New method of the chemical state imaging by EPMA-EXEFS

T. Watanabe,[a,b]* A. Kawano,[a] K. Ueda,[a] N. Umesaki[c] and H. Wakita[d]

[a]*Kobelco Research Institute, Inc., Hyogo 651-2271, Japan,* [b]*The Graduate School of Science and Technology, Kobe University, Hyogo 657-8501, Japan,* [c]*Department of Optical Materials, Osaka National Research Institute, AIST, Osaka 563-8577, Japan,* [d]*Department of Chemistry, Faculty of Science, Fukuoka University, Fukuoka 814-0180, Japan. E-mail: bnm0096@notice.kobelco.co.jp*

A novel two dimensional imaging technique of the chemical bonding state was developed by combining the extended X-ray emission fine structure method with an electron probe X-ray microanalyzer mapping technology. With this method, chemical state images of some aluminum standard samples were obtained. It was confirmed that the obtained images provide correct information of chemical states.

Keywords: extended X-ray emission fine structure; electron probe micro analysis; radiative Auger effect; chemical stste imaging; Al *K*-edge.

1. Introduction

Recently, an extended X-ray emission fine structure (EXEFS) method with an electron probe X-ray microanalyzer (EPMA) or a wavelength dispersive X-ray fluorescence spectrometer (WDXRF) attracts an attention as a new tool for the chemical state and local structural analysis of the material. Recently, the EXEFS spectrum of *K-LL* radiative Auger effect (RAE) peak has been observed to the low energy side of the *K*α lines for the element of atomic number 9-20. By using this spectrum, an equivalent analysis to the X-ray absorption fine structure (XAFS) method, especially, to the extended X-ray absorption fine structure (EXAFS) may become possible. (Kawai, *et al*, 1998; Kawai, Hayashi, *et al*, 1998; Kawai, Takahashi, *et al*, 1999). The applicable samples are limited by this analysis because the peak of the characteristic line of the impurity and other elements in bulk appears in the EXEFS region. That is why it is generally difficult to apply this method to the structural analysis in the same way as the EXAFS method.

We have found that the difference of X-ray absorption near edge structure (XANES) appeared in the shape of the *K-LL* RAE peak, and developed a novel two dimensional imaging technique according to a chemical bonding state using a mapping characteristics of EPMA. An attempt was made to apply this method to aluminum standard samples.

2. Experimental results and discussion

2.1. *Two dimensional imaging of the chemical bonding state of aluminum standard samples*

Pure aluminum metal, aluminum oxides and aluminum hydroxides were used for the experiment. After these samples were embeded in the resin and polished, carbon powder was deposited on the surface. The Al *K-LL* RAE EXEFS spectrum of each sample was measured by using an EPMA (JEOL JXA--8800RL) spectrometer in KOBELCO Research Institute Inc. by controlling the electron beam voltage 15kV, beam current 0.3μA, and electron beam diameter 30μm, and analyzing crystal was used a Johann type TAP(001), 2*d*=25.75Å. The minimum measurering necessary time for a spectrum with sufficient energy resolution was about six hours.

Figure 1 shows Al *K-LL* EXEFS spectra of each standard sample obtained by 24 hour measurement. Peak A represents a peak by the Raman scattering of the characteristic X-ray. Moreover, peak B represents a peak of Mg *K*α. The spectrum of each sample reflects the difference of chemical bonding state and shows different shape. However, a remarkable difference is not observed among the three kinds of the aluminum hydroxide samples.

Next, each spectrum enlarging RAE peak is shown in Fig. 2. Here, we pay attention the energy position at 1394eV. It is possibly expected that Al, α-Al_2O_3, γ-Al_2O_3 or three kinds of the aluminum hydroxide samples can be distinguished according to the intensity difference.

