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Article

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Morphology and dissolution rate of wear debris from silicon nitride coatings

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Abstract

Silicon nitride (SiN_x) coatings have recently been introduced as a potential material for joint implant bearing surfaces, but there is no data on wear debris morphology nor their dissolution rate, something that could play a central role to implant longevity. In this study, wear debris was generated in a ball-on-disc setup in simulated body fluid. After serum digestion the debris was analysed with scanning electron microscopy and energy-dispersive x-ray spectroscopy. The particle dissolution rate was evaluated using inductively coupled plasma techniques, on model SiN_x particles. The wear debris from SiN_x coatings was found to be round, in the nm range and formed agglomerates in the sub-micron to micron range. Model particles dissolved in simulated body fluid at a rate of: $c(t)=39.45[1-\exp(-1.11 \cdot 10^{-6}t)]$, where $[c(t)]=\text{mg/l}$ and $[t]=\text{s}$. This study can be used as a preliminary prediction of size, shape and dissolution rate of wear debris from SiN_x coatings.

Keywords: wear debris, silicon nitride, coatings, hip joint replacement, dissolution, particles

Introduction

When targeting increased longevity for joint replacements, the wear debris is central as it may trigger a negative biological response.¹ A combination of size distribution, volume, shape, surface area, and chemical composition determines the biological reaction to the debris. The materials commonly used in the bearing surfaces are metals such as cobalt chromium alloys (CoCr) and stainless steel; polymers such as conventional ultra-high molecular weight polyethylene (UHMWPE) and highly cross-linked UHMWPE (HXLPE); and ceramics, commonly zirconia-toughened alumina (ZTA) or alumina, combined as Metal-on-Polymer (MoP), MoM, CoP, and CoC. Even if MoP can show three to four orders of magnitude higher wear volume than CoC, the longevity cannot be linked only to the amount of debris, as the specific debris characteristics may also influence the biological response, as mentioned above.

Debris from UHMWPE liners in hip replacements is reported to be round to fibril shaped and ranges from 30 nm to 1 mm in size, with a majority of particles between 0.1 to 1.0 μm .²⁻⁵ Sub-micron sized UHMWPE particles have been found to activate macrophages, and can lead to bone resorption and late aseptic loosening of the implant.⁶ In Sweden, more than 80% of the total hip replacements are MoP combinations, and more than half of all reoperations between 1979 and 2013 were due to aseptic loosening.⁷ The more wear resistant HXLPE has, in recent years, been the most implanted polyethylene type in several countries.⁷⁻⁹ Its debris is similar in size and shape to the conventional UHMWPE,¹⁰⁻¹¹ however the reduction in wear volume by an order of magnitude could reduce the secondary effects.¹¹ The *in vivo* results till date are promising in terms of reducing, although not eliminating, the risk of osteolysis and revision.^{7-9, 11}

The majority of debris from CoCr alloys is reported to be round, oval, or needle shaped and smaller than 50 nm, but ranges from 6 to 834 nm.¹²⁻¹³ Metal wear debris, corrosion products and free ions have in rare cases been associated with high metal ion levels in the blood, metallosis, hypersensitivity and pseudotumours, especially for MoM implants.¹⁴⁻¹⁵

Debris generated from alumina bearings has been reported to be polygonal shaped and lie between 5 nm and 3.2 μm , with a mean of 24 (± 19) nm.¹⁶ Here, the biological response to the wear debris itself (including osteolysis) has not been regarded as a major concern, it has rather been mechanical issues related to the implant itself, caused by incorrect positioning, instability, or implant design that have caused failure.¹⁶⁻¹⁹ It should be noted, however, that ceramic debris, while scarce, could be abrasive, and hence increase the wear of other implant parts as well as any following revision prostheses.²⁰

Hip simulator studies have also investigated CoCr parts coated with titanium nitride and chromium nitride (TiNoTiN and CrNoCrN), where the debris was generally less than 30 nm in size, with some shards greater than 100 nm.²¹ Ceramic coatings on metallic implants could be beneficial both in a hard-on-hard (coating against coating or against a ceramic) and a hard-on-soft (coating against HXLPE) setting, since they would give: 1) a hard, wear-resistant surface, on a tough bulk material (i.e. better wear resistance than the underlying metal²²⁻²³ and potentially a lower risk for catastrophic failure than for a bulk ceramic); 2) potential for a reduced metallic ion release²⁴; and 3) a low-roughness, homogeneous surface (reduced risk for wear of softer surfaces due to asperities). They could also give benefits in a taper connection²⁵⁻²⁶, for the above-cited reasons.

