Materials Analysis Using Synchrotron Radiation and Neutron Beams

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To develop high-performance and high-reliability products that do not contain any hazardous substances, Fujitsu uses many analysis techniques and various types of equipment. To add to these, we have been developing materials analysis techniques using synchrotron radiation and neutron beams, which cannot easily be handled by general analysis equipment. For this analysis, we make use of national public research facilities. In this paper, we introduce the "SUNBEAM" beamline constructed by a consortium of 13 companies at the SPring-8 synchrotron radiation facility managed by RIKEN and give examples of how Fujitsu Laboratories is applying this beamline to materials analysis. We also introduce two future analysis technologies: analysis using the X-ray free electron laser now under construction at SPring-8 and neutron beam analysis at the Japan Proton Accelerator Research Complex (J-PARC) built in Tokaimura, Ibaraki prefecture, by the Japan Atomic Energy Agency (JAEA).

1. Introduction

Many types of analysis techniques and equipment can be used for materials analysis as part of the product development process, but for some analysis targets, special-purpose analysis methods that can provide ultrahigh accuracy or trace element detection—characteristics that are difficult to achieve with standard equipment—may be necessary. Against this background, we are developing analysis techniques and assessing materials by using synchrotron radiation and neutron beams. For work of this type, we make use of large-scale national facilities.

In this paper, we introduce examples of materials analysis performed by Fujitsu Laboratories using SPring-8 (Super Photon ring 8 GeV), a large synchrotron radiation facility managed by RIKEN. Furthermore, as examples of future analysis techniques, we introduce analysis using the X-ray free electron laser (XFEL) now under construction at SPring-8 and analysis using neutron beams at the Japan Proton Accelerator Research Complex (J-PARC) built in Tokaimura, Ibaraki prefecture, by the Japan Atomic Energy Agency (JAEA).

2. SPring-8

Synchrotron radiation is electromagnetic radiation emitted from electrons that are accelerated in the storage ring. Its energy distribution depends on the energy of the accelerated electrons and on the applied magnetic field. The main features of synchrotron radiation are high intensity, high brilliance (parallelism), and tunable energy. A large-scale accelerator is needed to accumulate high-energy electrons, and the circumference of the SPring-8 synchrotron radiation facility built in Hyogo prefecture, Japan, is 1436 m. To make effective use of SPring-8, 13 companies, including Fujitsu Laboratories, have formed the SUNBEAM consortium and constructed the SUNBEAM beamline for

industrial use. Beam time is divided equally among the member companies, enabling each company to analyze its key materials on a regular basis. The SUNBEAM beamline is equipped with X-ray absorption fine structure (XAFS) analysis equipment, an 8-axis diffractometer, an X-ray fluorescence spectrometer, and X-ray microbeam equipment.

2.1 XAFS analysis equipment

XAFS analysis makes use of the tunability of synchrotron radiation energy. It can provide inter-atomic distances, bonding valence, and other information in the periphery of absorption atoms from the X-ray absorption near-edge structure caused by the excitation of electrons in inner-shell orbitals of the sample. As such, XAFS analysis can be applied to a wide range of samples including amorphous materials, liquids, and gases in addition to crystalline systems. As an example of XAFS analysis results, **Figure 1** shows the results of using this technology for nondestructive analysis of chromate conversion coatings, which are used to prevent rust in electronic components.[1] The author would like to change this part to the following sentences.

The trivalent and hexavalent states of chromium can be found in chromate conversion coatings. While trivalent chromium is stable and nontoxic to humans, hexavalent chromium is a toxic substance associated with allergies, cancer, and other conditions. Consequently, the use of hexavalent chromium has been banned in electrical and electronic products by the RoHS[note 1] Directive in the EU. XAFS analysis can nondestructively isolate and quantify trivalent and hexavalent chromium.

note 1) Restriction on Hazardous Substances is legislation on toxic substances enacted by the European Union (EU) on July 1, 2006. It prohibits the use of lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyl, and polybrominated diphenyl ethers in electrical and electronic equipment and products within the EU region.

