BL14B1
(QST Quantum Dynamics II)

1. Overview

BL14B1 is designed for various experiments on diffraction and X-ray absorption fine structure (XAFS)-type spectroscopy in the energy range of 5–90 keV for monochromatized beams and 5–150 keV for white beams. The main optics refers to the standard SPring-8 bending magnet system with two mirrors and a fixed-exit double-crystal monochromator. These optical elements can be removed completely for experiments with white X-rays. This beamline has two experimental hutches. One is dedicated to high-pressure and dispersive XAFS experiments with white X-rays. The other is dedicated to structure analysis of surfaces, interfaces, glass, ferroelectrics, catalysts, and metals with monochromatized X-rays. BL14B1 can be a one-stop platform for the development of novel functional materials by complemental use of white and monochromatized X-rays.

2. High-pressure and high-temperature experiments

High-pressure and high-temperature synthesis studies have been carried out at the high-pressure experimental station. *In situ* synchrotron radiation X-ray diffraction measurements allow structural changes of a sample to be detected under high pressure and high temperature. Thus, we can easily search the synthetic conditions of novel materials. Additionally, the system can be used to investigate reaction mechanisms.

We are trying to synthesize novel aluminum-based hydrides. Here, 3*d* transition metals are selected to alloy with aluminum. These metals are known to have a low hydrogen affinity. In other words, they do not form hydrides around ambient pressure. However, some form hydrides under high pressure around 10 GPa by alloying with aluminum. In FY2018, we found formations of novel Al–Cr and Al–Mn hydrides under high pressure. As the formed hydrides can be recovered at ambient conditions, we are currently characterizing their thermodynamic and crystallographic properties.

We have also been investigating hydrogenation reactions of pure 3*d* metals. As described above, they are hydrogenated only at high pressures and cannot be recovered at ambient conditions. Thus, such reactions should be investigated using *in situ* measurement techniques such as synchrotron and neutron diffractions.

We have reported the formation of FeH_x where Fe atoms form a hexagonal closed packed structure (hereafter referred to hcp-FeH_x) for a hydrogen concentration $x < 0.6$ [1]. Hcp-FeH_x was absent from previously reported phase diagrams of the Fe–H system because previous works were conducted for hydrogen-rich conditions $x >> 1$. The crystal structure of hcp-FeD_x was investigated by an *in situ* neutron diffraction technique. Here, deuterization conditions were carefully investigated using synchrotron radiation X-rays. Additionally, the complementary use of synchrotron and neutrons allows hydrogenation reaction of metals to be studied under high pressure efficiently and quickly.

3. Stress

Since 2017, we have been developing a two-dimensional detector for white X-rays and a new stress measurement method using this detector [2]. One of the problems of stress measurements using the X-ray diffraction method is difficulty applying to materials with coarse grains. To solve this problem, the double-exposure method (DEM) using monochromatic X-rays was developed [3]. However, the method has a problem in which the Bragg diffraction from crystal grains in the X-ray irradiation region does not occur unless the sample is rotated.

We developed a new method, which is a combination of the DEM and the developed detector with white X-rays (DEM-WX) [4]. In this method, by measuring the Laue spots from the sample while changing the distance between the sample and the camera, the position of each Laue spot in the sample and the stress at that position can be calculated by geometric analysis.

Figure 1 shows the strain distribution of austenitic four points. The dotted line represents the strain calculated by a strain gauge placed on both sides. The measured strain using the DEM-WX corresponded to the applied strain. We revealed that the DEM-WX is useful for strain measurements of coarse-grained materials.

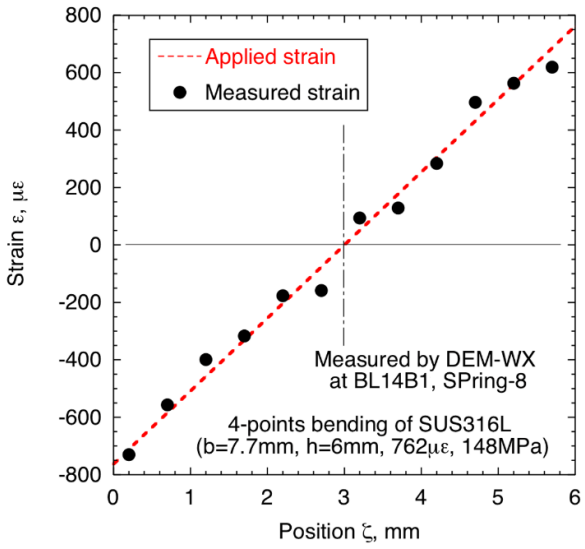

Fig. 1. Strain distribution of austenitic stainless steel with a grain size of 300 μm bent at four points.

