BL22XU JAEA Actinide Science I

1. Introduction

BL22XU was constructed as a hard X-ray undulator beamline extending from the Storage Ring building to the RI Laboratory, and has been operational since May 2002 as a supplementary beamline to the soft X-ray undulator beamlines BL23SU and BL22XU ^[1]. In accordance with the new vision of JAEA, which is "A new future pioneered by the synergy of nuclear and renewable energies," the following research and development activities are currently underway: "Synergy: R&D for pursuing the synergy of nuclear and renewable energies," "Sustainability: R&D for making nuclear energy itself sustainable," and "Ubiquitousness: R&D for applying nuclear technology widely to society, not limited to the energy field." In September 2022, a limited quantity of sealed nuclear fuel material was approved for use, with operations scheduled to begin in September 2023. Subsequently, in January 2024, the radioactive particles containing nuclear fuel, collected from within the containment vessel of the Fukushima Daiichi Nuclear Power Plant, were subjected to measurement.

BL22XU has two double-crystal monochromators. One is a single-cam-type monochromator with a multicrystal switching system. This monochromator can utilize wideenergy-range X-rays from 4 to 72 keV by using Si(111) and Si(311) crystals. The other is a calculation-and-combination-type monochromator. This monochromator can utilize high-flux X-rays from 35 to 70 keV by using Si(111) crystals.

BL22XU has mirrors for focusing and higher harmonics rejection. They focus X-rays of 1 mm

height and 3 mm width to 0.2 and 0.4 mm, respectively, in the RI Laboratory at 120 m from the light source. The three mirrors are switched to reject harmonics higher than 7, 16, and 30 keV. A beryllium diffraction lens system for the higher energy and a Kirkpatrick–Baez (KB) microfocusing system for less than 40 keV are also used.

2. Experimental Hutch 1 (EH1)

2-1. Large diffractometer

Currently, an apparatus for Bragg coherent X-ray diffraction imaging (Bragg-CDI) is under development. Bragg-CDI is expected to be a powerful technique for investigating isolated nanosized crystalline particles. Furthermore, it is expected to enable studies of particles located within devices, which are inaccessible by electron beam techniques. This technique now enables us to study particles from 40 to 1000 nm in size and from room temperature to 1373 K.

In 2023, the Bragg-CDI contributed to the development of negative thermal expansion (NTE) materials with 11.1% volume shrinkage ^[2]. The complementary use of a transmission electron microscope and Bragg-CDI have revealed the coexistence of cubic and tetragonal phases with a large volume difference. It was suggested that the change in the heterophase structure dominates the NTE character.

We also succeeded in visualizing a 500 nm single grain of BaTiO₃ in polycrystalline ceramics ^[3]. The lattice strain distribution of grains in the paraelectric phase and a pair of 90° domains of the ferroelectric phase were imaged in three dimensions.

These results suggest that the domain boundaries correlate with the strain induced by stress from adjacent grains.

Furthermore, it is worth noting that we have conducted position-resolved diffraction experiments on samples with a temperature gradient ^[4] and composition gradient ^[5], accurately detecting the phase boundary by precisely adjusting the sample position. In this work, we introduce a novel approach for the future study of phase transitions, utilizing the positional resolution capabilities of synchrotron radiation with exceptional precision.

2-2. Diamond-anvil-cell diffractometer

The diamond-anvil-cell diffractometer was designed for X-ray diffraction experiments under high pressure. The equipped large-area twodimensional detectors cover a wide diffraction angle. By using these detectors and high-energy monochromatic X-rays up to 70 keV, this diffractometer enables us to measure the X-ray total scattering pattern even in a high-Q range with a short exposure time. The measured X-ray total scattering pattern transforms into an atomic pairdistribution function (PDF), which corresponds to the probability of finding atom pairs at a distance in real space.

PDF analysis is one of the powerful methods to analyze the local structure with the scale of subnanometers to several nanometers. The structural information of functional materials in local to middle-range structures has been regarded as important for understanding their properties. Our rapid-acquisition PDF measurement system has been applied to a wide variety of functional materials, such as hydrogen-absorbing materials ^[6– 8], negative thermal expansion materials ^[9], and cement materials ^[10–12]. The conventional PDF profiles include correlations among all pairs of atoms. To obtain the atom-selective PDF, anomalous X-ray scattering (AXS) measurements were applied. The formation processes of zeolites containing alkaline earth metal cations were investigated by using the atom-selective PDFs focusing on the alkaline earth metal ^[13, 14].