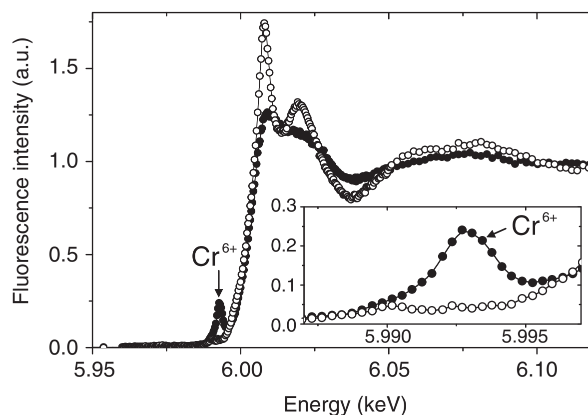


Figure 1
Hexavalent chromium in chromate conversion coatings.

In Figure 1, the sample of chromate conversion coating indicated by the open circles contains no hexavalent chromium while the sample indicated by the closed circles does contain hexavalent chromium.

Other typical applications of XAFS analysis include the structural analysis of battery materials with the aim of improving performance and the analysis of emissions-processing reactions in automobile catalytic converters. XAFS analysis is also widely used for in-situ analysis of reactions in progress.

2.2 8-axis diffractometer

The 8-axis diffractometer on the SUNBEAM beamline has an X-ray intensity about one million times stronger than that of diffractometers used in many laboratories. This feature makes it possible to perform ultrathin-film analysis such as X-ray reflectometry of the gate insulation film in metal oxide semiconductor devices.[2] The ability to use highly parallel X-rays and high-energy X-rays in this manner also enables high-accuracy stress evaluations to be performed.

2.3 X-ray fluorescence spectrometer

X-ray fluorescence spectrometry at SPring-8 became famous as a result of the Wakayama

toxic-curry incident[note 2)]. The X-ray fluorescence spectrometer installed on the SUNBEAM beamline can perform fluorescence spectrometry and mapping within an area with a diameter of 10 µm by making use of intense, parallel X-rays. Moreover, fluorescence XAFS measurements can be performed with the equipment using tunable energy. The spectrometer is also equipped with a high-efficiency silicon drift detector and a high-resolution wavelength-dispersion detector, enabling trace-element analysis.[3)]

2.4 X-ray microbeam equipment

To enable X-ray analysis within a submicrometer area, the SUNBEAM beamline includes Kirkpatrick-Baez mirror optics and Fresnel zone plate optics for microfocusing, enabling local-area fluorescence and diffraction measurements to be performed.

3. Use of public beamlines

For analysis in areas not covered by the abovementioned general-purpose equipment, we make use of public beamlines developed within the SPring-8 facility provided by the Japan Synchrotron Radiation Research Institute (JASRI). At SPring-8, calls for research proposals are made twice a year, and in recent years, about 20% of all selected proposal have dealt with industrial themes.

3.1 BL19B2 beamline for industrial use

This beamline is equipped with a powder diffractometer, which enables the high-resolution diffraction data needed for Rietveld analysis of crystalline materials to be obtained in only about five minutes. It also includes an automatic sample exchanger that enables measurements to be performed on more than 100 samples in a relatively short time. We have used this beamline to analyze the photocatalyst titanium apatite[4)] and other materials.

3.2 BL25SU beamline for circularly polarized soft X-rays

Soft X-rays have energy in the range of 0.1–2 keV, and on this beamline, high-quality circularly polarized X-rays can be used for magnetic circular dichroism (MCD) analysis and X-ray photoemission electron microscopy measurements of magnetic materials. We used this beamline to measure the magnetic structure of a MnIr/CoFe exchange bias system used in spin-valve films.[5)]

4. XFEL

An XFEL produces a pulse-shaped beam of X-rays from the interference of electromagnetic waves generated from bunched electrons in a linear accelerator. It has attracted attention as a new type of X-ray source having almost 100% (full) coherency.

