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Applied Surface Science 252 (2006) 3760–3766

applied surface science

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Analysis of prosthetic knee wear debris extracted from synovial fluid

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Received 31 December 2004; received in revised form 27 April 2005; accepted 31 May 2005
Available online 11 July 2005

Abstract

We report on the use of X-ray photoelectron spectroscopy and scanning electron microscopy equipped with energy dispersive spectroscopy to investigate the metallic content of wear debris from prosthetic knees. Synovial fluid aspirated from patients with prosthetic knees was centrifuged, rinsed and dried, resulting in small deposits of wear debris. We identify the presence and composition of metal wear debris from the femoral, tibial, and in some cases the patellar prosthetic components. We also demonstrate the inhomogeneous size, shape, and distribution of the wear particles, and both lateral and vertical elemental inhomogeneity. This points to the necessity of using a combination of techniques for studying such wear debris. The ability to detect the presence of certain metals within the synovial fluid of patients, even when surgical inspection did not identify wear of specific components, may have far reaching implications in the biomedical and prosthetics communities.

Keywords: Knee arthroplasty; Wear debris; XPS; SEM; EDS; Ti–6Al–4V; Co–Cr–Mo

1. Introduction

Joint arthroplasty involves the placement of man-made materials into the joints of the human body, which are intended to withstand mechanical wear in a biological environment for many years. After joint replacement surgery, the inevitable generation of wear debris that dislodges from the artificial joint during normal usage can lead to localized inflammation, pain, and ultimately bone loss [1]. This loss of bone adjacent to the prosthetic device, a process known as aseptic osteolysis, continues to be a common problem with joint replacements and is responsible for the majority of their failures. However, the composition of this in situ wear debris is presently unclear. It is thought to contain various

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0169-4332/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.apsusc.2005.05.060

metals in addition to ultrahigh molecular weight polyethylene (UHMWPE), polymethylmethacrylate, and human tissue, but has yet to be adequately identified.

We are trying to answer some of the open questions in the biomedical community concerning the biocompatibility and fate of prosthetic metals [2–6]. In a recent study performed in our laboratories [2], knee synovial fluid, obtained from seven patients with different prosthetic knee designs, was aspirated and centrifuged, resulting in small wear deposits. These deposits were washed and dried, and then analyzed by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. We identified titanium in five of the seven debris samples, indicating femoral and patellar component wear, and in some, the potential for backside wear of the metal tibial tray. From these earlier results we hypothesized that the metallic species were inhomogeneously distributed throughout the wear debris samples. The present study, analyzing a different set of synovial fluid aspirates with XPS in conjunction with scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS), verifies this previous hypothesis.

The deposits are primarily carbonaceous in nature, but XPS data indicate that some of the new samples contain titanium as well. Energy dispersive spectroscopy data generally show evidence for titanium, aluminum and vanadium, consistent with the Ti–6%Al–4%V (Ti–6Al–4V) alloys used for the prostheses. Some samples also contain cobalt, chromium, and other trace elements consistent with the F–75Co–Cr–Mo (Co–Cr–Mo) prosthetic alloys used. Most importantly, SEM images show metallic-appearing particles of varying sizes and shapes. These data indicate that wear of prosthetic knees cannot be limited to the polyethylene articular inserts. Therefore, models of prosthetic failure need to include metallic wear and the interaction of this metal debris with the synovial fluid and surrounding tissue, as well as the effects of dissemination throughout the body.

2. Methods

All patients enrolled in this study (approved by the Summa Health System and The University of Akron Institutional Review Boards) signed an informed consent form. These patients had a total knee replacement (TKR) previously, and were scheduled to undergo revision TKR. After anesthetization in the operating room, an 18-gauge needle was inserted into the TKR joint, and synovial fluid was aspirated. Immediately following aspiration the fluid was transferred into lavender topped Vacutainer® tubes (Ryan Medical, Brentwood, TN) containing ethylenediaminetetraacetic acid (EDTA), and mixed to prevent clotting. Aliquots (1.9 mL) were then transferred to dolphin microcentrifuge tubes (Sorenson, West Salt Lake City, UT, USA) and stored at −80 °C.

When needed for analysis, the microcentrifuge tubes were brought to room temperature, mixed thoroughly and centrifuged at $14250 \times g_{\mathrm{av}}$ for 7 min. Following centrifugation, a deposit of debris resembling a small flake was visible at the bottom of each tube. The synovial fluid was removed from the sample and the debris flake was thoroughly washed with deionized water and dried. The samples were numbered so that the identities of the patients remained confidential but the data could be correlated with the actual prosthetic history. Analyses by XPS were performed in fixed analyzer transmission mode, under high vacuum conditions, using a Kratos ES-300 spectrometer, with an Al anode source operated at 12 kV. SEM imaging and EDS were performed under low vacuum conditions, with a JEOL JSM-6480LV instrument using an electron gun operated at 20 kV.