3. Experimental Hutch 3 (EH3)

3-1. Hard X-ray photoemission spectroscopy (HAXPES)

We have developed a transfer case that is powerless, lightweight, and compact by applying a technology invented at the J-PARC Center; the chamber itself is used as an ultrahigh-vacuum getter pump ^[15]. The prototype has successfully maintained a high vacuum without the need for a conventional vacuum pump. An external view of the developed transfer case is shown in Fig. 1. This case is extremely compact and weighs only approximately 6 kg.



Fig. 1. External view of the developed transfer case.

To evaluate the performance of the transfer case, a land transportation test was conducted using air and rail transport from the Japan Atomic Energy Agency (JAEA) in Ibaraki Prefecture to SPring-8 in Hyogo Prefecture. During the test, the NEG-

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material-based transport case was used to prevent exposure to the atmosphere during transportation and to maintain a vacuum inside the case. Upon arrival, the oxidation states of Ti in the Ti-V-Zr alloy samples transported with and without the transport case were compared and evaluated using the HAXPES system installed at the JAEA Contract Beamline BL22XU. The results from HAXPES are presented in Fig. 2. The results confirmed that the use of the transport case effectively suppressed Ti oxidation and minimized the formation of an oxide layer. On the other hand, without the transport case, Ti oxidation progressed, leading to the formation of an oxide layer. This evaluation demonstrated that the NEG-material-based transfer case is highly effective in preventing the oxidation of the easily oxidizable Ti-V-Zr alloy and in preserving the quality of the material. The developed vacuum transfer case allows for the transport of samples, such as nanomaterials and semiconductor wafers, which are prone to oxidation, from manufacturing equipment to analytical devices or between different analytical instruments, while keeping the surfaces clean and avoiding atmospheric exposure.



Fig. 2. Ti1s HAXPES spectra of alloy with and without transfer case.

3-2. X-ray absorption fine structure (XAFS) (1) Structural and electronic properties of lightwater reactor (LWR) fuel melting phenomena In the event of a loss-of-coolant accident (LOCA) exceeding the design basis, it has been reported that the fuel UO₂ and zirconium alloys comprising the nuclear reactor coolant system rapidly melt at temperatures above 1900°C owing to a chemical reaction between the fuel and coolant. However, the model uncertainty of the actual fuel assembly melting phenomenon is considerable because experimental conditions are not precisely controlled, particularly with regard to sample size and shape. Accordingly, it is essential to adopt an evaluation approach that is founded upon a comprehensive understanding of the physical and structural characteristics.



Fig. 3. High-temperature XAFS/XRD measurement system.

We evaluate the fuel melting behavior of UO₂/Zr mixed oxides heated to 1900–2200°C by analyzing the electronic state transitions and structural information during the heating process using the high-temperature XAFS method.A recently developed combination of a furnace and

synchrotron radiation experimental apparatus is employed to elucidate the rapid melting conditions resulting from this phenomenon ^[16, 17]. The objective of this study is to elucidate the conditions that precipitate rapid melting as a consequence of this phenomenon. Y_2O_3 , which is resistant to oxidation at elevated temperatures, was prepared as a high-temperature alternative to UO_2 , and its compatibility with existing equipment was evaluated. Furthermore, a deoxidizer developed to inhibit Zr oxidation during the reaction process was connected to the measurement system.

The sample loading section is equipped with a 0.06 mm slit, which permits the passage of X-rays. The heating chamber in which the sample is loaded is equipped with glass windows in the incident and transmission sections, allowing for the passage of X-rays. The loaded sample holder can be remotely heated to a high temperature with low power consumption via an electrical current. Simultaneous XAFS and XRD measurements were performed with an ionization chamber situated in front of and behind the heating chamber, as well as a twodimensional detector for capturing diffraction images of transmitted X-rays at a position slightly offset from the optical path. In this experiment, energy spectra in the vicinity of the K absorption edges of Zr and Y were measured simultaneously.

Spectral measurements were performed on mixtures of Zr and Y_2O_3 during the temperature increase process. The temperature of the sample was increased from a point above the melting point of Zr (2128 K) to approximately 2500 K. The intensity of the metallic Zr peak, identified at the beginning of the measurement, decreased with increasing temperature, and a tetragonal ZrO₂ peak appeared at temperatures above 1500 K, as

observed in the XRD spectrum obtained from the 2D diffraction image. Subsequently, the solid-state reaction between ZrO₂ and Y₂O₃ proceeded, and a Zr chemical shift from the Zr–Zr coordination to the Zr–O coordination became notable in the XAFS spectrum at the Zr-K edge and by the EXAFS vibration analysis. This is a high-temperature reaction between ZrO₂ and Y₂O₃.

(2) X-ray analysis for radioactive particulates from Fukushima-Daiichi Nuclear Power Plant

Because of the 2011 Tohoku earthquake and tsunami in the northeast area of Japan, the Fukushima Daiichi Nuclear Power Plant (1F) lost all electric supplies, and Units 1, 2, and 3 were seriously damaged. These units underwent meltdown, resulting in a large amount of debris inside their primary containment vessels (PCVs).