Silicon nitride (Si_3N_4) based materials, including SiN_x coatings, are currently being studied for potential use in joint replacements^{22-24, 27-30}. One additional potential advantage of these materials is the chemical composition of the debris, which only contains elements that are considered non-toxic. N is naturally present in the body and Si-ions have *in vitro* been found to inhibit osteoclast formation and bone resorption.³¹ Furthermore, silicon nitride has been found to slowly dissolve in aqueous solutions,³²⁻³⁴ and if the formed debris is small and has a high surface area, this could result in an increased dissolution rate compared to the bulk material. A recent study on the dissolution of SiN_x coatings found a dissolution rate of 0.2-1.4 nm/day, where a higher nitrogen content (N/Si atomic ratio of 1.1) gave the lowest values.²⁴ Reference CoCr alloy gave dissolution rates of 0.7-1.2 nm/day. *In vivo* the dissolution of small SiN_x debris

with a high surface area may reduce the amount of debris present over time, and hence also limit a potential negative biological response to the debris.

In this study, a ball-on-disc setup was used to generate SiN_x coating wear debris. It was hypothesized that SiN_x coatings would generate smaller and less wear debris than UHMWPE, which could decrease the risk for negative biological reactions. Since a relatively fast dissolution of the SiN_x particles could be beneficial from a biological point of view, its dissolution rate was also investigated. The debris was first studied using semi-automatic image analysis and scanning electron microscopy (SEM), and then more in detail with higher resolution SEM in combination with chemical analysis with energy-dispersive x-ray spectroscopy (EDS), in order to characterize debris size, shape and chemical composition. Since a high enough amount of wear debris could not be obtained, model particles, similar in size and shape to the coating wear debris, were evaluated for dissolution rate of in simulated body fluid, using inductively coupled plasma techniques.

Materials and Methods

Materials: SiN_x coatings were deposited using reactive high power impulse magnetron sputtering (HiPIMS) on cast CoCr alloy (average surface roughness, R_a ~ 5 nm, ASTM F-75, Sandvik AB, Sweden), in a similar manner as SiN (1/-/I) studied previously^{24, 29, 35}, i.e. the coatings had a N/Si ratio of approx. 0.8 at. %, as evaluated by x-ray photoelectron spectroscopy (XPS)²⁴, Figure 1. The featureless coatings had a thickness of 8 ± 0.2 µm, and an R_a ~ 7 nm. As a reference, non-irradiated conventional UHMWPE (GUR 1050) was evaluated. The UHMWPE was machined and not polished to prevent embedded hard particles, i.e. it had a rough surface with R_a ~ 4 µm.

Debris generation: Wear debris was generated in a reciprocating ball-on-disc setup (Figure 2) using an Al₂O₃ ball (Ø 19 mm, purity 99.5 %, R_a ~ 150 nm, Spekuma Kullagar AB, Sweden), applied with a load of 1.5 N on the sample. This corresponds to an initial maximum Hertzian contact pressure of 0.41 GPa, this

was selected higher than what can be expected in a CoC hip replacement (~ 90 MPa)³⁶ in order to generate a high amount of debris. With a stroke length of 10 mm and a frequency of 3 Hz, the test was run for 2 h with three replicates generating parallel wear scars. The tested material was fitted in a heated PTFE bath, and a testing temperature of $37 \pm 3^\circ\text{C}$ was used. A simulated body fluid of 20 ml of a 25 vol.% fetal bovine serum (FBS, Gibco, EU approved, origin South America), with 0.075 wt. % sodium azide (Sigma-Aldrich, S8032) and 18.75 mM ethylene-diaminetetraacetic acid (EDTA, Amresco, E522) was used, according to ASTM F732–00 (2006). The simulated body fluid with wear debris was stored in a freezer at -30°C until digestion of the serum.

Digestion protocol: A hydrochloric acid digestion protocol, previously described by Scott et al. and in ISO17853:2011, was applied^{32, 33}. Hydrochloric acid of 37 vol. % (Fisher Scientific, code: 124620025) and methanol (VWR, product no: 20903.368) were used.

