

Surface analysis of prosthetic wear debris[†]

J. C. Tokash,¹ N. Stojilovic,¹ R. D. Ramsier,^{1*} M. W. Kovacic² and R. A. Mostardi²

¹ Departments of Physics, Chemistry and Chemical Engineering, The University of Akron, Akron, OH 44325-4001, USA

² Walter A. Hoyt Jr. Musculoskeletal Research Laboratory, Department of Orthopaedic Surgery, Summa Health System, Akron, OH 44309-2090, USA

Received 10 June 2004; Revised 23 August 2004; Accepted 25 August 2004

Total knee arthroplasty introduces foreign materials into the body that are intended to withstand significant biological and mechanical stresses while maintaining biocompatibility. Unfortunately many arthroplasty patients experience inflammation and pain, presumably due to wear debris that dislodges from the artificial joint over time. The failure mechanisms of prosthetic devices and the chemical make-up of the associated wear debris are presently unclear. In this study, we use x-ray photoelectron spectroscopy and Raman microscopy to identify the chemical composition of the wear debris. Knee synovial fluid was aspirated from seven different prosthetics patients and centrifuged, resulting in small deposits of wear debris. Our analysis identifies oxidized titanium in five of the seven sets of samples, indicating femoral component wear and potentially back-side wear of the tibial base plates of the prosthetics. Furthermore, samples with large percentages of titanium also contain sodium, whereas the others contain chlorine. This may indicate differences in the chemical composition of synovial fluid under different inflammatory conditions.
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KEYWORDS: knee arthroplasty; wear debris; XPS; titanium; Raman; UHMWPE

INTRODUCTION

Surgical replacement of worn articular surfaces that line the major joints of the human body (i.e. hip, knee and shoulder) with prosthetic devices, made of various metal alloys and plastics, remains the only definitive treatment available for severe osteo and rheumatoid arthritis. Arthroplasty involves the introduction of foreign materials into the body that are intended to withstand significant biological and mechanical stresses for many years. Unfortunately, many arthroplasty patients experience inflammation, pain and bone loss due to particles that dislodge from the artificial joint during normal wear over time.¹ Today, although joint replacement surgery is a highly successful therapy, the inevitable generation of the aforementioned particles during normal use invokes a cellular reaction known as aseptic loosening. This culminates with a loss of bone surrounding the prosthetic device, which continues to be a common problem with joint replacements and accounts for the majority of total joint replacement failures.

The device failure mechanisms and even the chemical identity of these wear particles are unclear at present. The alloys most commonly used as prosthetic-bearing surfaces are primarily composed of either titanium or cobalt–chromium. The titanium alloys ASTM F-136 and

F-1108 (Ti–6Al–4V), for example, are comprised of titanium (88–92%), aluminum (5.5–6.8%) and vanadium (3.5–4.5%), along with other trace metals. The cobalt–chromium alloy ASTM F-75 contains cobalt (57–65%), chromium (27–30%), molybdenum (5–7%) and nickel (2.5%), along with other minor constituents. It is possible that wear particles contain some of these metallic elements in addition to ultrahigh-molecular-weight polyethylene (UHMWPE) from articular inserts, polymethylmethacrylate (PMMA) from bone cement and organic tissue from the human body.

Many studies of wear in prosthetics devices have focused on simulator testing,^{2–6} whereas others have studied materials extracted from patients.^{7–14} Some of these investigations involve characterization of the wear surfaces and their morphology,^{2,3,5,7,8,11} and others have concentrated on the wear debris.^{4,6,9,10,12–14} These latter studies have been concerned mainly with the size and shape distributions of the small (submicron to tens of microns) polyethylene particles found in the synovial fluid. However, some micro-Raman work has shown that although some of these particles are polyethylene some also contain beta-carotene or are classified as distinctly non-polyethylene.^{9,13}

Our current and ongoing studies are aimed at determining whether spectroscopic methods can be used to answer some of the open questions in the biomedical community concerning the biocompatibility of prosthetic metal alloys¹⁵ and the nature of prosthetic failure.^{16,17} In this study, we use x-ray photoelectron spectroscopy (XPS) and Raman microscopy to identify the nature of wear particles. Knee synovial fluid was aspirated from different prosthetics patients and centrifuged, resulting in small wear deposits resembling flakes or pellets. These deposits were washed and dried and

*Correspondence to: R. D. Ramsier, Departments of Physics, Chemistry and Chemical Engineering, Ayer Hall Room 111, 250 Buchtel Commons, The University of Akron, Akron, OH 44325-4001, USA. E-mail: rex@uakron.edu

[†]Paper presented at the 26th Symposium on Applied Surface Analysis. 15–18 June 2004, Pacific Northwest National Laboratory, Richland, Washington, USA.