However, the nature of the debris is not well understood owing to difficulties in collecting samples from inside the PCVs. On the other hand, micron-sized radioactive particulates were collected during an investigation inside the PCVs. These particulates contain important information for understanding the characteristics of the debris.

X-ray fluorescence (XRF), X-ray absorption spectroscopy (XAS), and X-ray diffraction (XRD) analyses were performed on the radioactive particulates collected during an investigation inside the 1F Unit 2 PCV using micro-focused X-rays.

The mappings of radioactive particulates at U L3, Pu L3, and Zr K fluorescence were obtained. The incident photon energy was 20 keV, and the size of the particulates was about 20 μ m. Furthermore, U L3 and Pu L3 XAS spectra of the particulates were measured and found to coincide with those of UO₂ and PuO₂.

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3-3. Stress/imaging measurements

In this device, deformation and state changes inside a material are determined by a diffraction method and an imaging method using high-energy synchrotron radiation X-rays.

Figure 4 shows a real-time X-ray image of the molten metal wire taken during the arc welding process. The metallic wire material was an aluminum alloy of 1.2 mm diameter, sealed inside with tungsten particles (approximately 50 μ m in diameter) that serve as tracer particles for measuring the flow velocity. The metal wire melted and ejected by the arc plasma was irradiated with a 30 keV synchrotron X-ray, and 3,000 X-ray transmission images were taken per second using a high-speed camera. The change in the tracer position was read from the obtained images, and the flow velocity inside the molten metal wire was calculated.



Fig. 4. Real-time X-ray image of the molten metal wire material taken during the arc welding process.

As a result, it was clarified that the flow inside the metal wire material is greatly accelerated in a space of only about 1 mm after it is melted by the arc plasma. It was also revealed that the magnitude of the arc plasma discharge current and the contact condition between the arc plasma and the metal wire material significantly change the acceleration behavior, and that these factors affect the ejection morphology of the molten metal wire material. When the current is large and the arc plasma is in contact with the molten metal surrounding the wire material, it has been found that the molten metal is ejected as a jet and the internal velocity is greatly accelerated ^[18].

3-4. Surface X-ray scattering

A κ -type diffractometer equipped with an electrochemical measurement system was installed in EH3. Electrochemical and surface X-ray scattering (SXS) measurements can be carried out simultaneously; that is, SXS measurements can be carried out under electrode potential control *in situ*. The structure of the electrode of an all-solid-state Li-ion battery during charge/discharge cycles, the electrode potential dependence of the structure of the novel electrode materials, and the electrode surface structure during the underpotential deposition (UPD) reaction in an ionic liquid (IL) were studied.

Here, we report a study on the UPD reaction process on a Au(111) electrode in 1-butyl-3methylimidazolium tetrafluoroborate ([BMIM]BF₄) using SXS. The UPD reaction is a part of the electrodeposition reaction, which occurs at a more positive electrode potential than the redox potential. In many cases, the metal layer formed by the UPD reaction (the UPD layer) is a monolayer with a specific structure, depending on the coverage. Previously, we reported Bi that was underpotentially deposited on a Au(111) electrode in [BMIM]BF₄. However, the precise coverage of Bi and the in-plane structure of UPD Bi were uncovered. Therefore, we analyzed the coverage of Bi and the in-plane structure using SXS. Figure 5 shows the reflectivity profile, known as the (00) rod. A parameter fitting analysis was performed, and it

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was found that the UPD Bi layer was a monolayer with a coverage of 0.75 at E = -0.57 V. Using this result, the potential dependence of the Bi coverage during the UPD reaction was evaluated, and the result suggested that the UPD Bi layer can form a (2 \times 2) or ($\sqrt{3} \times \sqrt{3}$) structure. Therefore, we carried out surface X-ray diffraction (SXRD) measurements. The diffracted intensity along (X, X) was measured, and a diffraction peak was observed at (1/2, 1/2), indicating the existence of the (2×2) structure. Furthermore, the potential dependence of the diffracted intensity observed at (1/2, 1/2) was evaluated. During both the negative and positive scans, the diffracted intensity at (1/2, 1/2) was observed at a particular electrode potential, as expected, indicating that during the Bi UPD reaction and the dissolution of the UPD Bi layer, the Bi layer may form a (2×2) structure between the coverages of 1/4 and 1/2, as observed in the 1 M HClO₄ electrolyte.



Fig. 5. The (00) rod profile obtained at E = -0.57 V in [BMIM]BF₄ containing 10 mM BiCl₃.

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