3. Results and discussion

The debris flakes were difficult to handle due to their small size and fragile nature. As a result of centrifuging, the debris collected at the bottom of the microcentrifuge tubes forming a bowl-like shape. As we noted previously [2], if the debris is mounted such that the concave side is analyzed by XPS, the results may not indicate any metals. However, if the convex side of the debris is probed, XPS analysis showed the presence of metals in five of the seven samples studied.

3.1. SEM/EDS

Fig. 1, from sample 17, provides one example of the type of materials we have analyzed in this study. This SEM image at low magnification illustrates the

Fig. 1. SEM image of sample 17 under low magnification.

brittle nature of the flakes of wear debris, and the inhomogeneous distribution of materials. This sample was from a patient who experienced femoral wear, based on surgical notes taken at the time of prosthetic replacement. Both the femoral and tibial components were constructed from Ti–6Al–4V alloys.

Fig. 2 provides an EDS area scan of one part of sample 17 containing, based on the corresponding SEM image, a significant amount of particles with a bright (metallic-like) appearance. Note that the major elements detected are carbon, titanium and oxygen, with aluminum and vanadium also identifiable. Table 1 provides the weight and atomic percentages determined from these data. This area of the sample, although appearing mostly bright under electron imaging, is predominantly carbonaceous in the volume sampled by EDS. Most important is the Ti:Al:V weight percent ratio, which, within experimental uncertainty, is close to that of the original alloy. The size and shape of these wear debris particles vary significantly, as might be expected from relevant simulator tests [7–9].

Fig. 3 and Table 2 contain data from a different region of sample 17. Note that in this case the carbon content is much smaller than in Fig. 2, and that we now detect sodium, phosphorus and sulfur in small quantities. Within the experimental uncertainty of EDS, it seems that the Ti:Al:V ratios in this and other samples are consistent with that of the original alloys. The introduction of metals into the body can affect local tissue and cells [3,6,10,11] as well as result in build-up in vital organs if disseminated throughout the body [12,13], which points to the potential importance of these findings.

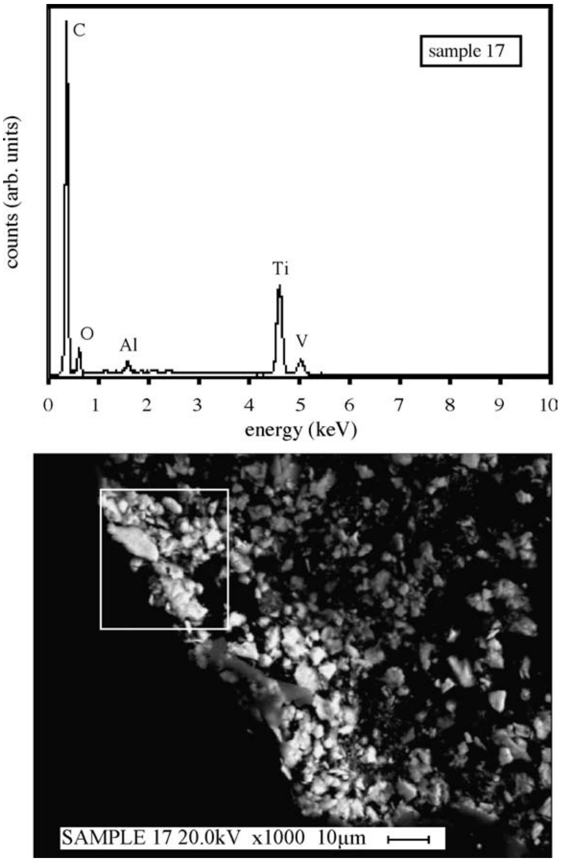

Fig. 2. Top: EDS area scan of sample 17, showing mostly carbon. Bottom: SEM image of sample 17 under higher magnification showing many particles that appear as metallic. The inset box is where the EDS data were taken.