Contract/grant sponsor: NIH-NIBIB; Contract/grant number: EB003397-01.

then analyzed by XPS and Raman spectroscopy. In general the deposits are carbonaceous, but several contain titanium as well. This indicates that wear in prosthetic knees is not necessarily limited to the articular inserts but can involve the metallic components, therefore our models of prosthetic knee failure mechanisms need to include metallic wear and the interaction of this debris with both the synovial fluid and surrounding human tissue.

METHODOLOGY

Patients who had undergone a previous total knee replacement and were now scheduled to undergo a primary total knee replacement on the contralateral side were identified. All patients enrolled in this study (which had been approved by the Summa Health System and the University of Akron Institutional Review Boards) signed an informed consent form. After the patient had been anesthetized in the operating room, an 18-gauge needle was inserted into the previous replacement joint and the synovial fluid was aspirated. Immediately following aspiration the fluid was transferred into lavender-topped Vacutainer® tubes (Ryan Medical, Brentwood, TN) containing the anticoagulant ethylenediaminetetraacetic acid (EDTA) and mixed thoroughly. Aliquots of 1.9 ml were transferred to dolphin microcentrifuge tubes (Sorenson, West Salt Lake City, UT) and stored at -80°C . For the present study, microcentrifuge tubes from seven knees were brought to room temperature and centrifuged at 14250 g for 7 min. Following centrifugation of the synovial fluid, a deposit was visible at the bottom of each of the microcentrifuge tubes. The synovial fluid was removed and the debris was washed thoroughly with deionized water. After the samples were completely dry they were hand-carried to the University of Akron for study. The samples were numbered at Summa Health System as 002, 004, 005, 007, 008, 009 and 011 so that the identities of the patient donors remained confidential but the data could be correlated with the actual prosthetic history after analysis. Figure 1(a) is a photograph of one of the microcentrifuge tubes containing wear debris (sample 004) in order to give the reader an indication of the appearance of the materials studied here.

The dried knee joint debris was kept at room temperature and the chemical composition was analyzed using XPS. The XPS analysis was performed in fixed analyzer transmission mode under high vacuum conditions with pressures of $<5 \times 10^{-8}$ Torr and often $<8 \times 10^{-9}$ Torr. We used a Kratos ES 300 electron spectrometer with a dual-anode (Al and Mg) source. For all measurements the aluminum source was used for the primary survey and detail scans, however the magnesium anode was selected to verify the identity of some Auger features in the spectra. The x-ray source was operated at 12 kV and 10 mA and the samples were ~ 1 cm away from the source.

The debris particles were difficult to mount to the load-lock sample holder owing to their small size and fragile nature. A method used in the past to mount and analyze fragile titania nanofibers¹⁸ was chosen for the knee debris. This method uses a small (~ 2 mm wide) copper sample probe

