XAFS Analysis of the Bronchoalveolar Lavage Fluid of a Tungsten Carbide Pneumoconiosis Patient

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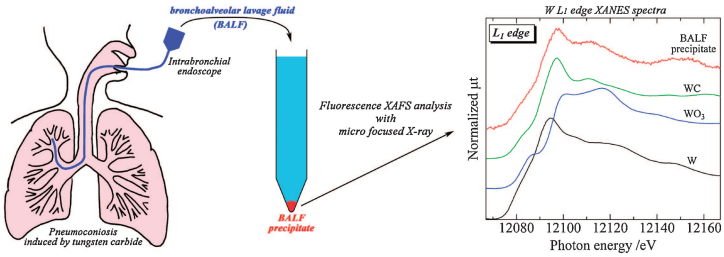

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The bronchoalveolar lavage fluid (BALF) from a patient with pneumoconiosis induced by cemented tungsten carbide (WC) was analyzed by micro-X-ray absorption fine structure (XAFS) analysis. The BALF precipitate was dried and subjected to fluorescence XAFS using polycapillary focused X-rays. The W L_1-edge XANES spectrum of the BALF precipitate could be identified as that of WC. Thus, a low concentration of WC could be detected from BALF using micro-XAFS without excess biopsy.

Cemented tungsten carbide (WC) has very high hardness, next to that of diamond and is, therefore, widely used for cutting tools and rock drills. During the work with cemented WC, fine particle dust is generated, and this can cause severe pneumoconiosis.[1,2] For the diagnosis of tungsten carbide pneumoconiosis, histologic and elemental analyses of a lung biopsy are often employed. However, excess biopsy for elemental analysis is invasive and involves pain and risk to the patient. On the other hand, bronchoalveolar lavage is conducted by instilling saline into the lung via an intrabronchial endoscope, after which the wash-out fluid is retracted through the endoscope. The bronchoalveolar lavage fluid (BALF) contains a small amount of cells and solid components detached from the alveolar surface. If the detection of WC from the solid component in BALF were possible, less invasive diagnosis of tungsten carbide pneumoconiosis could be carried out. However, the volume of the solid component of BALF is quite small, and the concentration of WC in it is low. Also, the biopsy specimens and BALF should be applied for histologic analysis. Thus, a nondestructive analytical method applicable for small specimens and low concentrations is required. In this study, fluorescence X-ray absorption fine structure (XAFS) analysis using microfocused synchrotron radiation was employed for the chemical-state analysis of low concentrations of tungsten in the solid component of BALF.

BALF was obtained from a patient who was suspected of having tungsten carbide pneumoconiosis. 15 mL of the BALF was centrifuged and its precipitate was dried and subjected to fluorescence XAFS analysis, which is favorable for the analysis of low elemental concentrations.[3] The precipitate was smaller than 0.5 mm; thus the incident X-ray needed to be focused with polycapillary optics. The X-ray absorption near-edge structure (XANES) spectra were measured at beamline 9A in the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF). The incident X-ray was focused using the polycapillary optics (X-ray Optical Systems, NY, USA) into 50 μmϕ. The focusing length was designed to be 9.5 mm from the capillary end. The W L_1- and L_3-edge XANES spectra of the BALF precipitate were measured with fluorescent XAFS using a multielement solid-state detector (SSD, Camberra, 19 elements). Spectra were scanned with 0.35 eV steps and the integration time in each step was 15 (L_3) and 25 s (L_1), respectively. I_0 signals were monitored using an ionization chamber. The XANES spectra of reference materials (metallic tungsten, WC, and WO_3) were measured by transmission. In order to compare with the conventional elemental analysis, three lung biopsy specimens from deferent positions of the same patient were also analyzed using a fluorescence X-ray (XRF) spectrometer (XGT-2000V, Horiba, Japan) for elemental analysis. The energy-dispersive spectra of fluorescence X-rays of paraffin-embedded specimens were measured with focused incident X-ray (ca. 100 μmϕ) for 600 s per specimen at 50 kV, 1 mA (Rh target).

Figure 1 shows the fluorescence X-ray spectra of the lung biopsy specimens. Fe, Ni, and Cu peaks were caused by the background. Hg and Br were derived from mercurochrome, which was used for biopsy specimen staining. Weak peaks assigned to tungsten, presumably derived from inhaled WC, were found in specimens 1 and 3, which suggested the existence of tungsten or its compound in lung tissue. However, tungsten could not be detected in specimen 2. Thus, WC content would depend on the position in the excised biopsy specimen.

