shift (*IS*), which reflects the spectral center shift, is proportional to the *s*-electron density at the ^{57}Fe nucleus site. *IS* is particularly useful for determining the valence state of iron and for identifying oxide species in solids. The quadrupole shift (*QS*), caused by the interaction between the nuclear electric quadrupole moment and the electric field gradient, leads to doublet spectra in nonmagnetic materials. *QS* is valuable for examining the site symmetry and ligand configurations. Additionally, the hyperfine field (H_{int}) generated by the spin-polarized *s*-electrons at the ^{57}Fe nucleus site provides important information about the local magnetism.

Mössbauer spectroscopy is commonly performed in a transmission geometry. However, for opaque steel samples, conversion electron Mössbauer spectroscopy (CEMS) is conducted in a backscattering geometry. In CEMS, γ-rays are directed onto the sample, which is placed in a gas flow proportional counter, and the resulting conversion electrons are detected. A CEMS typically provides a surface sensitivity of approximately 100 nm, which corresponds to the escape depth of conversion electrons. This sensitivity can be enhanced by analyzing the electron energy using a method known as depth-selective CEMS (DCEMS). The DCEMS exploits the fact that electrons emitted near the surface lose less energy during their escape. It is a powerful tool for analyzing steel surfaces, with applications in surface modification, corrosion, and welding. In principle, DCEMS enables 3D analysis by scanning the sample surface with a focused probe beam, making it sensitive to both depth and lateral position. However, the non-directional nature of γ-rays emitted from traditional radioactive isotopic sources poses challenges for achieving a small probe γ-ray with sufficient photon flux for practical 3D surface analysis. Recently, we developed an “iron microscope” using a highly brilliant synchrotron Mössbauer source (SMS), beam-focusing mirrors, a precision stage, a gas-flow proportional counter, and multiple multichannel scalers (MCS). This system was successfully applied to the 3D chemical state analysis near the surface of a laser-ablated ^{57}Fe foil [1].

A ^{57}Fe [90%] foil, irradiated with a pulsed YAG laser with a focal spot size of φ19 μm in air, was prepared as the sample (Fig. 1). The SMS study was conducted at the SPring-8 **BL11XU**. The SMS γ-rays were focused to approximately 10 μm (vertical) × 30 μm (horizontal) using a K–B focusing mirror (Fig. 2). The vertical and horizontal beam sizes were evaluated as the FWHM values of the differential peaks of the knife-edge scan profile. The sample, placed inside the CEMS detector, was positioned at the focal point, with the γ-rays incident normal to the foil plane. The γ-ray irradiation positions in this study are indicated by yellow ellipses in Fig. 1. The DCEMS and transmission spectra were measured using a four-pulse-height analyzer-equipped MCSs. The DCEMS spectra were recorded in three distinct energy regions: low energy (2–6.5 keV), medium energy (6.5–11 keV), and high energy (>11 keV) corresponding to approximate depths of 90, 60, and 30 nm, respectively.

Figure 3 shows typical DCEMS and transmission spectra observed near the center of the laser-irradiated region. In the DCEMS spectra, a magnetic sextet (green line) and a nonmagnetic doublet (red line) were observed. The magnetic phase displayed typical hyperfine parameters of α-Fe: H_{int} = 33 T, *QS* = 0 mm/s, and *IS* = 0 mm/s. By contrast, the nonmagnetic phase exhibited *QS* = 0.68 mm/s and *IS* = 0.85 mm/s, corresponding to iron monoxide (wüstite) with a non-stoichiometric crystal structure formed during the rapid cooling of the iron foil surface in air after pulsed laser heating. The abundances of the nonmagnetic phase, estimated from the data analysis, were 28.0%, 17.6%, and 10.3% at different depths. A

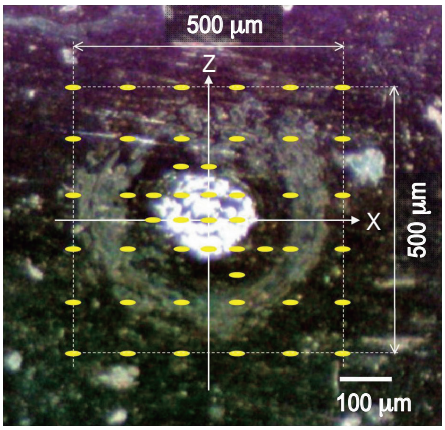

Fig. 1. Photograph of the laser-ablated ^{57}Fe foil for the DCEMS measurements.