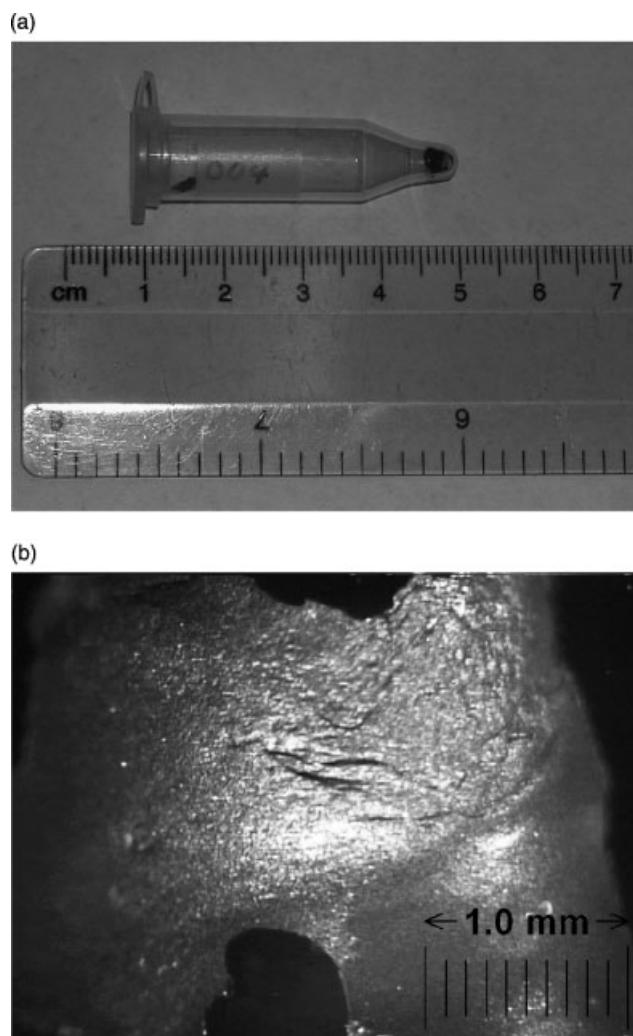


Figure 1. (a) Photograph of a microcentrifuge tube containing dry prosthetic wear debris. (b) Low-power optical microscope image of wear debris in the concave-down geometry.

tip (sometimes coated with gold) of triangular cross-section to which double-sided tape is fixed along one face. The wear debris was placed onto the top face of the tape, taking care not to contaminate the sample. We did not experience significant sample charging, and referencing was performed with respect to the copper/gold probe tip. The spectrometer entrance slits were set so that the entire sample was analyzed during data collection.

As a result of centrifuging the fluid, the debris collects at the bottom of the microcentrifuge tubes, forming a bowl-like shape. If the debris is placed onto the tape such that the concave side is up (this is the side analyzed by XPS), the results did not indicate any metallic content. However, if the debris is placed such that the concave side is down, then XPS analysis shows the presence of metals in some samples. This sample mounting method was reproducible and reversible. The debris particles were not damaged in the process and could be studied later by optical microscopy and Raman techniques. Figure 1(b) shows a low-power optical microscope image of one of the debris particles (sample 004) studied in this work. The sample is positioned with the concave side down in the image, and its curvature is apparent.

Sputtering was performed on all samples to remove surface contamination and also to remove more material to analyze the atomic composition deeper within the bulk by XPS. The sputtering gun can be focused and rastered, and was operated at 2.5 keV. The ion beam was rastered over an area larger than the sample such that the entire sample was uniformly sputtered. Using ultrahigh-purity argon gas at a total pressure of 2×10^{-5} Torr, the sputtering rate of a gold standard was $\sim 0.63 \text{ nm min}^{-1}$. Samples were sputtered for as little as 35 min and as long as 7 h, corresponding to removal of 22.1 and 265 nm, respectively. These depth-profiling values are with respect to a gold standard, and we have not determined differential sputtering rates in this study.

Raman microscopy was used to provide information about metal oxides and UHMWPE potentially present in the wear debris. The Raman system consisted of a custom-built excitation source utilizing a He-Ne laser (632.8 nm wavelength) and various beam splitters and fiber optics. The beam was focused to $\sim 25 \mu\text{m}$, providing $\sim 27 \text{ mW}$ of power at the sample surface. The Raman data were collected using an ACTON InSpectrum CCD spectrogram detector operating at -20°C . The instrument was controlled through a computer interface using SpectroSense software. An integration time of 30 s and a resolution of 2.58 cm^{-1} were used for the studies discussed here.

RESULTS AND DISCUSSION

Figure 2 presents a representative photoelectron survey spectrum from sample 002 in which no metallic elements were found. The elemental atomic percentages derived from integrating detailed spectra are presented in Table 1, after correction with the appropriate sensitivity factors. Details on the actual alloys used for the prosthetics are given in Table 2. As seen in Fig. 2, sample 002 is mostly carbon with traces of nitrogen, oxygen and chlorine. Depth profiling for several hours did not change the results and we conclude that this sample is mostly carbonaceous. Interestingly, the presence of chlorine as observed in Fig. 2 is only detected in debris that contains no or very little titanium. This is a consistent

