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Application of synchrotron radiation in investigation of metal-ion release from a hip replacement prosthesis

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The aim of the present study was to measure very low concentrations of Al, V, Fe, Cr and other metal elements in a matrix of P, S, Cl, Ca and other constituent elements of the human body. These metal elements were released from a failed total hip replacement prosthesis into the surrounding tissues. The experimental results have been compared with those from proton-induced X-ray emission spectroscopy of the same specimen.

Keywords: ion release; XRF; prosthesis.

1. Introduction

Dental and orthopaedic implants are used in different surgical processes. Fig. 1, a hip prosthesis, is a typical example of the several hundred implants that exist with different shapes and materials. Fig. 1(*a*) shows a stem, Fig. 1(*b*) a head, and Fig. 1(*c*) a cup. Most of these implants are made of cobalt-based alloys. However, there has been a general trend in the past three decades, and in the past decade in particular, to replace some of the cobalt-based materials with titanium, despite the fact that the material strength of titanium is lower than that of cobalt-based materials.

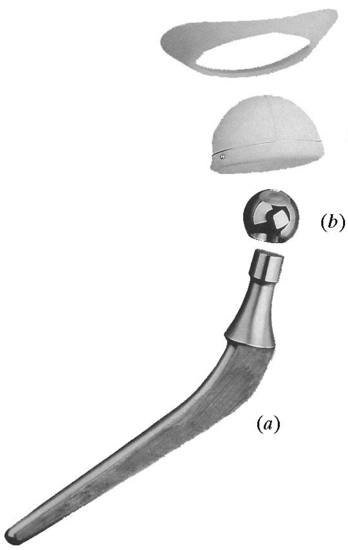

Figure 1
A total hip replacement system.

The material from implants dissolves in the human body and releases metallic and polymeric elements during the long periods of time while inserted in the human body. The chemical interactions between the tissues and surface of the implants, and the mechanical friction of implants are responsible for the release of metals into the human body.

Ion release (Ducheyne *et al.*, 1984; Osborn *et al.*, 1990; Lugowski *et al.*, 1991; Ektessabi *et al.*, 1994; Jacobs *et al.*, 1996) and evaluation of the toxicity of the released elements have been the subject of several *in vivo* and *in vitro* studies. Experimental results from cytotoxicity tests of the ions released from the implant materials show that V in concentrations from 0.1 to 1.67 p.p.m. resulted in altered metabolic cell responses. The cytotoxic effect of V in those concentrations is comparable with that of other elements such as Cr, and more than one order of magnitude higher than the cytotoxicity of Ti (Yamamoto *et al.*, 1996). It is highly probable that there exists a strong relation between the toxicity and the chemical nature of the released ions. The release of less toxic elements such as Ti and Al may have undesirable consequences when they are accumulated in other human organs.

Several studies have been carried out using different methods, such as EPMA (electron-probe microanalyser), SIMS (secondary ion mass spectroscopy) and PIXE (proton-induced X-ray emission) techniques to investigate ion release from implant materials. The release of titanium into human bone from titanium implants was investigated by Osborn *et al.* (1990) using the EPMA method, where the surface of the implant was coated by plasma-sprayed titanium. SIMS was used by Lodding *et al.* (1990) to measure element distribution in recovering tissues around implants in rabbit tibia bone. These studies confirm the release of metals into the tissues surrounding implants, but the detection limit was low, and in the case of the EPMA study the noise-to-signal ratio was high. Ektessabi *et al.* (1994, 1996) and Ektessabi & Wennerberg (1995) used ion microbeam PIXE and confirmed metal-ion release from Ti-alloy implants inserted in rabbit bone. One of the serious problems in the application of microbeam PIXE to the analysis of biomedical samples is the low yield of the emitted X-rays when the analysis is localized and the diameter of the ion beam is very small (a few μm).

The aim of the present study was to measure Al, V, Fe, Cr and other metal elements which were released from a failed total hip replacement prosthesis into the surrounding tissues, in an *in vivo* process, using synchrotron-radiation-excited X-ray fluorescence (XRF) spectroscopy (Horowitz & Howell, 1972; Sparks *et al.*, 1977; Iida & Gohshi, 1991; Saisho & Gohshi, 1996) as a tool for this kind of biomedical sample investigation. The experimental results are compared with those from PIXE spectroscopy of the same specimen.

2. Experimental

2.1. *Specimen*

The specimens were provided from one female patient, 55 years of age and with a diagnosed arthrosis. The patient had a total hip replacement with a hydroxyapatite (HAp)-coated prosthesis. The implant consisted of a stem and a metal backing made of Ti–6 Al–4 V, an implant head made of stainless steel, and a polyethylene (PE) cup. Both the stem and the metal backing had a plasma-sprayed HAp surface coating (155 μm). Accelerating PE wear was diagnosed, leading to reoperation 5.4 years after insertion. This hip functioned painlessly until a few months before reoperation. At revision, one could observe excessive wear, *i.e.* the femoral head had created a wear hole through the PE inlay and the steel was fretting directly on the Ti-alloy-made backing. Histologically stained ground sections (10 μm) were prepared for light microscopy observations as well as thin (50 μm) unstained loose ground sections for synchrotron radiation XRF and PIXE analyses. The method of preparation has been explained in detail by Donath (1995). The thin section was placed on ultra-high-purity carbon. Fig. 2 shows a thin specimen used for the measurements before being placed on the ultra-high-purity carbon.