Debris sample 14 is from a patient whose prosthesis was constructed from F–75Co–Cr–Mo for the femoral component and Ti–6Al–4V for the tibial tray. Intraoperative notes only indicated visual evidence

Table 1
Composition of wear debris from sample 17 from the EDS data of Fig. 2

Element	Wt.%	At.%
C	71.1	84.4
O	11.5	10.2
Al	0.8	0.4
Ti	16.2	4.8
V	0.4	0.1

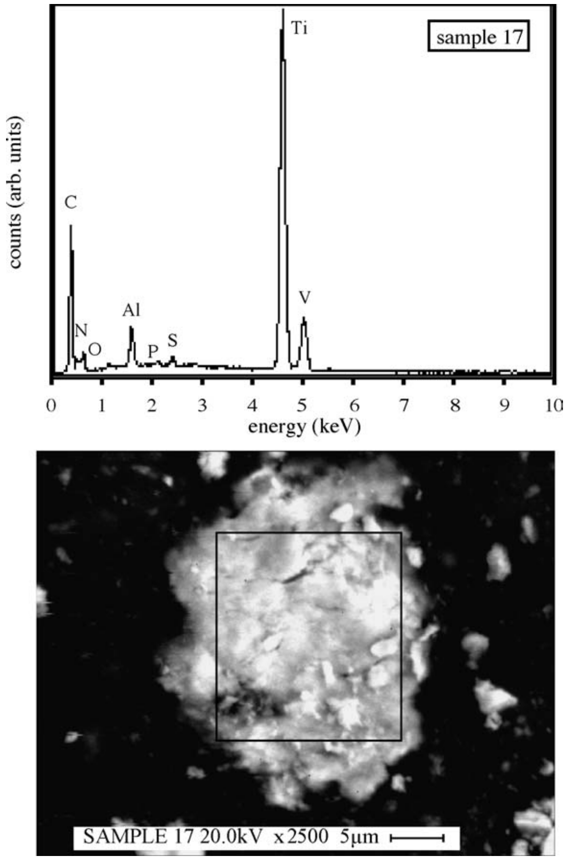

Fig. 3. Top: EDS scan of a particular metallic particle in sample 17, showing mostly titanium. Bottom: SEM image of sample 17 under higher magnification, with an inset box showing where the EDS data were taken.

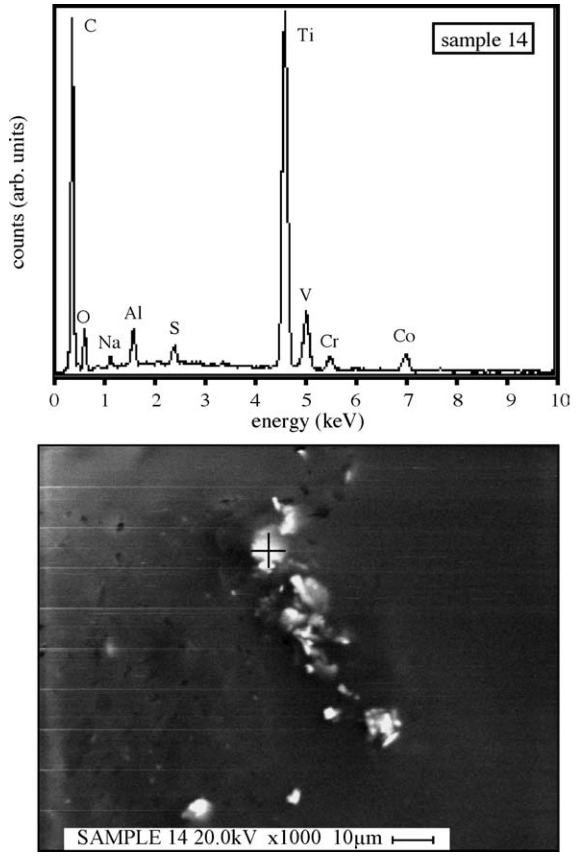

Fig. 4. Top: Energy dispersive spectrum from sample 14. Bottom: SEM image of sample 14 under high magnification showing a few metallic looking particles. The cross hairs indicate where the EDS data were taken.

of femoral wear. However, Fig. 4 and Table 3 indicate that tibial wear also occurred. This result is consistent with what we reported previously for samples from other patients [2], where we proposed that the unexpected presence of titanium was due to backside wear of the tibial tray. It is relevant that the work

Table 2
Composition of wear debris from sample 17 from the EDS data of Fig. 3

Element	Wt.%	At.%
C	34.7	58.2
N	6.0	8.6
O	8.3	10.5
Na	0.4	0.4
Al	2.5	1.9
P	0.3	0.2
S	0.5	0.3
Ti	46.4	19.6
V	1.0	0.4

Table 3
Composition of wear debris from sample 14 from the EDS data of Fig. 4

Element	Wt.%	At.%
C	51.2	74.9
O	9.2	10.1
Na	0.8	0.6
Al	1.5	1.0
S	0.7	0.4
Ti	30.4	11.1
V	0.9	0.3
Cr	1.6	0.6
Co	3.7	1.1

of Decking et al. [14] shows unexpected metals from failed hip prosthetics present on the surface of the removed components. In the present study, we find a similar result, but from the synovial fluid of failed knee devices.