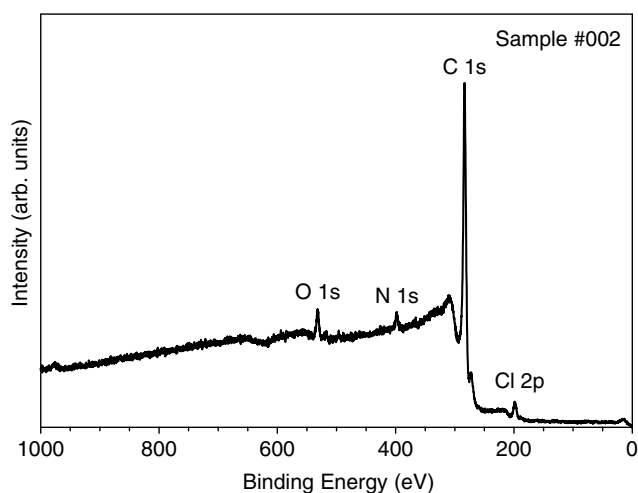


Figure 2. X-ray photoelectron survey spectrum of wear debris that does not contain metallic elements.

trend in the data that we have acquired so far, and will be discussed in more detail below.

In contrast to sample 002, XPS data from sample 004 indicate a large percentage of titanium and oxygen. Figure 3 is a representative survey scan from this type of wear debris, and Table 1 contains the average elemental composition determined from integrating detailed spectra. As mentioned previously, sputtering was needed to remove surface carbon before we could identify the metals and other elements, and there was an asymmetry depending on how samples containing metals were mounted. It is logical that the centrifuge process carries the heavier metallic species outwards to the 'concave-down' side of the debris, which has been our observation.

There are some interesting trends in these XPS data that are best seen graphically. Figure 4 is a plot of the average percentage compositions of each of the seven samples that we have studied to date. The five main elements that we detected are shown, with the sixth (carbon) not plotted because it always has the highest concentration. We have conclusively identified titanium in four of these seven knee debris samples, three of which have quite large percentages

Table 1. Atomic percentage compositions (the balance is carbon in each case) of the wear debris as determined in this study by XPS, along with the identity of the femoral components and tibial base plates of the associated prosthetic devices

Sample no.	Femoral component	Tibial base plate	Cl	N	Ti	O	Na	Observed wear ^a
002	Ti-6Al-4V ^b	Ti-6Al-4V ^c	1.4	2.6	0.0	3.4	0.0	Femoral
004	Ti-6Al-4V ^b	Ti-6Al-4V ^c	0.0	5.1	8.4	33.0	1.5	Femoral
005	Ti-6Al-4V ^b	Ti-6Al-4V ^c	0.0	6.7	6.2	10.6	1.0	Femoral/tibial
007	Co-Cr-Mo ^d	Ti-6Al-4V ^e	0.0	5.2	4.5	10.3	1.1	—
008	Co-Cr-Mo ^d	Co-Cr-Mo ^d	1.1	2.8	0.3	0.0	0.0	Femoral
009	Co-Cr-Mo ^d	Ti-6Al-4V ^e	3.4	3.2	0.0	2.9	0.0	Femoral/tibial
011	Co-Cr-Mo ^d	Ti-6Al-4V ^e	1.6	3.7	1.0	2.8	0.0	Femoral/tibial

^a The prosthetic components that exhibited visible signs of wear after they were extracted from the patients.

^b F-136.

^c F-1108.

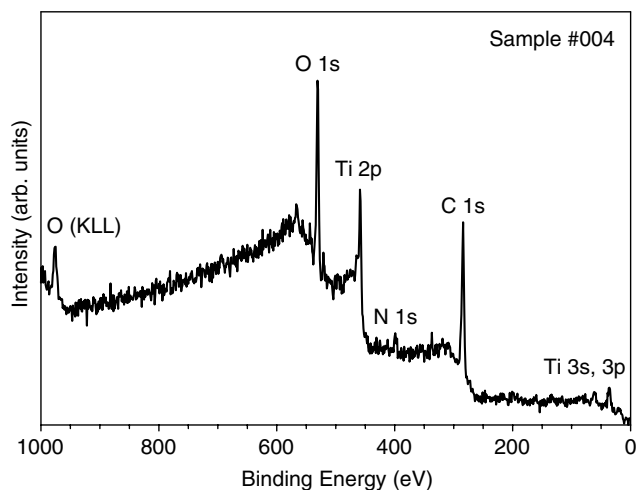
^d F-75.