Particle characterization: The debris was evaluated using two different methods, referred to as screening and high-resolution analysis, respectively. To get a high debris count and obtain an overview of the particle morphology, a screening method (with a lower resolution and semi-automatic debris count) was first applied. Model silicon nitride particles (Sigma-Aldrich, Product nr: 636703), used for dissolution analysis (see next section), were characterized using the high-resolution technique.

Screening of debris: The digested solution with debris was first sonicated for 5 min then pipetted on Si wafers. The samples were dried at 60°C . The debris was evaluated in a SEM run at 15 kV using a backscatter detector (Tabletop Microscope TM-1000, Hitachi), with no sputtered conductive layer. The SEM images were processed using a modified MATLAB-script originating from Cervera Gontard et al.³⁷, identifying the debris and calculating their mean diameter, illustrated in Figure 3C.

High-resolution analysis of debris and model particles: The digested solution with debris was placed on a polycarbonate filter membrane with pore sizes $0.1\ \mu\text{m}$ (Whatman, cat. no: 7060-4701). Dried filters

where mounted on stubs using carbon tape and sputtered with a thin (< 5 nm) layer of gold-palladium. Debris and agglomerates were analysed for size, shape and composition. The size and shape were determined using a field-emission gun SEM (FEG-SEM), with in-lens detector at 5 kV (Merlin, Carl Zeiss Microscopy GmbH) with an integrated EDS (X-Max 80 mm², and Aztec software). Each agglomerate or particle was characterized with EDS to distinguish the SiN_x or UHMWPE debris from possible debris from the Al₂O₃ ball, protein residuals, salts etc. The maximum diameter was individually measured in image software (GIMP 2.6) to determine the sizes.

Model particle dissolution: Model silicon nitride particles were evaluated for dissolution rate in a simulated body fluid. Particles, 4.00 ± 0.05 mg, were tested in 40 ml solution of a 25 vol.% FBS (HyClone, SV30180.03), with 0.075 wt. % sodium azide (Sigma-Aldrich, S8032) and 5 mM EDTA in aqueous solution (Amresco, E522) in tubes, obtaining a SiN_x particle concentration of 100 mg/l. Only plastics, and no glassware, were used for all handling of the particles and solution to avoid Si contamination.

For each time point, three tubes with particles and three without (controls) were incubated at 37°C on a tipping table at 0.5 Hz for 0, 0.125, 3, 1, 3, 7, 20 and 30 days. At each time point the pH was measured, and 15 ml of the top solution was extracted to a new tube and centrifuged for 15 min, then 10 ml from the top was extracted to a new tube and centrifuged another 15 min, and 5 ml was extracted and centrifuged a third time for 15 min and the top 2 ml solution was extracted and stored in a freezer. Prior to ICP analysis 0.5 ml defrosted solution was diluted 1:10 with de-ionized water. ICP-MS (NexION 300d, PerkinElmer) and ICP-AES (Ciros CCD, Spectro) were used to determine the Si concentration. The ICP-MS instrument is more sensitive at low ion concentrations (applied for all blanks and time points 0 and 0.125 where the concentration was < 250 µg/l) while ICP-AES is more accurate at higher concentrations (applied for time points >0.125 days where the concentration was >250 µg/l; <5000 µg/l). Indium was used as internal standard element. The controls were subtracted from the results to determine the zero concentration at each time point. ICP-MS evaluated the ion concentration of isotope Si 28 and for ICP-

AES the emission line at 251.612 nm was used for the quantitative measurements. The pH was recorded as samples were taken out from the incubation within 30 min, at a temperature of ~26°C [22°C to 29°C].

Results

Screening of debris

The UHMWPE debris was round to fibril shaped, Figure 3A, with a size range between 0.11 and 7.24 μm , with a median size of 0.29 μm , Figure 4A and Table 1. According to the screening, SiN_x was round in shape, Figure 3B. The size distribution was between 0.08 and 3.25 μm , and the median size was 0.29 μm .

High-resolution analysis of debris and model particles

Chemical evaluation: For UHMWPE the debris was evaluated with EDS point analysis and expressed C, O, and Au (from a conducting layer), Figure 5A. Even if the debris was analysed on a polymer membrane in which C, O, and Au can be expected, it confirmed the absence of other elements. It could hence be excluded that the debris originated from the Al_2O_3 ball, protein residuals or salts. Evaluation of debris from SiN_x showed a presence of Si, C, O and Au (Figure 5A). The signal from Si could be linked to SiN_x debris, and the absence of other elements excluded contaminations.

