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Yasuhiro Niwa1, a), Yasuo Takeichi1, 2, Toshiki Watanabe1 and Masao Kimura1, 2

1Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan
2Department of Materials Structure Science, School of High Energy Accelerator Science, Sokendai (the Graduate University for Advanced Studies), 1-1 Oho, Tsukuba, Ibaraki 305-0801, Japan

a)Corresponding author: yasuhiro.niwa@kek.jp

Abstract. We have developed hard X-ray spectromicroscopes at various scales using synchrotron radiation to elucidate the origin of the function of materials at Photon Factory (PF), Institute of Materials Structure Science (IMSS), High Energy Accelerator Research Organization (KEK) in Japan. One is a 2D scanning X-ray microscope with ~20-µm spatial resolution at BL-15A1 in PF; another is full-field 3D X-ray computed tomography (X-CT) with a resolution down to 30 nm at NW2A in PF-AR. In both techniques, not only morphological images but also X-ray absorption spectra (XAS) at any pixel or voxel of interest can be obtained by changing the X-ray energy. These XAS imaging techniques are useful for understanding the chemical states of specific elements and investigating reaction mechanisms. We have applied these techniques to various materials and elucidated the change of heterogeneity in chemical states which determines macroscopic properties. Application to heterogeneous reduction in iron ore sinters demonstrated clearly the impact of this approach; the multi-scale heterogeneity from 50 nm to 20 µm was shown to be related to trigger sites, which determine the degradation of iron ore sinters during reduction.

INTRODUCTION

Microscopy using energy-tunable X-rays is an imaging technique which inherently includes XAS information and thus provides not only the shape or morphology, but also useful information about the chemical properties and local atomic structure of a specimen. This method, called spectromicroscopy, has been widely introduced at second- and third-generation synchrotron light sources [1-8]. Recently, the spatial resolution of some spectromicroscopy techniques has reached nanometer scale, enabling the distribution of chemical states and the morphology of materials to be observed simultaneously with nanometer scale.

Functional materials often have hierarchical structures both in the shape of morphologies (microstructure) and the chemical states, which have a wide range of scale from nm to mm. In order to control macroscopic properties such as mechanical behavior, heat resistance and environmental resistance, it is necessary to elucidate trigger sites which are real-space points of origin of function in materials from the hierarchical structures. To achieve this, not only observations of the microstructures with electron microscopes but also mapping of various heterogeneities such as chemical states with spectromicroscopy are required. It is especially important to identify the trigger sites by observing chemical states in three-dimensional space together with the microstructures of materials. Thus, we have developed spectromicroscopy techniques at various scales for diverse materials at PF, IMSS, KEK in Japan, and have applied both systems to iron ore sinter. By combining these 2D semi-micro and 3D nano mapping techniques, we have tried to elucidate the mechanism of the reduction process of iron ore sinters in a blast furnace.
INSTRUMENTATION

We have installed two different types of spectromicroscopes with different spatial resolutions. One has semi-micro spatial resolution (down to 20 μm) with two-dimensional (2D) scanning or mapping of XAS and XRF (X-ray fluorescence), and the other has nano-spatial resolution (down to 30 nm) with three-dimensional (3D) X-CT with a full-field transmission X-ray microscope (TXM).

The semi-micro XAS and XRF system has been developed at the hard X-ray undulator beamline BL-15A1 of PF [9, 10]. The mirror optics of the beamline provide an X-ray beam of ~10¹² photons/sec focused down to ~20 μm. This system has been used for mapping of elements (XRF), chemical states (XAS) and crystal structures (XRD) by “on-the-fly” mapping in 2D.

The TXM system for 3D nano X-CT has been installed in the tapered undulator beamline NW2A at PF-AR [11]. The X-ray energy dependence of the X-CT image, called XAFS-CT, also can be measured by changing the energy of the system [5-8]. The TXM system is equipped with optics optimized for X-ray energy range from 5 to 11 keV, and the minimum spatial resolution is 30 nm. Principal components of this system are a capillary condenser, zone plate, phase ring, scintillator and detector (CCD camera). A conceptual diagram of the system in the NW2A beamline is shown in Fig. 1. The phase ring is used for Zernike phase contrast imaging, which can obtain images of a specimen that has a low-contrast signal of hard X-ray absorption, such as carbon fiber. More details about the instrument can be found elsewhere [5-8].

![Conceptual diagram of the TXM](image)

**FIGURE 1.** Conceptual diagram of the TXM installed in the NW2A beamline at PF-AR.

EXPERIMENTAL

Iron ore sinter, which is reduced in a modeled blast furnace to produce pig iron, was used as a specimen. It consisted mainly of iron oxides (Fe₂O₃ and Fe₃O₄) and calcium ferrites (CaFe₂O₄ and other Ca-Fe-O phases), and a small amount of gauge phases such as silica (SiO₂) and alumina (Al₂O₃). Iron ore sinters were reduced in reductive gas (CO) and specimens with a size of 6 × 3 × 3 mm were mechanically cut from the sinter.

The semi-micro 2D mappings were performed at the BL-15A1 beamline of PF. The X-ray beam was focused to 20 μm (H) × 10 μm (V) at the sample position. Fluorescence X-rays from the specimen at 7080, 7117, 7157 and 7600 eV were obtained to make 2D valence maps of iron by a silicon drift detector. The specimen was scanned in increments of 20 μm. The FOV of the images was about 1 × 1 mm. Iron valence images with spatial resolution of 20 μm were obtained to map the ratio of the fluorescent X-ray intensity around the iron K edge energy of 7117 eV [12].