^e F-1472.

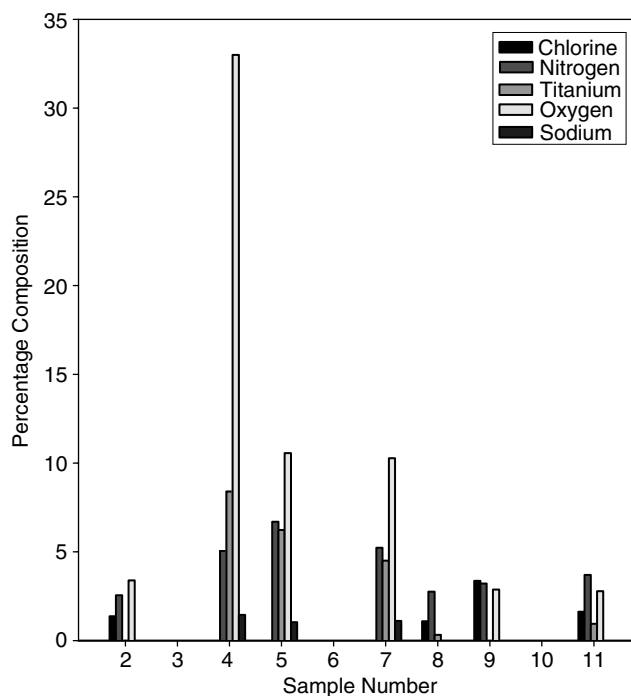
Table 2. Percentage compositions (wt.%) of the alloys used for the prosthetics

	ASTM F-136 (Ti-6Al-4V)	ASTM F-1108 (Ti-6Al-4V)	ASTM F-1472 (Ti-6Al-4V)
Titanium (Ti)	88.5–92.0	88.2–91.0	88.1–91.0
Aluminum (Al)	5.5–6.5	5.5–6.75	5.5–6.75
Vanadium (V)	3.5–4.5	3.5–4.5	3.5–4.5
Iron (Fe)	0.25	0.30	0.30
Carbon (C)	0.08	0.08	0.08
Oxygen (O)	0.13	0.13	0.20
Nitrogen (N)	0.05	0.05	0.05
Hydrogen (H)	0.015	0.015	0.015
Yttrium (Y)	—	—	0.005

	ASTM F-75 (Co-Cr-Mo)	
Cobalt (Co)	58.2–67.8	57.4–65.0
Chromium (Cr)	27.0–30.0	27.0–30.0
Molybdenum (Mo)	5.0–7.0	5.0–7.0
Nickel (Ni)	1.0	2.5
Iron (Fe)	0.75	0.75
Carbon (C)	0.26	0.35
Manganese (Mn)	1.0	1.0
Sulfur (S)	0.010	—
Silicon (Si)	1.0	1.0
Tungsten (W)	0.20	—
Boron (B)	0.01	—
Nitrogen (N)	0.25	—
Aluminum (Al)	0.30	—

**Figure 3.** X-ray photoelectron survey spectrum of wear debris that contains oxidized titanium.

of metals (samples 004, 005 and 007). Sample 011 also has ~1.0% titanium, but we feel that the 0.3% value shown in Table 1 for sample 008 is below our detection limit because we know that no titanium is present in this prosthetic device. Identifying metals in the knee debris is important because it proves that UHMWPE is not the only material that wears *in situ*. In addition, results from sample 007 indicate not only

**Figure 4.** Atomic percentage compositions of the wear debris studied in this work as determined from XPS data. The elements identified are Cl, O, Ti, N and Na. The balance in each case is carbon. The sample numbering nomenclature has no significance, except that it allows us to track the history of the associated prosthetic components while keeping the identity of the patient donors confidential.

that the articulating surfaces wear but also that backside wear (between the inferior surface of the UHMWPE insert and the metal base plate) can occur on the tibial base plate. Intraoperative notes that describe visual observations of the actual components after extraction from the patients were used to form the right-hand column of Table 1. From these, there is no conclusive evidence of tibial base plate wear for sample 007, although we detect titanium in the wear debris. This is another important finding of this work that requires future investigations with more samples from patients who experienced different types of prosthetic failure.