4. XAFS

XAFS measurements using an energy-dispersive optical system were performed in the white X-ray hutch as well as a conventional optical system in the monochromatic X-ray hutch [5-9]. Various XAFS measurements from high-speed real-time to low concentration observations can be performed.

Several *in situ* observation conditions can be prepared in the energy dispersive optics hutch. Remote control systems such as gas flow controllers, switching valves, potentiostats, and injectors are always available. Time-resolved measurements are performed for gas conversion reactions, electrode reactions, ligand substitution reactions, etc. In FY2018, the reduction reaction of Pd ions induced by laser irradiation was observed by time-resolved XAFS measurements and the reaction mechanism was clarified [5].

In the conventional optics system, low concentration XAFS measurements are performed using a 36-element solid stated detector. For example, local structure measurements of Cs-including clay minerals at Cs K-edge XAFS were carried out for stable storage and volume reduction of radioactive wastes. We are continuing research to determine the relationship between the layer structure of clays and the sorption state of Cs ions, thereby leading to mobility evaluation and selective collection of radioactive Cs.

5. Diffractometer

Studies on the electrolyte/electrode interfaces were conducted using a kappa-type multi-axis diffractometer installed at BL14B1. The surface structure of the Li-ion battery electrode during charge/discharge cycles, interface structure between solid electrolyte and Pt electrodes, and electrode surface structures in an ionic liquid (IL) during the electrodeposition reaction were studied.

Here, we report a study of the electrodeposition reaction in ILs using a surface X-ray scattering (SXS) technique. IL is defined as a salt, which is in the liquid state at the room temperature. ILs exhibit physical properties such as non-volatility, high conductivity, and inflammability. Because most ILs consist of organic compounds, their properties can be easily changed by altering the molecular structure of ILs. One application of ILs is an electrolyte for electrochemical devices. However, the reactivity of the electrochemical reaction differs between ILs and aqueous electrolytes. We, therefore, studied the electrodeposition of Bi on the Au(111) electrode in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) using SXS. A continuous ad(de)sorption of Bi atom and/or solvation Bi complex on the Au(111) electrode surface occurred during electrodeposition reaction. On the other hand, the Au(111) electrode surface structure discontinuously changed during the reaction. These results suggest that Bi atoms (or complexes) may form distinct adlattice structures and the structure changes depend on the coverage.

6. Pare distribution function analysis

The feature of Pare Distribution function (PDF) analysis at BL14B1 is that the average and local

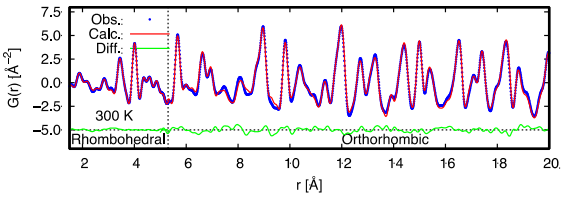

Fig. 2. Results of a box-car refinement of $KNbO_3$ at 300 K. Fit is performed by assuming a rhombohedral structure in the range of $1.5 \leq r \leq 5.3$ Å and an average structure in the range of $5 \leq r \leq 20$ Å. Note that the difference between the local and average structures vanishes above 5 Å.

structures can be obtained from the consistent data set by collecting data of high-energy X-ray diffraction patterns using a large X-ray diffractometer. Utilizing this feature, the difference between the average structure and the local structure can be strictly visualized. Moreover, structural analysis can be performed efficiently using the average structure obtained with the same dataset as the initial value of the local structure model. These two features are indispensable conditions at present to experimentally improve the real spatial resolution of PDF.

Figure 2 shows the results of the local structure analysis of potassium niobate ($KNbO_3$) that causes successive phase transitions [10]. The crystal structure of $KNbO_3$ at room temperature was an orthorhombic structure, but the local structure was reproduced as a rhombohedral structure. By comparing with the average structure obtained from the same dataset, we observed how the local structure changes to the average structure in a real scale.

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