2.2. *Measurement and results*

The synchrotron radiation ring, with the following parameters, was used for the total reflection X-ray florescence spectroscopy. The beam energy was 575 MeV, the beam current 300 mA, the bending field 3.8 T, the critical wavelength 1.5 nm and the ring radius 1.0 m. The beam, with the quasi monochromatic photon energy of 10 keV and a glancing angle of 30°, was incident on the specimen with a cross section of 10 × 15 mm. The synchrotron radiation XRF analysis result is shown in Fig. 3, without any absorption corrections. In addition to comparatively high concentrations of Ti, V, Cr and Fe in a matrix of P, S, K, Ca and Cl, Al was also detected with a clear peak in the low-energy side of the spectrum.

PIXE (Johansson & Campbell, 1988; Vis, 1985; Watt & Grime, 1987) spectroscopy was performed on two pieces of the specimen, over 30 different points. A tandem accelerator with an energy of 2.0 MeV and a beam size of 0.5 × 0.5 mm was used. The measurement points were chosen from tissues probably including the metal particles. Two typical spectra are shown in Figs. 4 and 5. Fig. 4 shows the spectrum at a point with a low concentration of metallic elements and Fig. 5 shows the spectrum at a point with a high concentration of metallic elements.

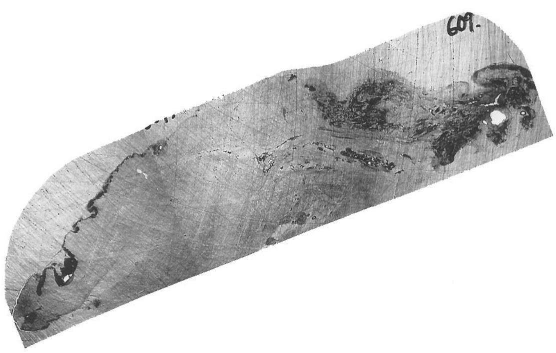

Figure 2
A photograph of a thin specimen from soft tissues around a failed implant.

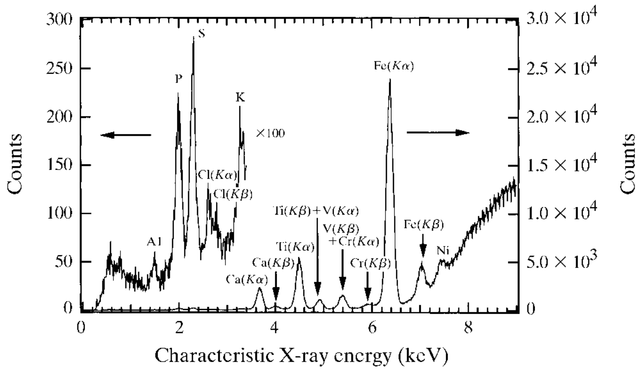

Figure 3
XRF analysis result of the soft tissues around a failed hip replacement prosthesis.

3. Discussion

Cr–Co-based materials, commercially pure titanium (Cp-Ti) and titanium alloys (Ti–6 Al–4 V) are materials which are often used as dental and orthopaedic implants. Owing to mechanical friction or chemical reactions which cause dissolution of the implant material, metal ions are released into the surrounding tissues from a metal implant. Large areas of black stained tissue as well as large PE particles, internalized in multinucleated cells, were observed by light microscopy in the specimens used in this study. Synchrotron radiation XRF analysis demonstrated the presence of different metals, such as Al, Ti, Fe and Cr. A comparison between the synchrotron radiation XRF spectrum and the PIXE spectra shows that under the experimental conditions reported in this paper, XRF using synchrotron radiation has a better sensitivity for detecting the low-mass elements, Al being a significant example. Both the synchrotron radiation XRF and PIXE spectra show the presence of metallic elements in the soft tissues and support the clinical observation of friction between the two metals used in the prosthesis.

The application of synchrotron radiation XRF to the detection of metal-ion release, measurement of the distribution of the

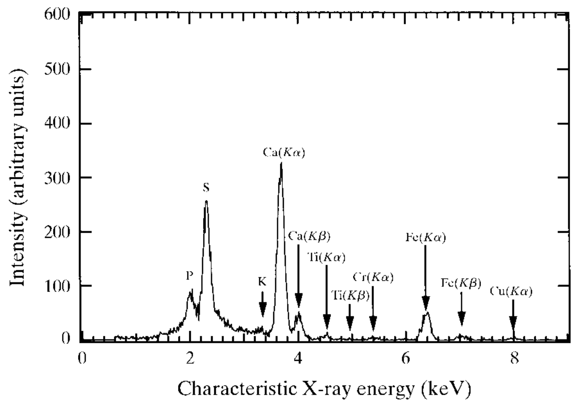

Figure 4
PIXE analysis result of the soft tissues around a failed hip replacement prosthesis at a point with a low concentration of Ti.

