ORIGINAL ARTICLE

Analysis of Wear Debris Generated from the Metal-on-metal Hip Joint

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Synopsis
The elemental concentration, shape and chemical state of debris contained in the articular capsules of metal-on-metal hip joints were examined. Co derived from Co-Cr alloy was detected with high concentration. By TEM observation, some larger debris in several hundred nanometers and a lot of smaller debris smaller than several ten nanometers were observed. The debris could be observed in the severe metallosis region. Most of Co contained in the articular capsules could be estimated as the metallic state by fluorescence XAFS analysis, which provides high sensitivity for chemical state analysis. Therefore, the metallosis of the articular capsule could be assumed as mainly caused by the metallic debris.

Key words: *wear debris, hip joint, Co-Cr alloy, XAFS*

Introduction

Metal-on-metal bearings have been widely used as the hip joint bearings because of its high wear resistance than other type of joints such as metal-on-polyethylene [1-3]. Even a metal-on-metal hip joints, metal debris were generated and accumulated in the surrounding tissues and synovial fluids of the joints. Failure of the hip joint prothesis caused by the metal debris are also concerned [4, 5]. The bulk metallic materials used for the metal-on-metal bearings such as Co-Cr alloy show high corrosion resistance and low toxicity. However, the inflammatory response induced by debris of worn metals was suggested even in case of the biocompatible metals. Tamura et al. showed the cytotoxicity of titanium particles increased in the smaller particles (2μm) [6]. Therefore, the size, shape, concentration and chemical state of the wear debris in the surrounding tissues of the metal-on-metal hip joints would be necessary to estimate the endurance of the joints.

The aim of this study was to investigate the elemental concentration, shape and chemical state of debris contained in the articular capsules of metal-on-metal hip joints.

Materials and Methods

1 Specimens

Two cases of the surrounding tissues of metal-on-metal hip joints were studied. A part of articular capsules of hip joints were retrieved while the replacement operations of hip joints. The materials used in those hip joints (acetabular cup, femoral head and stem) were tabulated in Table 1. Specimen 1 was retrieved from the articular capsule of the hip joint for 6 months. Specimen 2 was retrieved from that for 14 years, then, the inner surface of the capsule showed stained black and severe metallosis was suggested. Then, the specimen 2 was separated into the black-stained inner region (specimen 2-B) and the outer region with white color (specimen 2-W). Those specimens were applied for the following analysis.

2 Quantification of metal concentration

Two replicates of each specimen of the articular capsules were weighed to be 0.1~0.3g in wet weight and dissolved in 5M HCl(aq) at 80^{o}C for 12 hours. Then, the concentrations of Co, Cr and Ti in the dissolved solutions were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES; P-4010, Hitachi, Japan). The concentration of those elements in the articlar capsules were evaluated by the concentrations in the solutions and wet weights of the specimens.

3 Transmission electron microscope observation

The specimens were fixed, dehydrated, embedded and thin-sectioned by the conventional method and applied for the transmission electron microscope (TEM). TEM observation was carried by JSM-6500F (JEOL, Japan) under 200kV of the acceleration voltage.

4 X-ray absorption fine structure (XAFS) analysis

The X-ray absorption fine structure (XAFS) spectra were measured at beamline 12C in the Photon Factory at the National Laboratory for High Energy Physics (KEK-PF). The electron storage ring was operated at 3 GeV with 450 mA. The synchrotron radiation was monochromatized with a Si(111) double-crystal monochromator. The incident X-ray was focused 1mm in diameter using two bent conical mirrors, and the specified areas of the specimens were irradiated. The X-ray absorption near-edge structure (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 material (Co foil) were measured by a transmission method.

Table 1 Components of the examined hip joints

	Cup	Head	Stem	Implanted period
Specimen 1	Co-Cr	Co-Cr	Ti alloy	6 months
Specimen 2	Ti alloy	Co-Cr	Ti alloy	14 years

Table 2 Concentration of metallic elements in articular capsules of hip joints

	Co (ppm)	Cr (ppm)	Ti (ppm)
Specimen 1	530	8.6	14
Specimen 2-B	1060	1.6	420
Specimen 2-W	160	1.1	5.1

Results and discussion

The concentration of metallic elements in the specimens were shown in Table 2. Both femoral heads consisted of Co-Cr alloy, then, Co was detected from both specimens with high concentration. The acetabular cup was consist of Ti alloy, then, high concentration of Ti (400ppm) was detected in specimen 2-B. The inner region of specimen 2 (2-B) showed high Co and Ti concentration compared to the outer region (specimen 2-W). Then, the severe metallosis was confirmed in the specimen 2. In contrast, Cr concentrations were several ppm. Generally, Cr and Co content in the Co-Cr alloy is 50~60wt% and 20~30wt%, respectively. If the Co and Cr in the tissues were derived from the wear debris of Co-Cr alloy, Cr concentration should be one third to half of Co concentration. The reason of the low Cr concentration is not clear, but, the selective dissolution of Cr could be assumed.

Fig.1 shows the debris observed in the specimen 2-B. Some larger debris in several hundred nanometers and a lot of smaller debris smaller than several ten nanometers were observed. The debris could be observed in the severe metallosis region in the specimen 2-B, but, no debris could be found in other two specimens by TEM observation.