After fixing the detection system to the point (1394eV for instance) where the intensity difference of Al *K*α RAE peak is large, two dimensional distribution measurement of X-ray intensity was done by scanning the sample stage with a beam diameter 120μm. The two dimensional image of the chemical bonding state of the aluminum standard samples are presented in Fig. 3. It was possibly found to distinguish the intensity differences among Al, α-Al_2O_3, and γ-Al_2O_3. On the other hand, the intensity difference between three kinds of the aluminum hydroxide and γ-Al_2O_3 was too small to identify.

2.2. *Verification experiment by aluminum K-edge*

Aluminum *K*-edge XAFS of the same samples were corrected by a total electron yield (TEY) XAFS method at the BL7A station in the UVSOR Facility, Institute for Molecular Science, Okazaki,

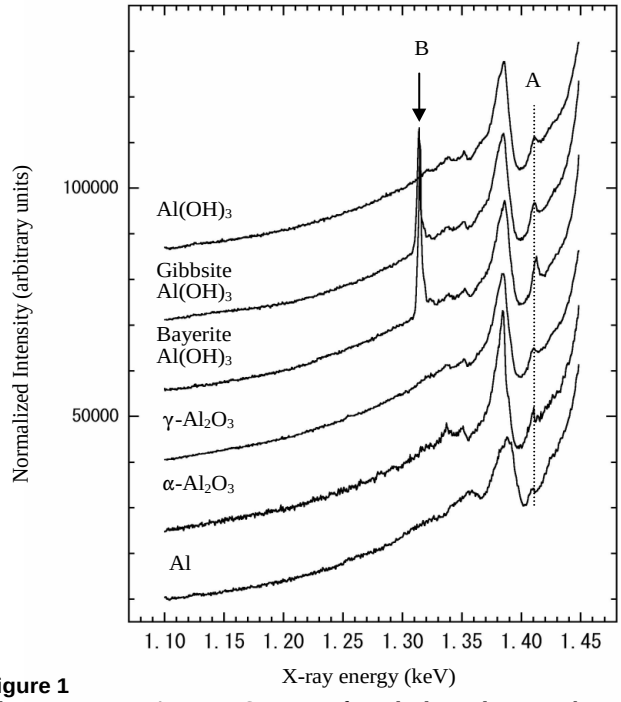

Figure 1
Aluminum *K-LL* RAE EXEFS spectra of standard samples. Here the peak A are the internal X-ray Raman scattering peaks, and the peak B are Mg *K*α lines.

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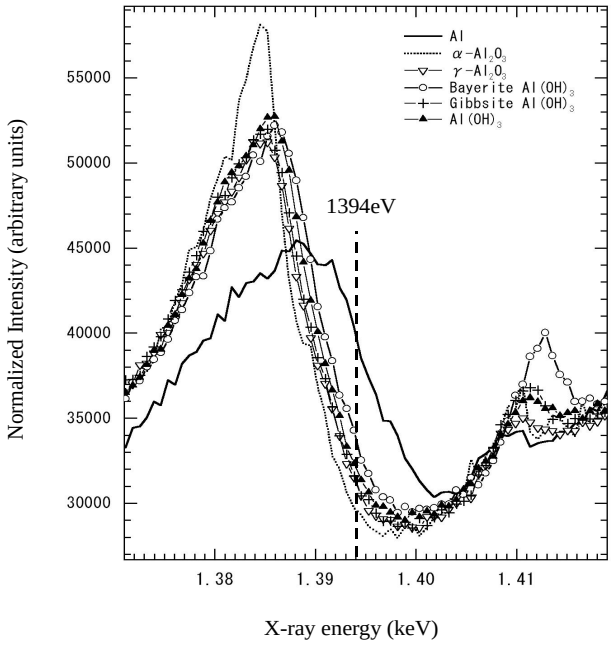

Figure 2
Enlarged view of Al *K-LL* RAE peaks of the aluminum standard samples.