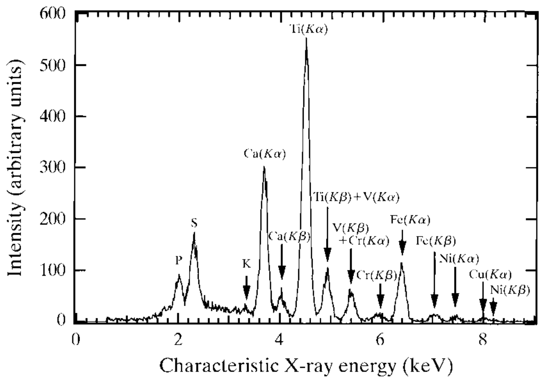

Figure 5
PIXE analysis result of the soft tissues around a failed hip replacement prosthesis at a point with a high concentration of Ti.

released materials around the metal implants and the chemical state of the released elements makes it possible to investigate further the mechanism of ion release and cell interactions with an implant surface.

The synchrotron radiation XRF analysis was performed at the Synchrotron Radiation Center, Ritsumeikan University, Kusatsu, Shiga, Japan. The PIXE analysis was performed at the Radiation Laboratory, Department of Nuclear Energy, Kyoto University. The authors would like to express their thanks to many colleagues in the above-mentioned institutions for their support of this study.

References

Donath, K. (1995). *Preparation of Histologic Sections*. Norderstedt: Exakt-Kulzer Publication.

Ducheyne, P., Willems, G., Martens, M. & Helsen, J. (1984). *J. Biomed. Mater. Res.* **18**, 293–308.

Ektessabi, A. M., Otsuka, T., Tsuboi, Y., Horino, Y., Mokuno, Y., Fujii, K., Albrektsson, T., Sennerby, L. & Johansson, C. (1996). *Nucl. Instrum. Methods B*, **109**/**110**, 278–283.

Ektessabi, A. M., Otsuka, T., Tsuboi, Y., Yokoyama, K., Albrektsson, T., Sennerby, L. & Johansson, C. (1994). *Int. J. PIXE*, **4**, 81–91.

Ektessabi, A. M. & Wennerberg, A. (1995). *Int. J. PIXE*, **5**(2,3), 145–152.

Horowitz, P. & Howell, J. A. (1972). *Science*, **178**, 608.

Iida, A. & Gohshi, Y. (1991). *Handbook on Synchrotron Radiation*, Vol. 4, ch. 9, edited by S. Ebashi, M. Koch & E. R. Rubenstein, p. 307. Amsterdam: North Holland.

Jacobs, J. J., Black, J., Skipor, A. K., Paprosky, W. P., Patterson, L. M. & Galante, J. O. (1996). *Proceedings of the Fifth World Biomaterials Congress*, p. 243. University of Toronto Press.

Johansson, S. A. E. & Campbell, J. L. (1988). *PIXE, a Novel Technique for Elemental Analysis*. Chichester: Wiley.

Lodding, A. R., Fischer, P. M., Odelius, H., Noren, J. G., Sennerby, L., Johansson, C. B., Chabala, J. M. & Levi-Setti, R. (1990). *Anal. Chim. Acta*, **241**, 299–314.

Lugowski, S. J., Smith, C., Mchugh, A. D. & Van Loon, J. C. (1991). *J. Biomed. Mater. Res.* **1**, 1443–1458.

Osborn, J. F., Wallet, P. & Meenen, N. (1990). *Clinical Implant Materials, Advances in Biomaterials*, Vol. 9, edited by G. Heimke, U. Soltesz & A. J. C. Lee, pp. 75–80. Amsterdam: Elsevier.

Saisho, H. & Gohshi, Y. (1996). *Application of Synchrotron Radiation to Material Analysis*, ch. 2, edited by H. Saisho & Y. Gohshi, p. 79. Amsterdam: Elsevier.

Sparks, C. J. Jr, Raman, S., Yakel, H. L., Gentry, R. V. & Krause, M. O. (1977). *Phys. Rev. Lett.* **38**, 205.

Vis, R. D. (1985). *The Proton Microprobe: Applications in the Biomedical Field*. New York: CRC.

Watt, F. & Grime, G. W. (1987). In *Principles and Applications of High Energy Ion Micro Beams*, ch. 5, 6. Bristol: Adam Hilger.

Yamamoto, A., Honma, R. & Sumita, M. (1996). *Proceedings of the Fifth World Biomaterials Congress*, p. 679. University of Toronto Press.