XAFS Analysis of Ti and Ni Dissolution from Pure Ti, Ni–Ti Alloy, and SUS304 in Soft Tissues

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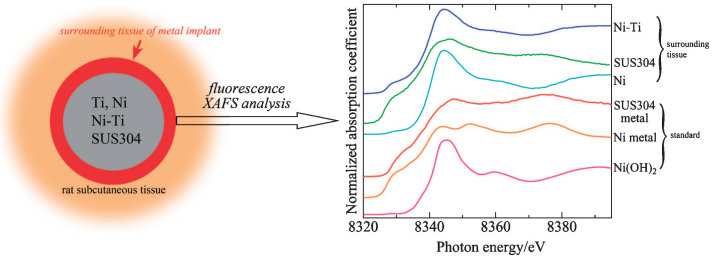

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Ti, a Ni–Ti alloy, and stainless steel (SUS304) were implanted in rat soft tissues for 6 months. The chemical states of the component elements contained in the tissues surrounding those metallic implants were analyzed by fluorescence X-ray absorption fine structure (XAFS). Titanium oxide and a nickel aquo complex, which would be caused by the erosion of Ti and Ni, were detected in the surrounding tissues. The concentrations of Ti and Ni in the tissues were 1–3 and 300 ppm, respectively. Thus, the dissolved conditions and concentrations of those practical metallic materials in vivo were successfully confirmed.

Corrosion-resistant metallic materials, e.g., stainless steel, chromium- and titanium-based alloys, and pure titanium, are widely used for medical and dental implants.[1] Titanium and its alloys are quite chemically stable and biocompatible materials, so they are widely used for dental implants and artificial bones and joints. Stainless steels and chromium-based alloys also have high corrosion resistance and good mechanical properties, so they are widely used for various medical and dental devices. The Ni–Ti alloy, Nitinol, is used for orthodontic wires and some medical implants because of its good corrosion resistance and unique mechanical properties. However, even for highly corrosion-resistant materials, corrosion of these materials in vivo and in vitro has been reported.[2] Stainless steels, chromium-based alloys, and Ni–Ti contain Ni, Cr, and Co, which are known to cause acute and chronic toxicity and metal allergies. However, the in vitro corrosion of these alloys has been reported.[3] Determining the chemical states of eroded metallic elements is important for the estimation of their biocompatibility, but it is difficult by conventional methods because of their quite low concentrations.

The authors have employed fluorescence X-ray absorption fine structure (XAFS) analysis using synchrotron radiation for chemical-state analysis of low concentrations of metallic elements in the tissues surrounding dental titanium implants and other dental alloys.[4] In those studies, pure Ti, a Ni–Ti alloy, and SUS304 were implanted into rat soft tissue for a long period (6 months) and eroded Ti and Ni in the surrounding tissue were analyzed using fluorescence XAFS.

Pure Ti (99.99%), a Ni–Ti alloy (55%Ni–45%Ti) and SUS304 (Fe–18%Cr–8%Ni) (1 mmϕ, Nilaco Co., Ltd., Tokyo, Japan) were cut into 10-mm lengths, and their surfaces were polished with 0.05-μm alumina paste. The polished specimens were sterilized with ethylene oxide gas and implanted into subcutaneous loose connective tissue in the dorsal thoracic region of 12 week-old Wistar rats. After 24 weeks of implantation, the rats were euthanized and tissue blocks with metallic specimens were obtained. After fixation in 10% neutral buffered formalin, the thin fibrous tissue layers that encapsulated the implanted specimens were carefully removed, freeze-dried, and used for XAFS analysis. The weight of the dried specimens were 2–3 mg. Two replicates were prepared for each specimen. The X-ray absorption near-edge structure (XANES) spectra were measured at beamlines 9A and 12C in 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 1 mm in diameter using two bent conical mirrors, and the specified areas of the specimens enriched in Ti or Ni were irradiated. Higher harmonics were removed by a total reflection mirror. The XANES spectra of tissue specimens were measured with the fluorescent XAFS method using a multielement solid-state detector (SSD, Camberra, 19 elements). I_0 signals were monitored using an N_2-filled ionization chamber. The XANES spectra of reference materials (Ti and Ni foil, anatase and $Ni(OH)_2$) were measured by a transmission method. After XAFS measurement, specimens were dissolved in 2 M HCl(aq) and total amounts of Ti and Ni in the soft tissues were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; P-4010, Hitachi, Japan).