Figure 2 shows the W L_3-edge XANES spectra of the BALF precipitate, metallic tungsten, WC, and WO_3. Using the polycapillary focused X-rays, the XANES spectrum of a small BALF precipitate was successfully measured. The shapes of the

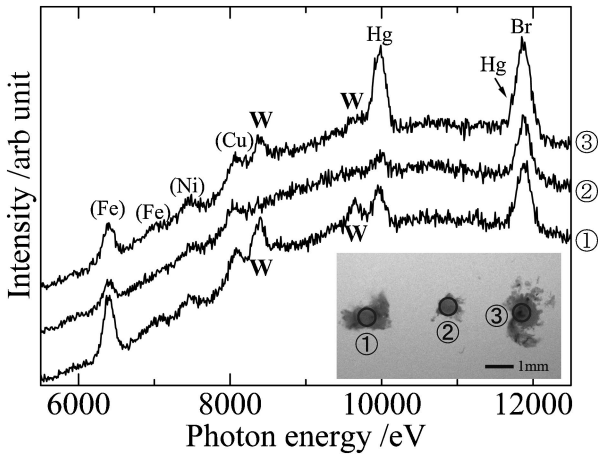

Figure 1. The fluorescence X-ray spectra of lung biopsy specimens.

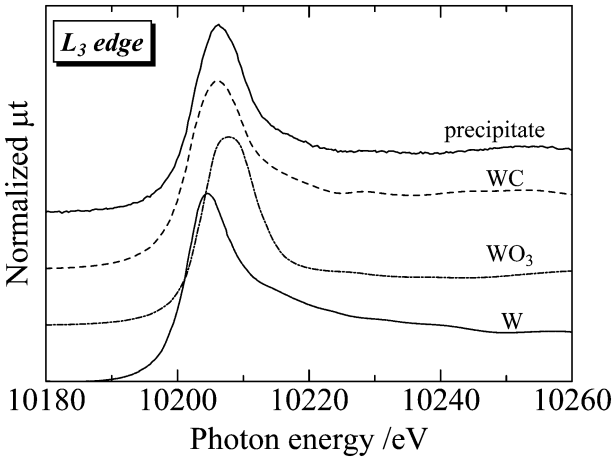

Figure 2. The W L_3-edge XANES spectra of BALF precipitate, metallic W, WC, and WO_3.

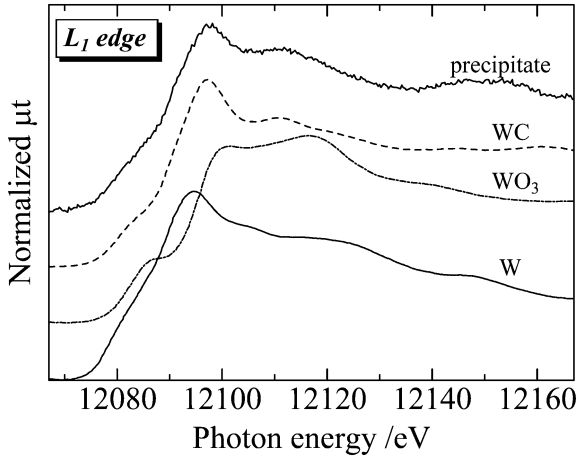

Figure 3. The W L_1-edge XANES spectra of BALF precipitate, metallic W, WC, and WO_3.

XANES spectra were similar in WC and WO_3, but the absorption edge energy was slightly different. Judging from the edge energy, the state of tungsten in the precipitate was close to that of WC; however, clear identification was difficult.

Figure 3 shows the W L_1-edge XANES spectra of the BALF precipitate and standards. The absorption coefficient at the L_1-edge was weaker than that at the L_3-edge; however, a clear difference between the XANES spectra of WC, WO_3, and metallic tungsten could be observed in the W L_1-edge XANES spectra, and the peak edge position and edge height of the BALF precipitate were similar to those of WC. Thus, the W L_1-edge XANES spectra gives clear identification of the state and structure of the BALF precipitate, and the tungsten in the BALF precipitate was identified as WC.

Tungsten concentrations in the lung tissue and BALF of pneumoconiosis patients were reported to be 1.3 and 1.5 ng g^{-1}, as determined by neutron activation analysis.[4] Those are quite low concentrations. X-ray microanalysis (XMA) could detect tungsten in particles localized in lung tissue[1] but not those in BALF.[5] As shown in Figure 1, XRF could also detect tungsten in some of the lung tissue. However, the detection probability depended on the position of the biopsy, and tungsten was not always detected in all specimens. In addition, chemical species of inhaled materials could not be identified by these methods. Thus, elemental analysis (XMA or XRF) would not be conclusive for the diagnosis of tungsten carbide pneumoconiosis.

We have been employed flourescence XAFS analysis for low concentrations of metallic elements in biological specimens.[6] In this study, we used fluorescence XAFS analysis with a microfocused X-ray for the solid components of BALF, and the tungsten contained in the samples could be successfully detected and identified as WC. Bronchoalveolar lavage is less invasive, risky, and painful for the patient compared to biopsy. Inhaled materials attached to alveoli can be effectively washed out and contained in BALF. XAFS analysis of the BALF precipitate provides nondestructive detection and chemical state information on inhaled materials. We used this method to detect WC from a tungsten carbide pneumoconiosis patient in this study. This method should be useful for the diagnosis of low concentrations of foreign bodies in pneumoconiosis patients without excess biopsy.

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