With the aim of developing nanodevice imaging technology, we have been promoting research proposals as part of the XFEL Usage Promotion Project of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) in collaboration with Tohoku University and JASRI, and as a basic technology here, we have been developing an X-ray Fourier transform holography method. This method enables nondestructive analysis using X-rays that have strong penetrating power. With this method, sample images are obtained without arbitrariness by subjecting the intensities of X-rays scattered from the sample to an inverse Fourier transform. In addition, the equipment has a relatively simple configuration without any lenses, which means that the space around the sample is not occupied, making this method applicable to the

note 2) This incident, which occurred in 1998 in Wakayama prefecture, involved poison being mixed into curry served at a summer festival. Among the people who ate it, 67 people felt nauseous and suffered stomach pains and were taken to the hospital. Four people died. SPring-8 was used analyze the composition of the curry (the suspected cause) because the amount of poison was too small to be detected by ordinary means.

observation of device operation or high-speed temporal changes under an external applied field. This X-ray Fourier transform holography method is therefore expected to be an in-situ measurement technology targeting tiny areas and nanodevices.

It has also been reported that it can even be used to measure magnetic domains when making use of MCD effects.[6] Using it, we have performed a preliminary magnetic-domain-observation experiment on Co/Pt vertical-magnetization film. In this experiment, the measured sample was formed on a SiN membrane as shown in **Figure 2**. Specifically, an opaque Au film was formed on one side of the membrane as an X-ray shielding mask, and a Co/Pt vertical-magnetization film was formed on the other side. A sample-penetration window was then formed on a 2 × 2 μm^2 area of the thin film, and to provide reference lights for holography use, through holes of different sizes were formed at three locations (A, B, and C). Measurements were performed at the SPring-8 BL25SU beamline for circularly polarized soft X-rays at the Co-L absorption edge energy. The X-rays diffracted from the sample were measured with a CCD (charge coupled device) detector installed at a downstream location. An image (hologram) of diffracted X-rays measured in this way is shown in **Figure 3**. The data sets for left and right circular polarizations obtained here were separately subjected to an inverse Fourier transform and a magnetic image was obtained from the difference between the two data sets. Results are shown in **Figure 4**. The center of the figure is overlaid with the autocorrelation function of the image, and the surrounding area contains actual images of the sample along with their conjugate images

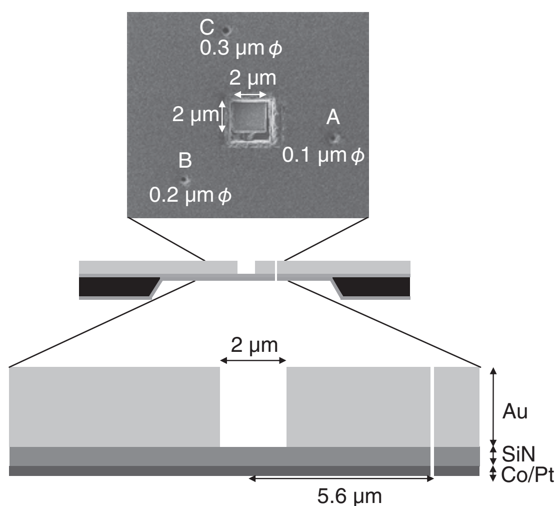


Figure 2
Scanning electron micrograph of X-ray holography sample.

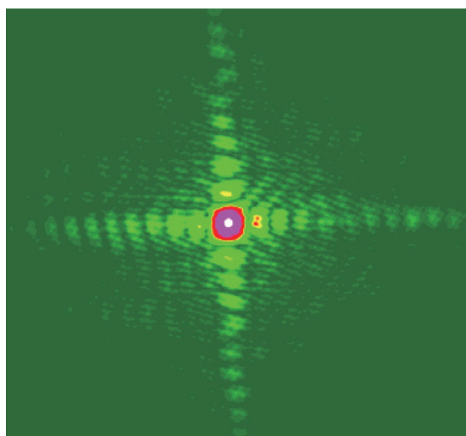


Figure 3
Intensity of X-rays diffracted from sample (hologram).

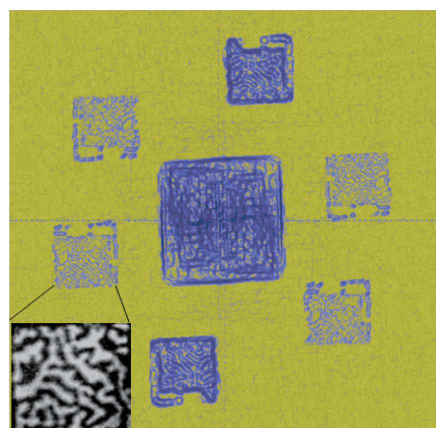


Figure 4
Magnetic domains obtained from the difference between Fourier transformed images using left and right circularly polarized X-rays.
Inset is a black and white chart of one image.