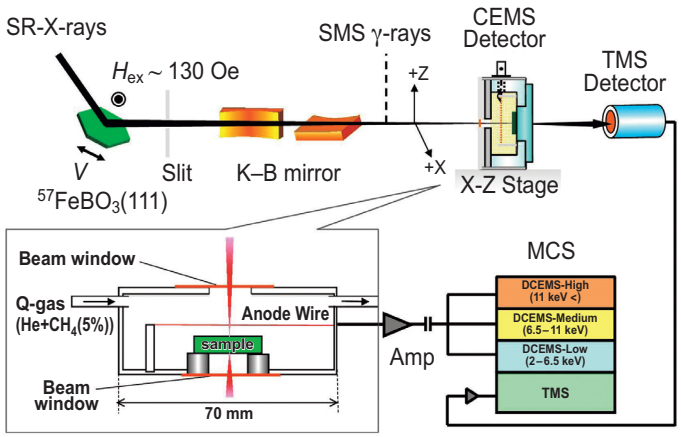

Fig. 2. Measurement system for 3D Mössbauer surface analysis. Multiple MCS were used for DCEMS and transmission measurements.

nonmagnetic oxide formed at a depth of approximately 100 nm from the surface. As expected, the transmission spectrum, which reflects bulk information, was dominated by the ferromagnetic α-Fe component, whereas the nonmagnetic component was negligible.

To visualize the oxidation state transition from the surface to the interior of the iron foil, the spatial distribution of the nonmagnetic phase was mapped using a 3D quadratic spline interpolation method (Fig. 3). The resulting visualization reveals three prominent columnar compositional variations, indicating heterogeneous oxide formation within the iron foil. This heterogeneous distribution is attributed to the complex detachment and scattering of molten fragments from the iron surface during the pulsed laser ablation process.

The developed system successfully visualized the heterogeneous formation of iron oxide near the surface of a laser-ablated iron foil. Currently, 3D surface analysis is primarily applied in fundamental research on ^{57}Fe-rich steel. However, it has considerable potential for practical applications, such as the pinpoint surface analysis of corrosion and welded areas in steel with a natural abundance of ^{57}Fe (2.2%) [2]. In future studies, this method is expected to make substantial contributions to advanced steel science research, including investigations of corrosion, welding, and surface modifications induced by processes such as laser ablation and peening.

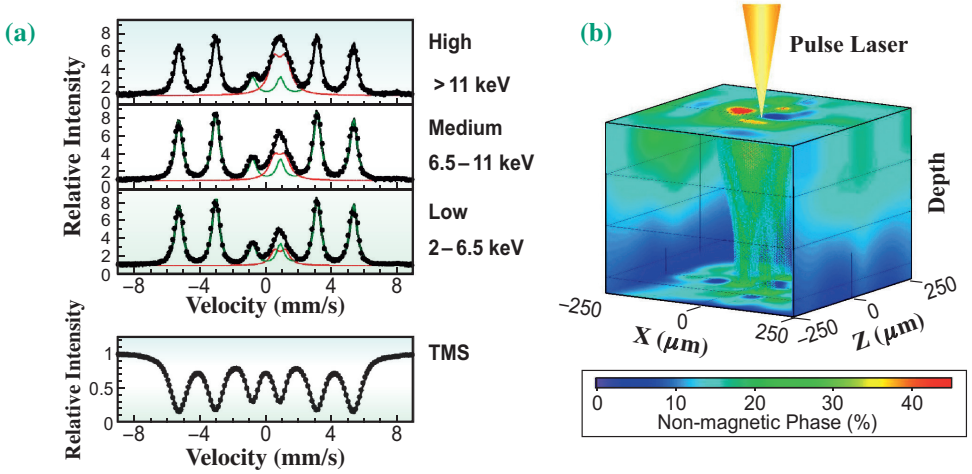

Fig. 3. **(a)** DCEMS and transmission spectra measured near the laser irradiation center [X = –100 μm, Z = 100 μm] on the laser-ablated ^{57}Fe iron foil. **(b)** 3D distribution of the nonmagnetic phase was calculated using spline interpolation.

Takaya Mitsui* and Kosuke Fujiwara

National Institutes for Quantum Science and Technology (QST)

*Email: mitsui.takaya@qst.go.jp

References

[1] *K. Fujiwara, T. Mitsui, N. Hasegawa, M. Nishikino, Y. Kobayashi, K. Mibu, K. Shinoda, R. Masuda and M. Seto: Appl. Phys. Express* ***17*** *(2024) 082002.*
[2] T. Mitsui *et al.*: Interactions **245** (2024) 347.