Note that the samples with the most titanium also have the most oxygen. This is anticipated because fresh titanium wear particulates would be expected to react immediately within the human body to form a passive titanium oxide complex. The Ti 2p_{3/2} feature of sample 004 resides at 458.4 eV, which is indicative of titanium dioxide, whereas that of sample 011 occurs at 455.5 eV, indicating a stoichiometry closer to TiO. All of the titanium features fall in this range of oxidation state. It should be noted that sputtering can alter the oxidation state and composition of materials, so these XPS data may not reflect accurately what is present in the wear debris before sputtering.

Another interesting trend seen in Fig. 4 is that the three samples containing the most titanium also contain sodium, whereas the other samples, with little or no titanium, have chlorine. In view of the fact that extreme care was used to avoid salt-containing water during sample preparation, we must conclude that this latter result is a consequence of the

biochemistry involved in the synovial fluid. Large amounts of titanium cause a reactive inflammatory response within the knee, and the local chemistry within the fluid presumably favors the ingress of sodium ions rather than chloride ions in these cases. Both Na^+ and Cl^- are membrane-permeable ions present in the human body, and the fact that we detect them is a potentially important finding for those studying the chemistry of synovial fluids interacting with artificial biomaterials.

Finally, the absence of any other metals (Al, V, Co, Cr, Mo or Ni) is of interest. It is understandable that with the small sample size and less-than-optimal sample geometry we do not have an excellent signal-to-noise ratio in all of our spectra. Thus, even though we see Ti from the Ti-6Al-4V components, we may not necessarily detect the aluminum and vanadium that were originally present in much smaller quantities in the alloy. However, based on our previous work with energy-dispersive spectroscopy (EDS) on other wear debris samples,¹⁷ we assumed that wear of the femoral component would be more predominant than that of the tibial base plate. Therefore, we would expect to detect cobalt and chromium in samples 007, 008, 009 and 011, but the XPS data do not support this assumption. Our future work will include direct comparisons of volumetric (EDS) measurements with surface-sensitive (XPS) data on the same samples, to investigate this issue in more detail.

Figure 5 shows a Raman spectrum from sample 004, the one containing the largest amount of titanium as determined by XPS. Here, we see two features at 401 cm^{-1} and 606 cm^{-1} , which we assign to the rutile phase of titanium oxide.¹⁹ These data are consistent with our XPS results, which indicated the presence of oxidized titanium. Sample 007 also contains these Raman features (not shown), but those from all the other samples were completely featureless in the range $200\text{--}2500\text{ cm}^{-1}$. Figure 5 indicates where we would expect to see features corresponding to UHMWPE,^{9,13,20} however there is no evidence for any articular insert material in any of the wear debris that we have studied. We propose that the washing performed on the debris removed any UHMWPE

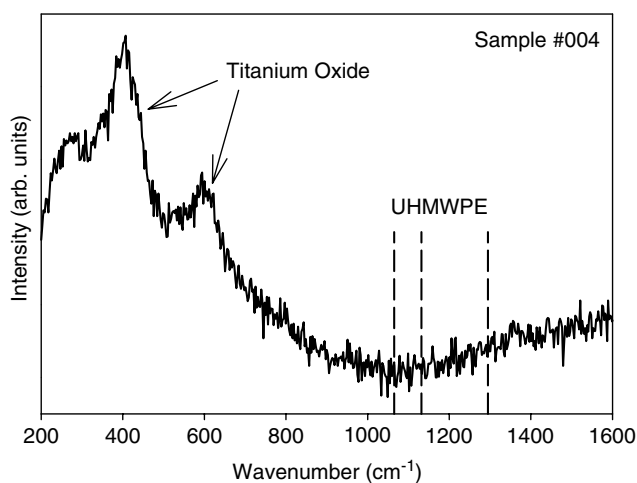


Figure 5. Raman spectrum from wear debris containing oxidized titanium. No UHMWPE was identified in any of the samples studied, and presumably it was removed by the washing performed as part of the sample preparation.

particles that were present, leaving only what appears to be a sintered flake of hard carbonaceous material (see Fig. 1(b)).