Figure 1 shows the background-removed Ti K-edge XANES spectra of pure Ti- and Ni–Ti alloy-implanted soft tissues and Ti foil and anatase as standards. The spectrum of Ni–Ti-implanted tissue was similar to that of anatase. However, the absorption edge was slightly shifted toward low energy. Thus, the existence of metallic Ti or other lower oxide was also expected. Therefore, in the tissues surrounding the Ni–Ti alloy, Ti would exist as not only metallic Ti but also anatase. Anatase was derived from eroded Ti in our previous studies,[4] and metallic Ti would be derived from the remaining debris during the polishing of the implants prior to the implantation. Pure Ti has high corrosion resistance so the absorption of pure Ti-implanted tissue was at lower S/N than that of Ni–Ti-implanted tissue. From the shape of the spectra and their absorption edges, the chemical state of Ti in the surrounding tissue of Ti was expected to be similar to that of Ni–Ti. The concentration of Ti in the surrounding tissue (dry weight) of Ti was approximately 1 ppm and that of Ni–Ti 3 ppm. Thus, the total amounts of Ti transferred from the implanted metals to the surrounding tissues were quite small, but their

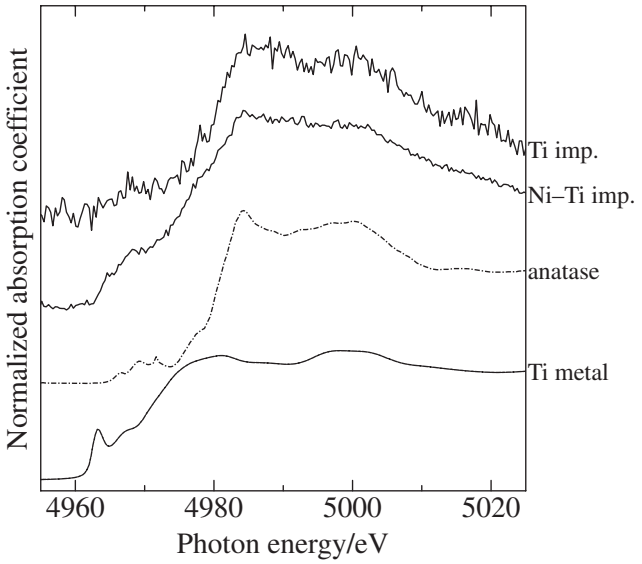

Figure 1. The Ti K-edge XANES spectra of pure Ti- and Ni–Ti alloy-implanted tissues and Ti foil and anatase[5] as standards.

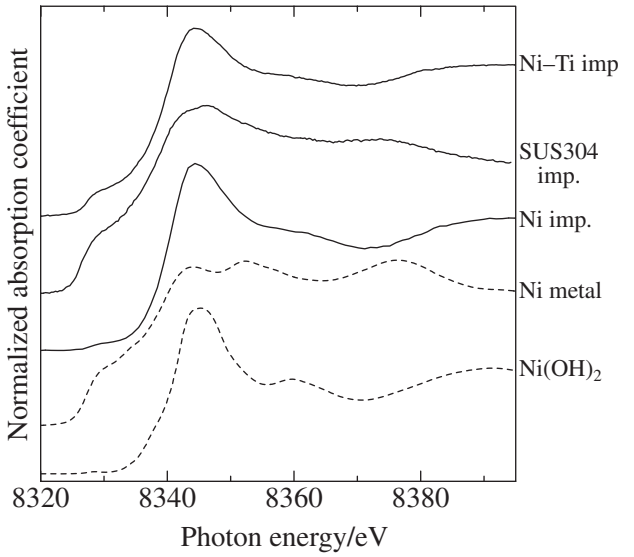

Figure 2. The Ni K-edge XAFS spectra of Ni–Ti alloy-, SUS304-, and Ni-implanted tissues, and Ni foil and $Ni(OH_2)$ as standards.

chemical states were successfully estimated by fluorescence XAFS.

Figure 2 shows the background-removed Ni K-edge XAFS spectra of Ni–Ti- and SUS304-implanted tissues. In a previous study, the chemical state of Ni in the tissue surrounding Ni implants was similar to that of $Ni(OH)_2$; therefore, Ni was expected as an aquo complex. The spectra in Ni–Ti- and SUS304-implanted tissues were explained as a mixture of metallic Ni and $Ni(OH)_2$. That means the Ni in those tissues were not only the metallic component but also the aquo complex. The metallic component would be derived from remaining debris during the polishing. The aquo complex would be caused by the erosion and dissolution of Ni. The percentages of the aquo complex estimated by curve-fitting were 50% for Ni–Ti and 20% for SUS304. The total Ni concentrations in the surrounding tissue determined by ICP-AES analysis were 330 ppm for Ni–Ti and 350 ppm for SUS304. Thus, the expected concentrations of nickel aquo complex were 165 ppm for Ni–Ti and 70 ppm for SUS304. That suggests the higher Ni dissolution was occured for Ni–Ti compared to SUS304. Cr was not detected in the tissue surrounding SUS304 by this method. Cr in the surface layer would be in an oxide state caused by passivation, so Cr would not dissolve into the surrounding tissue.

Takahashi et al. reported that Ni was selectively eroded from Ni–Ti and Ni–Cr alloys. Doi et al. reported the dissolution of Ti, Ni, Ni–Ti, and SUS316L under various pHs in vitro. In that report, SUS316L showed lower Ni dissolution than Ni–Ti, and Cr dissolution was negligible under neutral condition. Ryhanen et al. also reported higher Ni dissolution from Ni–Ti alloy than from SUS316L under cell culture conditions. This tendency is in good agreement with the present study.[3]

Ti, Ni–Ti, and SUS304 are well-known corrosion-resistant metals and are widely used as medical and dental materials. In this study, the dissolution of the component elements into the surrounding soft tissues in long-term implantation was confirmed by the fluorescence XAFS method.

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