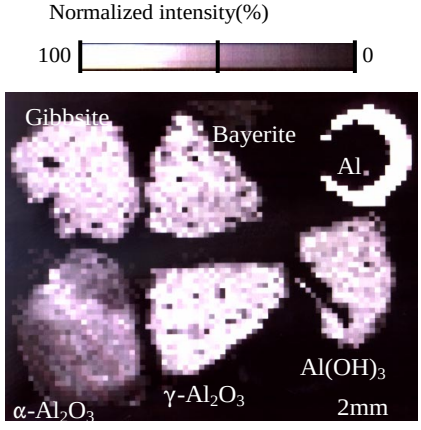

Figure 3
Chemical state image of the aluminum standard samples.

Japan (Kinoshita, *et al*, 1998), in order to confirm that two dimensional image of the chemical bonding state of the aluminum standard samples as seen in Fig.3, and the XANES parts between them were compared. The wiggler radiation source for 750MeV was used for the experiment, and beam diameter on the sample after two collection SiO_2 mirrors coated with Cr was approximately 1mm. Moreover, YB_{66}(400) (2*d*=11.76Å) was used for the double crystal monochromator. Aluminum *K*-edge XANES spectra of the samples are presented in Fig. 4. The x - axis is shown in the same direction as that of Fig. 2, which is opposite to the ordinary direction. Here, we pay attention the energy position at 1562eV of Al *K*-edge. It was found possible to distinguish the difference among Al, α-Al_2O_3, and γ-Al_2O_3, clearly. On the other hand, the difference of the electron yields between three kinds of the aluminum hydroxides and γ-Al_2O_3 are too small to identify. It is thought that the energy position at 1394eV in Fig. 2 corresponds to that at 1562.5eV in Fig. 4, as a

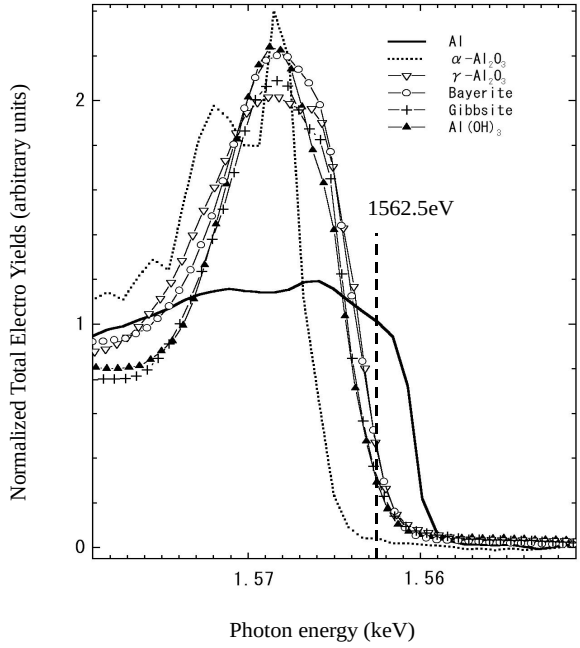

Figure 4
Al *K*-edge XANES of the aluminum standard samples.

results. This results supports the results of Fig. 3.

3. Summary

A novel technique of the two dimensional imaging of the chemical bonding state was developed by combining EXEFS measurement with EPMA mapping technology. This method made it relatiely easy to obtain the two dimensional image of the chemical bonding state in the device of the laboratory scale, because enough X-ray intensity was not obtained except for SR facilities, up to now. The intensity difference among Al, α-Al_2O_3, and γ-Al_2O_3 could be distinguished clearly as a result of the application to aluminum standard samples. On the other hand, three kinds of the aluminum hydroxide and γ-Al_2O_3 were too small in the intensity difference to identify. The Al *K*-edge of this sample was measured, and it was confirmed that it provides correct information of chemical states. Among these results, it is especially remarkable that the identification of a stabilized phase and an unstable aspect of aluminum became possible. An application of this technique is expected in the material corrosion field in the future.

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