3.2. XPS

Whereas SEM/EDS can be used to sample a small area of each sample, XPS samples from a large lateral area. However, XPS only probes vertically within the first few nanometers of the sample, while EDS data come from much deeper in the bulk of the material. In the present study, argon ion sputtering was used on XPS samples to remove surface contamination and to analyze deeper within the wear debris. The sputtering gun was operated at 2.5 kV, and the ion beam was rastered over an area larger than the sample. The sputtering rate of a gold standard was approximately 37.8 nm/h, and we have not determined differential sputtering rates in this study.

Fig. 5 presents a series of XPS survey scan spectra from sample 1 versus sputtering time. This wear debris is from a patient whose prosthetic was constructed solely from Ti–6Al–4V alloys. Both the femoral and patellar components exhibited signs of wear according to intraoperative notes. In addition to carbon, this sample contains oxygen at the surface before sputtering (bottom spectrum of Fig. 5). Sputtering reveals the presence of titanium deeper within the wear debris. Spectra like these indicate that the wear debris is inhomogeneous in the vertical direction. This is a complement to the use of SEM/EDS, which indicates lateral inhomogeneity for this type of wear debris.

Sample 6 originated from a patient with a Co–Cr–Mo femoral component and a Ti–6Al–4V tibial tray that was intraoperatively identified as having undergone femoral wear only. However, Fig. 6 indicates that titanium is the major metallic component found in this sample by XPS. The surface of this sample is predominantly carbon, oxygen and nitrogen to begin with, and sputtering reduces the signature of all of these elements and uncovers the presence of titanium. Once again, our data indicate vertical inhomogeneity, and identify wear debris from a component that had

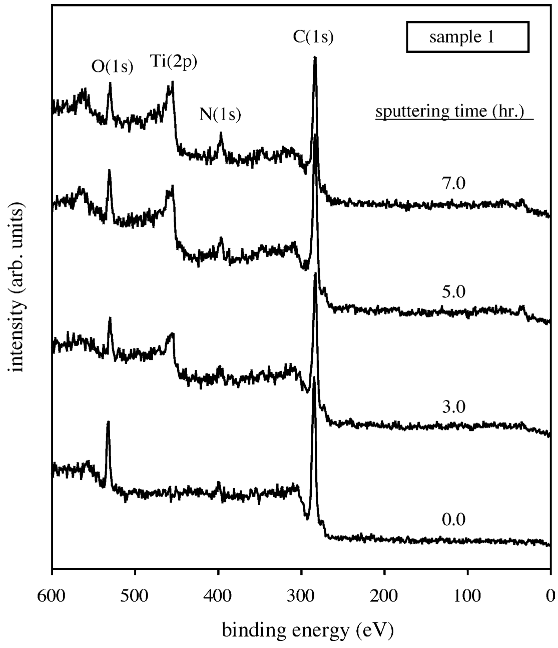

Fig. 5. X-ray photoelectron spectra of sample 1, with corresponding sputtering times. The spectra are offset vertically for clarity. Note the appearance of titanium with increased sputtering time.

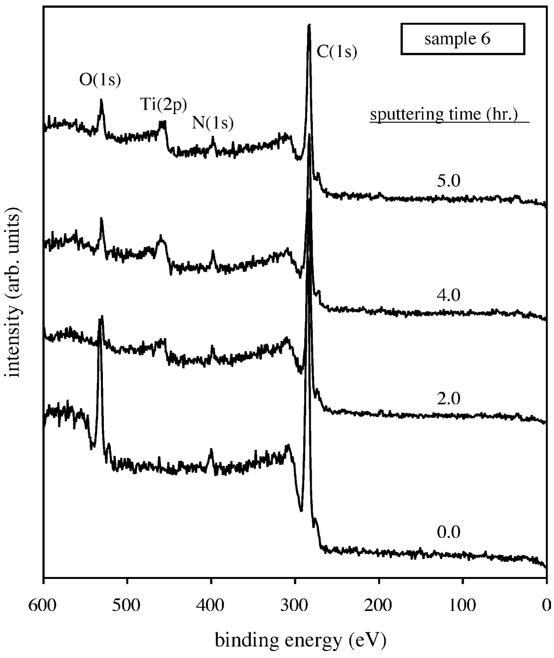

Fig. 6. X-ray photoelectron spectra of sample 6, with corresponding sputtering times. The spectra are offset vertically for clarity. Note the appearance of titanium with increased sputtering time.

