Analysis of Titanium Dental Implants Surrounding Soft Tissue Using X-ray Absorption Fine Structure (XAFS) Analysis

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X-ray absorption fine structure (XAFS) analysis was applied for the analysis of titanium (Ti) in the human oral mucosa in contact with Ti dental implants from two different patients. Metallic Ti and an oxide (anatase) were detected. The metallic Ti was distributed in particulate form, which would be debris formed by the abrasion during the operation of implantation. The possibility of using XAFS for the analysis of the chemical state of rarely contained elements in biological tissue was suggested.

Various metallic materials are widely used for medical and dental implants.[1] Erosion and mechanical wearing of metal implants placed in human body have been reported to be associated with localized and systemic problems.[2] Titanium (Ti) is one of the most biocompatible materials, but, even it erodes into surrounding bone.[3] We have studied the tissue reaction and biocompatibility for various metals using an X-ray scanning analytical microscope (XSAM).[4] However, the chemical states of eroded metallic elements in human body have not been reported because of their quite low concentrations detected by conventional methods, though they are important for the estimation of their biocompatibility.

X-ray absorption fine structure (XAFS) analysis is a useful method to reveal the chemical states of target elements. XAFS analysis using synchrotron radiation makes it possible to analyze the state of eroded metal in human body at low concentrations of around 1 to 100 ppm by using fluorescence XAFS.[5] In this study, fluorescence XAFS was applied 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.

Two oral mucosa specimens excised from two different patients through implant surgery were subjected to XAFS analysis. In the dental implant surgery, fixtures of the Brånemark® system were inserted into the jaw bone. The fixture was covered with a cover screw and the fixture and the cover screw were submerged under the mucosa in the first surgery. Both the fixtures and cover screw consisted of commercially pure Ti. Two tissues (specimen A and B) that closely contacted with the Ti cover screw for several months were excised roundly in a second operation to set the healing abutments. The excised specimens were freeze-dried and subjected to the following analysis. This study was carried out with the permission of the Ethical Society of the Graduate School of Dental Medicine of Hokkaido University.

Ti and other elemental distributions in the specimens were confirmed with an XSAM (XGT-2000V, Horiba). The elemental distribution images with XSAM were obtained with 50 scans (scan speed was 3000 seconds per scan). The incident X-ray was obtained under the conditions of 50 kV, 1 mA. Specimens that showed Ti localization with XSAM analysis were used for the following XAFS analysis.

The XAFS spectra were measured at beamline 9A of the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF). The electron storage ring was operated at 2.5 GeV with 300–500 mA. The synchrotron radiation was monochromatized with a Si(111) double-crystal monochromator. The incident X-ray was focused using two bent conical mirrors into 1 mm in diameter and irradiated to the specified area of the specimens where Ti was enriched. Higher harmonics were removed by a total reflection mirror. The XAFS spectra of oral mucosas were measured with a fluorescent XAFS method using the multi-element solid-state detector (SSD, Camberra, 19 elements). I_0 signals were monitored using a N_2 filled ionization chamber. The XAFS spectra of reference materials (Ti foil, anatase, and rutile) were measured with a transmission method.

Figure 1 shows the S and Ti distribution images of two oral

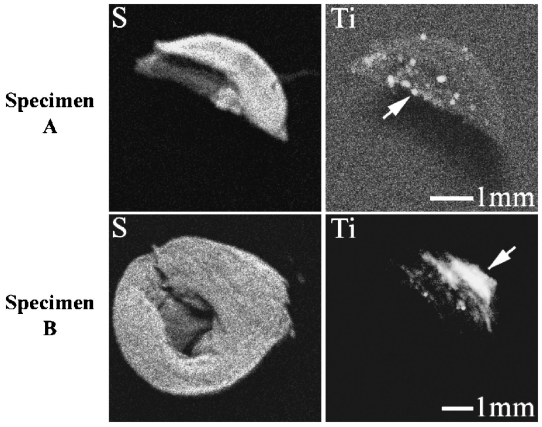

Figure 1. Elemental distribution images of two titanium implants and surrounding tissues using XSAM.

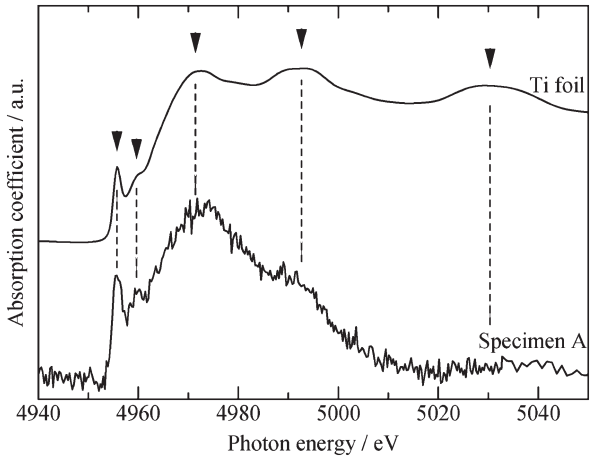

Figure 2. The Ti K-edge XAFS spectra of specimen A and Ti foil.