SUMMARY

The performance of biomaterials is an area receiving significant attention from the science and engineering communities. Quality-of-life issues and an aging population are causing an increase in the number of orthopedic implants that are in service, and this trend will continue. From the materials science point of view, understanding the behavior of materials in complex biological environments is a significant challenge. Synergistic effects can play a role, leading to enhanced corrosion and failure of materials. For orthopedic materials, especially those used for articulating joint replacements, wear is also a major concern. In an effort to design materials with better longevity for such applications, we need to understand the mechanisms of their failure. Corrosion and wear are properties of the surface of a material, implying that surface analytical methods are appropriate for studying biocompatibility. This work has identified several self-consistent trends that contribute to our understanding of these wear mechanisms and warrant further investigations with more wear debris samples.

Acknowledgements

We acknowledge support for this effort through NIH-NIBIB grant number EB003397-01. We also acknowledge approvals to carry out this work from the Institutional Review Boards of the University of Akron and Summa Health System, as well as from The Summa Health System Foundation and the Robertson-Hoyt Fund. We would like to thank Professor George Chase and Professor Jun Hu for access to the optical microscope and Raman system, respectively.

REFERENCES

- Bauer TW, Schils J. *Skel. Radiol.* 1999; **28**: 483.
- Walker PS, Blunn GW, Lilly PA. *J. Biomed. Mater. Res. (Appl. Biomater.)* 1996; **33**: 159.
- Hendry JA, Pilliar RM. *J. Biomed. Mater. Res. (Appl. Biomater.)* 2001; **58**: 156.
- Catelas J, Bobyn JD, Medley JB, Krygier JJ, Zukor DJ, Huk OL. *J. Biomed. Mater. Res.* 2003; **67A**: 312.
- Chandrasekaran M, Wei LY, Venkateshwaran KK, Batchelor AW, Loh NL. *Wear* 1998; **223**: 13.
- Scott M, Widding K, Jani S. *Wear* 2001; **251**: 1213.
- DeGiglio E, Motta A, Quagliarella L, Sabbatini L, Solarino G, Zambonin PG. *J. Mater. Sci.: Mater. Med.* 2001; **12**: 23.
- Decking R, Reuter P, Hüttner M, Puhl W, Claes LE, Scharf HP. *J. Biomed. Mater. Res. Part B: Appl. Biomater.* 2003; **64B**: 99.
- Wolfarth DL, Han DW, Bushar G, Parks NL. *J. Biomed. Mater. Res.* 1997; **34**: 57.
- Podsiadlo P, Stachowiak GW. *Wear* 1999; **230**: 184.
- Costa L, Bracco P, Brach del Prever E, Luda MP, Trossarelli L. *Biomaterials* 2001; **22**: 307.
- Mabrey JD, Afsar-Keshmiri A, McClung II GA, Pember II MA, Woolridge TM, Agrawal CM. *J. Biomed. Mater. Res. (Appl. Biomater.)* 2001; **58**: 196.
- Hahn DW, Wolfarth DL, Parks NL. *J. Biomed. Mater. Res.* 1997; **35**: 31.
- Podsiadlo P, Kuster M, Stachowiak GW. *Wear* 1997; **210**: 318.
- Buczynski BW, Kory MM, Steiner RP, Kittinger TA, Ramisier RD. *Coll. Surf. B: Biointerfaces* 2003; **30**: 167.
- Mostardi RA, Pentello A, Kovacik MW, Askew MJ. *J. Biomed. Mater. Res.* 2002; **59**: 605.

17. Kovacik MW, Gradisar IA, Haprian JJ, Alexander TS. *Clin. Orthopaed. Rel. Res.* 2000; **379**: 186.
18. Tomer V, Teye-Mensah R, Tokash JC, Stojilovic N, Kaphinan W, Evans EA, Chase GG, Ramsier RD, Smith DJ, Reneker DH. *Sol. Energy Mater. Sol. Cells* 2004 (In press).
19. Cassiers K, Linsen T, Mathieu M, Bai YQ, Zhu HY, Cool P, Vansant EF. *J. Phys. Chem. B* 2004; **108**: 3713.
20. Taddei P, Affatato S, Fagnano C, Bordini B, Tinti A, Toni A. *J. Mater. Struct.* 2002; **613**: 121.