2D nano XANES images were measured at NW2A of PF-AR. The XANES spectra were obtained from 7090 to 7200 eV in 4-eV steps. Pixel size and FOV were 39 nm with binning of 4 and 20 μm, respectively. The exposure time was 2 s in each image. 3D X-CT measurements were performed from 0 to 359° in steps of 1°. It took about 6 hours to obtain 360 projections (2 s per projection, 360 projections, 28 energy points). The specimen for XAFS-CT was cut out in a cylindrical shape of 10 μm diameter and 10 μm height from the specimen measured at BL-15A1 by a focused
RESULTS AND DISCUSSION

XAS spectra of some references, FeO, Fe$_2$O$_3$, Fe$_3$O$_4$, and CaFe$_2$O$_4$, are shown in Fig. 2 (a) [12]. The whole image of the specimen for semi-micro 2D XAS imaging is shown in Fig. 2 (b), which is rendered from the volume data obtained by an in-house macroscopic X-CT. Various sizes of pores, from 10 µm to mm, can be found in the sample (Fig. 2 (b)). The 2D valence maps obtained from the ratio of the fluorescent X-ray intensity at 7112 eV are shown in Figs. 2 (c) and (d). Red and blue indicate Fe(III) and Fe(II), respectively. It is found that the specimen, at an early stage of reduction, consists mainly of Fe(III) species, shown as white areas around the lips of pores. Iron around the lips of pores is in a more reductive state than that located far from pores. This indicates that the reducing gas flows through the pores, and the reduction of iron proceeds from the lips around the pores to bulk. White regions are also found in areas far from pores, suggesting that small pores or their network, smaller than the spatial resolution, also contribute to the flow of reduction gas. These results were useful for identifying the trigger sites of degradation during the reduction [14].

![FIGURE 2](image)

FIGURE 2. (a) XAS spectra of reference samples, (b) rendering image of the specimen, and (c) and (d) 2D valence mappings of iron in the areas indicated by white squares in (b).

We carried out further observations of the specimen in a nm scale to investigate the trigger sites in detail. The red circle in the right picture of Fig. 3 (a) indicates the sampling region. The diameter of the specimen is about 10 µm as described in an earlier section. An Fe K-edge jump 3D rendering image is shown in Fig. 3 (b). The XAS spectrum of every voxel was also obtained successfully. Figures 3 (c) and (d) show cross-sectional images of the dashed line in Fig. 3 (b). The amount of edge jump of Fe K-edge is shown as a gray-scale image in Figs. 3 (a) and (b). Since the amount of edge jump is proportional to the abundance of iron, Figs. 3 (b) and (c) show the abundance distribution of iron. The 3D abundance distribution of iron with a spatial resolution of 50 nm was obtained.

The chemical states of iron were also clearly observed with the same resolution (Fig. 3 (d)); red and blue correspond to larger and lower K-edge absorption energy, respectively. The iron K-edge energy in the area above and to the right of the crack is lower than that in the other areas. This indicates that iron in that area is in a more reductive state. The quantity of iron in the area above and to the right of the crack is less than that in the other areas. There are not only iron oxides but also calcium ferrites (CaFe$_2$O$_4$) and silica (SiO$_2$) in this specimen. The amount of iron of the calcium ferrites is less than that of the iron oxides. Thus, it is considered that the chemical species that contain less iron could exist in the area above and to the right of the crack, and the chemical state tends to be lower valence in that area. In other words, the iron-rich region remains more oxidative than other regions, suggesting that iron-rich phases

ion beam (FIB). The edge jump and energy maps from the 2D chemical images obtained at each angle were reconstructed using algebraic reconstruction techniques applying an iterative method [13].
such as Fe$_2$O$_3$ are less easily reduced than iron-poor phases such as CaFe$_3$O$_4$ and other calcium ferrites (Ca-Fe-O). This result is different from our previous macroscopic scale study [12]. This kind of heterogeneity with a scale of a few µm corresponds to trigger sites that were predicted by the analysis of macroscopic data using a persistent homology [14].

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<th>(a) The sampling region for X-CT</th>
<th>(c) Edge jump map</th>
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<td><img src="image1" alt="Sampling Region" /></td>
<td><img src="image2" alt="Edge Jump Map" /></td>
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<th>(b) Fe K-edge jump 3D rendering</th>
<th>(d) Edge energy map</th>
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<td><img src="image3" alt="Fe K-edge" /></td>
<td><img src="image4" alt="Edge Energy" /></td>
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**FIGURE 3.** (a) The sampling region for X-CT, (b) Fe K-edge jump 3D rendering image, (c) the amount of Fe edge jump and (d) mapping of the absorption energy. The red circle in the right picture of (a) indicates the sampling region. The 2D images (c) and (d) are cross-sectional images corresponding to the dashed plane in the 3D image (b).

**SUMMARY**

2D valence maps of iron were successfully obtained with 20-µm spatial resolution at BL-15A1 at PF. The valence of iron was found to be relatively higher around pores. This indicates that the reducing gas flowed through the pores, and reduction of iron selectively proceeded at the lips around the pores to bulk.

The 3D abundance distribution of iron was obtained with 50-nm spatial resolution at NW2A at PF-AR. In addition, 2D abundance distribution and valence maps were obtained. It was found that there are specific areas in which the concentration of iron is relatively lower and the iron chemical state is more reductive. These results cannot be obtained by 20-µm imaging alone, indicating the usefulness of observations at various scales from µm to nm.

We have developed X-ray microscopes with various scales (nm – µm) to investigate the heterogeneity of materials. Multi-dimensional volume data, chemical states and microstructures can yield information that may lead to a paradigm shift in materials research, as exemplified by this simple demonstration of heterogeneous reduction of iron ore sinters [12, 14].
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REFERENCES