9-1 XAFS Analysis of Titanium in the Soft Tissues Surrounding Dental Implants

Various metallic materials are in wide use for medical and dental implants [1]. Titanium (Ti) is one of the most biocompatible materials, but, even titanium erodes into the surrounding bone [2]. We have previously studied the tissue reaction and biocompatibility for various metals using an X-ray scanning analytical microscope (XSAM) [3]. However, the chemical states of the eroded metallic elements present in the human body were not reported due to their quite low concentrations as detected by conventional methods, even though such information is important for the estimation of biocompatibility. Therefore, we have applied fluorescence XAFS for the analysis of human soft tissue in contact with titanium dental implants to reveal the chemical state of titanium transferred from the placed implant into the surrounding tissue. This study was carried out with the permission of the Ethical Society of the Graduate School of Dental Medicine of Hokkaido University.

Two oral mucosa specimens which were in close contact with pure Ti cover screws for several months were excised (roundly) in the second operations to set healing abutments during the implant surgery treatment of two different patients. The excised specimens were freezedried and subjected to the following analysis. Firstly, the Ti distributions in the specimens were confirmed with an XSAM (XGT-2000V, Horiba). XAFS analyses were then carried for localised Ti sites in the specimens. The XAFS spectra were measured at BL-9A, where the incident X-ray beam was focused into a 1 mm diameter using two bent conical mirrors following monochromatisation with a Si (111) double-crystal. The resulting beam was used to irradiate the Ti-enriched areas of the specimens. Higher harmonics were removed using a total reflection mirror. The XAFS spectra of the oral mucosae were recorded by using a fluorescent XAFS method with a multi-element solid-state detector (SSD, Canberra, 19 elements).

Fig. 1 shows the Ti distribution images from the two oral mucosa specimens recorded with the XSAM. The two specimens show different types of Ti localization. In specimen A, the Ti is in localized in spots, suggesting the existence of particle-like Ti materials. In specimen B, Ti is widely distributed throughout part of the specimen.

Ti K-edge XANES spectra of specimens A and B are shown in Fig. 2. Some typical peaks characteristic of Ti foil were observed in the spectrum of specimen A, suggesting that the localized Ti in specimen A was in the metallic state. Considering the Ti distribution image obtained using the XSAM, the Ti in specimen A appears to exist as metallic particles. The implant treatment involves assembly with tapped pieces, and the tap surfaces were abraded during the implanting operation. Therefore, the origin of the Ti particles in specimen A can be considered to be as debris due to abrasion during the Ti implant operation. In contrast, the XANES spectrum of specimen B resembles that of anatase (TiO₂) [4]. The origin of the anatase in specimen B is unknown. However, it is possible to assume that the eroded Ti ion might be oxidized and localized in the surrounding tissue or that the TiO₂ layer on the implant surface was abraded and transferred into the tissue.

Study of the behavior of elements released into the human body is of great importance for the evaluation of biocompatibility and toxicity. In this study, the possibility of using XAFS for the analysis of the chemical state of trace quantities of elements in biological tissue was investigated [5].



Figure 1

Ti distribution in the surrounding tissue from two implants obtained using an XSAM. The S distribution (white image) shows the shapes of specimens, and the red image shows the Ti distribution.



Figure 2 Ti K-edge XANES spectra for the two specimens.

M. Uo, K. Asakura, A. Yokoyama, K. Tamura, Y. Totsuka, T. Akasaka and F. Watari (Hokkaido Univ.)

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9-2 Visualizing Human Articular Cartilage by X-ray Dark-field Imaging for Early Detection of Rheumatoid Arthritis

Rheumatoid arthritis (RA) is a common systemic autoimmune disease prevalent in around 1% of the worldwide population. It is characterized by the inflammation of the synovial membrane lining the articular capsule and the subsequent invasion of the bone and articular cartilage by the inflamed membrane. The proximal interphalangeal joint (PIPJ) is one of the common locations of RA. If the early degenerative changes before the point of irreversible damage can be detected, it may be possible to reduce the number of patients suffering from joint disease and to improve their quality of lives. The diagnosis of RA is primarily based on clinical, radiological and immunological findings. Of these, immunological research is powerfully done and radiological one is very poor since conventional radiography can only depict bones. Therefore the image diagnoses of early stage of RA are performed mainly by finding minute bone erosion around joints. If articular cartilages could be imaged directly using X-rays it may become possible to clarify changes in the articular cartilage in the early stages of RA.

In this study, X-ray Dark-Field Imaging (DFI) [1-3] was used to successfully visualize the articular cartilage of an intact human finger that had been fixed with formalin. DFI can reveal soft tissue with high contrast under almost no background illumination. The experiment was performed at BL-14B using the experimental apparatus shown in Fig. 3, which comprises of a monochro-collimator (MC) and a Laue case analyzer (A[L]) in a parallel arrangement. The MC uses a surface 9.9° to the Si (440) reflecting planes at an energy of 35 keV in order to achieve asymmetric diffraction leading to an asymmetric factor b = 0.04 and a beam size of 15mm (V) \times 40 mm (H). The 1.2 mm thick A[L] was adjusted to the symmetric Si (440) diffraction condition. The key manipulation to realize DFI is to tune the incident X-ray energy and the effective thickness of the A[L] by inclining it so as to make the reflectivity of the forward diffraction nearly zero. For the MC and



Figure 3

Experimental apparatus for X-ray DFI.



Figure 4 Representative (a) absorption contrast image and (b) DFI of PIPJ.

A[L] used here, an incident X-ray energy of 34.8 keV and a 5° inclination of the A[L] provided the optimum conditions for X-ray DFI.

A representative absorption contrast image and a DFI image of PIPJ are shown in Figs. 4(a) and 4(b). These images were stored on mammography film (Kodak Min-R 2000) without using an intensifying screen, in order to acquire images with high spatial resolution. The exposure time and the dose at object were 30 sec / 2.6 mGy for the absorption image and 50 sec / 4.8 mGy for the DFI image. Only the proximal phalanx (PP) and middle phalanx (MP) are visible in the absorption image of Fig. 4(a), while the articular cartilage on the head of the PP is also clearly visible (yellow arrows) in the DFI image of Fig. 4(b). This clear image of the articular cartilage may remarkably improve the diagnosis of RA. Furthermore this result may indicate that DFI will enable differential diagnosis between RA and other arthropathys.

D. Shimao¹, H. Sugiyama^{1,2}, T. Kunisada³ and M. Ando^{1,2} (¹Graduate Univ., ² KEK-PF, ³Okayama Univ.)

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