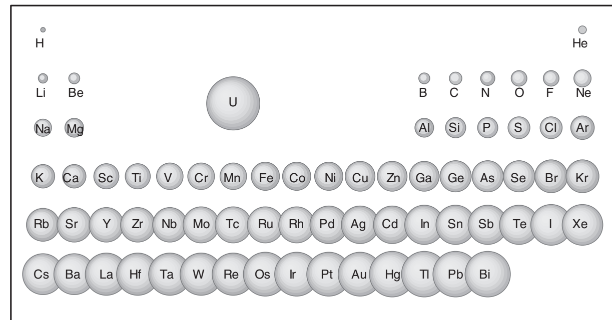
on opposite sides, with each pair corresponding to one of the three reference through-holes. This image shows that maze-like magnetic domains peculiar to a vertical-magnetization film have been formed.

Looking to the future, we can expect this method to be capable of one-shot imaging of nanodevices by using fully coherent X-rays from XFEL and to be applied to in-situ measurements during device operation.

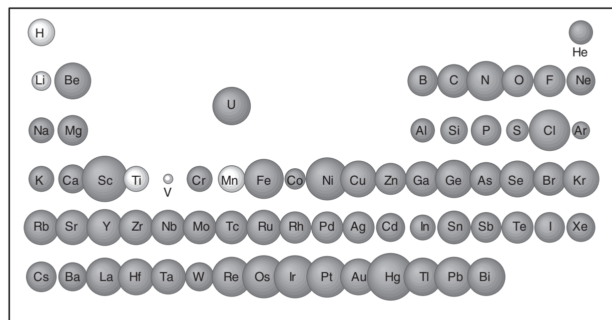
5. J-PARC

Neutrons, like X-rays, carry no electric charge. They react almost solely with the atomic nucleus. As a result, neutron beams penetrate further into materials than X-rays do. Here, we compare neutron beams with X-rays in terms of their use as analysis probes. First, given that X-rays are mainly scattered from electrons in an atom, the intensity of X-rays scattered from a sample is proportional to the atomic number, as shown in **Figure 5 (a)**, where the scattering cross-sectional area is indicated by the size of each element in the figure. This makes it difficult to differentiate and analyze atoms whose atomic numbers are nearly the same. In contrast, the intensity of neutron beams scattered from a sample changes from one element to another irregularly, as shown in **Figure 5 (b)**, where the scattering cross-sectional area is again indicated by the size of each element. This is because nuclear reactions pass through various resonance states. This property enables an element-specific materials analysis to be performed. For example, while it is difficult to "see" hydrogen with X-rays, it is possible to see this element with neutron beams. Differences in sensitivity due to the isotopes of an element can also provide contrast for analysis purposes.

The J-PARC built by JAEA in Tokaimura, Ibaraki prefecture, includes the Materials and Life Science Experimental Facility as one of its supplementary facilities. At this facility, materials analysis can be performed using pulsed neutrons. By using neutron beams, we can analyze materials having low atomic numbers that are hard to analyze by using X-rays. In some cases, a material with a similar atomic number can be resolved by using the different cross-section of neutrons. In our analysis work, we intend to make use of neutron beams as a complement to X-rays.



(a) Dependence of X-ray scattering cross-section on atomic number



(b) Dependence of neutron scattering cross-section on atomic number

Figure 5
X-ray and neutron scattering cross sections for different elements.

6. Conclusion

As the "eye" for examining samples, materials analysis is essential to the efficient development of diverse types of materials and devices. At the same time, information obtained from various types of analysis techniques is the result of investigating actual materials and devices from certain limited angles. To understand actual phenomena, we should combine various types of information to obtain more effective results. Analysis techniques using

synchrotron radiation and neutron beams provide information that cannot be obtained with only laboratory equipment, and in this complementary role, they should help deepen our understanding of materials.

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