Fig.2 shows the Co K-edge XANES spectra of the articular capsule specimens and Co foil as the standard. As shown in Fig.2(a), specimens 1 and 2-B showed clear Co K-edge absorption, while, the absorption ob the specimen 2-W was quite weak because of low Co concentration as shown in Table 2. Fig. 2(b) shows the comparison of normalized spectra of the specimens and Co foil standard. The spectra of specimen 1 and 2-B showed clear Co K absorption and those were close to that of Co foil. Therefore, the Co in the specimen 1 and 2-B was estimated to be in the metallic state. XANES spectrum of specimen 2-W was unclear, but the absorption edge was slightly shifted toward higher energy. Thus, Co would be existed as the aquo complex in the

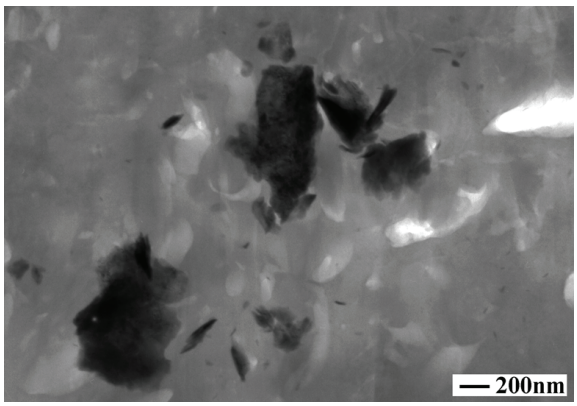

Fig. 1 TEM image of debris in the specimen 2-B.

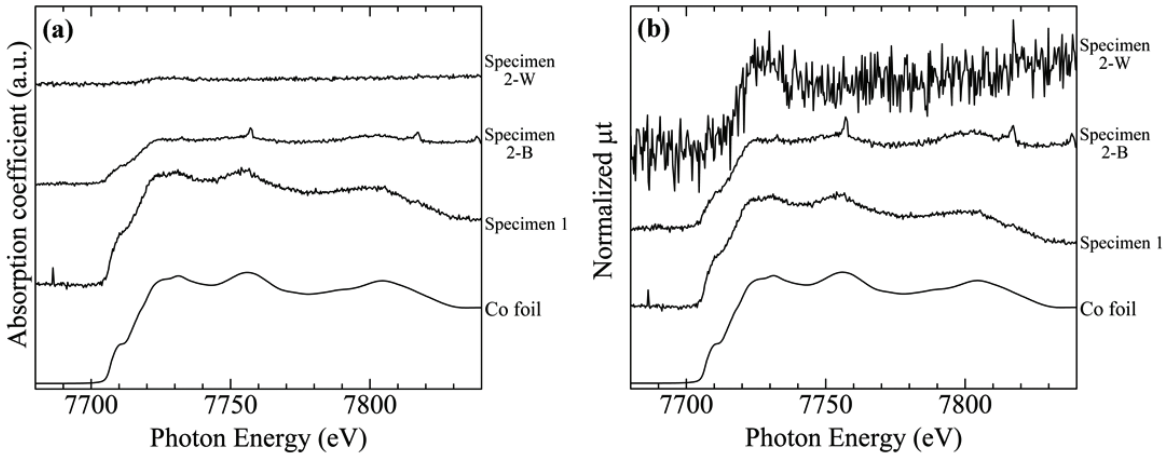

Fig.2 Co K-edge XANES spectra of the articular capsule specimens and Co foil as the standard. (a) background subtracted absorption spectra, (b) normalized absorption spectra

outer region of articular capsule, where was not stained by the metallosis. The absorption of Cr could not be detected because of its low concentration. Therefore, the most of Co contained in the articular capsules was estimated as the metallic Co which is the wear debris. Thus, the metallosis of the articular capsule would mainly caused by the metallic debris. In the outer region of articular capsule, where was not stained by the metallosis, the chemical state of Co was assumed as the aquo complex, then, the dissolution of Co from the wear debris was suspected.

The elemental analysis of wear debris of artificial joints had been carried by x-ray microanalysis with the electron microscope [4, 7]. However, that method could not analyze the chemical state of the metallic elements. We have been applied the fluorescence XAFS method with synchrotron radiation, which provide high sensitivity for chemical state analysis of rarely contained metallic elements in biological tissues [8, 9]. In case of Ti and Ni-Ti implants, dissolved Ti and Ni could be detected as TiO_2 and Ni aquo complex. In the present study, Co in the articular capsules of the hip joints could be estimated as metallic state and other component could not be detected.

Conclusion

The elemental concentration, shape and chemical state of debris contained in the articular capsules of metal-on-metal hip joints were examined. Co derived from Co-Cr alloy was detected with high concentration. By TEM observation, some larger debris in several hundred nanometers and a lot of smaller debris smaller than several ten nanometers were observed. The debris could be observed in the severe metallosis region. Most of Co contained in the articular capsules was estimated as the metallic state by XAFS analysis, then, the metallosis of the articular capsule could be assumed as mainly caused by the metallic debris.

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