Table 4
Atomic percentage composition of five samples as determined by XPS

Element	Sample 1	Sample 6	Sample 14	Sample 16	Sample 17
C	79.1	86.3	91.2	96.6	96.7
O	8.0	6.9	–	3.4	3.3
N	6.9	4.0	7.3	–	–
Na	–	–	1.6	–	–
Cl	–	–	0.9	–	–
Ti	6.0	2.9	–	–	–

not been identified as having any tibial tray abrasion by visual inspection. Table 4 summarizes our findings on the five samples studied in this work, with atomic percentages calculated from spectra at the longest sputtering times for each sample. Note that we did not detect significant Ti with XPS in samples 14 and 16, but did detect it with EDS as discussed above. This indicates the inhomogeneity of these samples, and the necessity to use a combination of techniques for studying such wear debris.

4. Concluding remarks

Our work demonstrates that metals from the prosthetic alloys, along with other minor impurities, can be present in synovial fluid of patients experiencing discomfort. The species are distributed inhomogeneously throughout the collected wear debris, proving problematic for only one technique to thoroughly characterize. While micro-Raman spectroscopy has previously shown some particles extracted from synovial fluids are polyethylene in nature, others are distinctly non-polyethylene [15]. These unidentified particles could be metals or metal oxides, as we have discussed previously [2]. The results presented here confirm that femoral component wear as well as back-side tibial tray wear cannot be neglected as we strive to understand the failure mechanisms and cellular reactivity following joint replacement surgery.

It may seem unusual that micro-motion between a Ti–6Al–4V tibial tray and an UHMWPE articular insert could lead to surface degradation of the alloy, but this has been shown to occur by simply sliding Ti–6Al–4V against UHMWPE pins under water-lubricated conditions, causing severe damage to the alloy surface [16]. In the same study, changes in the lubricant color indicated chemical changes were prevalent. Even though Ti–6Al–4V alloys in bulk exhibit excellent corrosion resistance, biocompatibility, and yield high strength properties, they have poor wear resistance [8,17,18]. Our findings clearly show that prosthetic knees containing the Ti–6Al–4V alloy, whether in the femoral or tibial components, can generate wear debris even if it is not visually verifiable. Since sub-micron metallic wear particulates and metal ions released within the joint capsule are known to pose a serious threat to the longevity of the prosthesis and possibly human health, this is an important conclusion of this work.

It was reported that the combination of Ti–6Al–4V and ultrahigh molecular weight polyethylene, in total joint arthroplasty prostheses, resulted in excessive wear of both the polymer and metal [19]. In another related study, dealing with the failure of a metal-backed patella, high levels of titanium within the intra- and extracellular deposits were observed by energy dispersive X-ray microanalysis [20]. On the other hand, in a study of the interaction between commercially pure titanium and bone using time-of-flight secondary ion mass spectrometry it was found that titanium diffuses into the bone tissue [21].

Therefore, the question is whether the titanium that we have identified in this study results from dissolution or actual wear of the alloy. In a study of the corrosion properties of Ti–6Al–4V in 0.05 M H_2SO_4/0.05 M NaCl solution, it was found that the aluminum percentage was higher than that for titanium and even reached 94% [22]. We point out that the Ti:Al:V ratios of the EDS-interrogated particles in this study are comparable to that of the original alloy. Also, within the signal to noise achievable with XPS, we do not see either Al or V. However, the particles that we observe with SEM appear bright, as if they are metallic flakes from the alloy. Based on the evidence we have thus far, we propose that the presence of metals in the samples we have studied is the result of wear of the alloys rather than chemical dissolution. While additional investigations are warranted, the use of XPS in conjunction with SEM and EDS for the early detection of these unwarranted metal concentrations within synovial fluid could be used as a means of monitoring prosthetic wear rate, and thus for the timing of interventions to extend prosthetic implant longevity.

Acknowledgements

We acknowledge support for this effort through NIH-NIBIB grant number EB003397-01. We also acknowledge approvals to carry out this work from by the Institutional Review Boards of both The University of Akron and Summa Health System, as well as from The Summa Health System Foundation and the Robertson-Hoyt Fund. We thank Jeanette Killius/Northeastern Ohio Universities College of Medicine, Ruth Murry/Oxford Instruments, and Donna Guarrera/JEOL Inc. USA, for their assistance with this work.

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