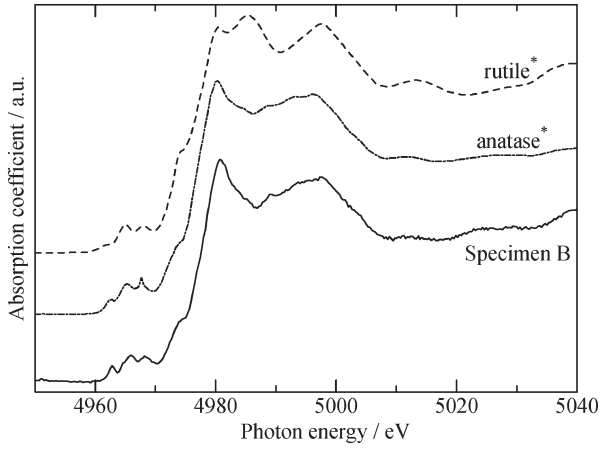

Figure 3. The Ti K-edge XAFS spectra of specimen B and TiO_2 in rutile and anatase form after Asakura et al.[6]

mucosa specimens with XSAM. The S distribution image shows the shapes of specimens. Specimens show different types of Ti localization. In specimen A, Ti is localized in spots, which suggests the existence of particle-like materials consisting of Ti. In specimen B, Ti is widely distibuted in part of the specimen and the distribution is different from specimen A.

The XAFS spectrum of specimen A was quite weak because of the low concentration of Ti. Figure 2 shows the background-removed Ti K-edge XAFS spectra of specimen A (arrow in Figure 1) and Ti foil. Some typical peaks characteristic of Ti foil were also observed in the spectrum of specimen A. This suggested that the localized Ti in specimen A was in the metallic state. Considering the Ti distribution image of XSAM, the Ti in specimen A would exist as metallic particles. The Ti dental implant was assembled with tapped pieces and the tap surfaces were abraded in the implanting operation. Therefore, the derivation of Ti particles in specimen A was considered to be debris due to the abration in the Ti implant operation.

The Ti K-edge XAFS spectra of specimen B (arrow in Figure 1) and TiO_2 (anatase and rutile)[6] are shown in Figure 3. The spectrum of specimen B was close to that of anatase. Therefore, the localized Ti in specimen B was considered to be anatase. The derivation 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 TiO_2 layer on the implant surface was abraded and transferred into the tissue.

The implants of these two patients were in stable in spite of the Ti transfer into the surrounding tissue. Therefore, the Ti transfer from implants to the tissues did not have a harmful influence on the stabilization of the Ti implant because stable Ti species such as metallic Ti and TiO_2 were localized around the tissue in contact with the implant and did not widely spread.

Pure Ti component of Ti dental implant have the highest chemical stability and biocompatibility among metals. In a previous study, it was evident that a small amount of Ti was transferred from the implant though its chemical state was unknown.[3] In this study, using XAFS analysis we found that the transferred and localized Ti in oral mucosa were metallic Ti and anatase, respectively. The estimation of behavior of elements released into the human body is important for the evaluation of biocompatibility and toxicity. In this study, the possibility of using XAFS for the analysis of the chemical state of rarely contained elements in biological tissue was suggested.

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References

1 A. McNamara and D. F. Williams, *Biomaterials*, **2**, 33 (1981).
2 A. McNamara and D. F. Williams, *Biomaterials*, **3**, 160 (1982); A. McNamara and D. F. Williams, *Biomaterials*, **3**, 165 (1982); H. Schliephake, G. Reiss, R. Urban, F. W. Newkam, and S. Guckel, *Int. J. Oral Maxillofac. Implants*, **8**, 502 (1993); N. J. Hallab, A. Skipor, and J. J. Jacobs, *J. Biomed. Mater. Res.*, **65A**, 311 (2002); Y. Kasai, R. Iida, and A. Uchida, *Spine*, **28**, 1320 (2003).
3 A. M. Ektessabi, T. Otsuka, Y. Tsuboi, K. Yokoyama, T. Albrektsson, L. Sennerby, and C. Johansson, *Int. J. PIXE*, **4**, 81 (1994).
4 M. Uo, F. Watari, A. Yokoyama, H. Matsuno, and T. Kawasaki, *Biomaterials*, **20**, 747 (1999); M. Uo, F. Watari, A. Yokoyama, H. Matsuno, and T. Kawasaki, *Biomaterials*, **22**, 677 (2001); M. Uo, F. Watari, A. Yokoyama, H. Matsuno, and T. Kawasaki, *Biomaterials*, **22**, 1787 (2001); M. Uo, M. Tanaka, and F. Watari, *J. Biomed. Mater. Res.*, **70B**, 146 (2004).
5 M. Nomura, *J. Synchrotron Radiat.*, **5**, 851 (1998); K. Asakura, *Shokubai (in Japanese)*, **42**, 328 (2000); W. J. Chun, Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, and K. Asakura, *J. Synchrotron Radiat.*, **8**, 168 (2001).
6 K. Asakura, J. Inukai, and Y. Iwasawa, *J. Phys. Chem.*, **96**, 829 (1992).

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