Size distribution and shape: A representative fibril shaped UHMWPE debris is shown in Figure 5B. At higher magnification, the shape and size from the screening was confirmed and found to be representative for UHMWPE debris. UHMWPE was not further evaluated with the high-resolution analysis. For SiN_x on the other hand, the high-resolution analysis prompted a reconsideration of the interpretation of the screening results. At a higher resolution, it was found that the SiN_x debris consisted of agglomerates of small debris, see Figures 5C and 6A-C. It is hence important to note that the size and size distribution evaluated with the screening method was mainly SiN_x agglomerates of debris. In the high-resolution analysis the agglomerates were found to have a size range between 0.15 and 1.96 μm

with a median of 0.59 μm , Figure 4B and Table 1, i.e. a similar size range as seen for the screening. In Figures 4C and D the agglomerate size distribution is plotted, along with the one order of magnitude smaller wear debris' individual particles, with a size range between 0.01 to 0.5 μm and a median of 0.04 μm .

Model particles and their dissolution

The model SiN_x particles are shown in Figure 7, also being round in shape, and forming agglomerates in the sub- μm range. The individual particles size range was between 0.02 to 0.08 μm , with a median of 0.04 μm (Figure 4E, Table 1). Agglomerates ranged between 0.05-0.51 μm , with a median of 0.17 μm (Figure 4F, Table 1).

The model particles dissolved in a simulated body fluid over 30 days, where the Si concentration measured by ICP techniques is shown in Figure 8A. The dissolution rate, in terms of Si concentration as a function of time was fitted to a kinetic dissolution equation given by Zhmud and Bergström.³² The equation, $c(t)=c_s[1-\exp(-kt)]$, where $c(t)$ is the concentration as a function of time, c_s is the saturation concentration and k is the dissolution rate constant, gave the following best fit parameters: $c_s=39.44$ mg/l, $k=1.11 \cdot 10^{-6} \text{ s}^{-1}$ ($R^2 = 0.992$). The pH in the solution increased from the initial pH of 7.45 to more alkaline pH of around 8 after 20 days and onwards for both the controls and the samples containing silicon nitride particles (Figure 8B). The variation in pH was larger for the silicon nitride-containing samples than the controls at days 20 and 30.

Discussion

This study used a laboratory test to generate wear debris from experimental SiN_x coatings for joint replacements, using an Al_2O_3 ball, with UHMWPE as reference material. The test generated UHMWPE

debris in similar shapes and sizes to those that have been found *in vivo*,²⁻⁵ with a majority in the critical range of macrophage activation¹.

The debris from the SiN_x coatings agglomerated to a critical size range for macrophage activation (median 0.59 μm), however the individual debris particles within the agglomerates were in the nm size range (median 40 nm). There are therefore two central questions to answer to understand the impact of these results. Firstly, what was the origin of the agglomerates, were they formed during the wear test or during the serum digestion? Commercially available nanoparticles typically agglomerate, which also applies to Si₃N₄,^{33, 38-39} (Figure 7) and Si₃N₄ debris also agglomerate during dry wear of bulk Si₃N₄.⁴⁰ Agglomerated debris has been reported after serum digestion also for other coatings (TiN, CrN, CrCN, and DLC), with individual debris particle sizes smaller than 40 nm, for a similar wear setup⁴¹, and debris particles smaller than 30 nm under steady-state wear in hip simulators.²¹ To investigate if the digestion protocol stimulated agglomeration, the same model SiN_x particles diluted in water were studied in SEM, after sonication for 30 min and pipetted onto a 0.1 μm filter, as in the high-resolution analysis. No difference in agglomeration was seen between the debris in water and the HCl digestion protocol. In histological analysis (no digestion) from *in vivo* generated debris in a CoC prosthesis, the same agglomeration behaviour of nm sized debris was seen¹⁶. It is therefore reasonable to assume that agglomeration at least starts already during the wear process.

To the second question, if agglomerates form *in vivo*, would the biological system treat them as sub-micron debris, or several nm sized debris? How strong is the inter bonding between the particles in the agglomerates? Commercially available nanoparticles of Al₂O₃, ZrO₂, and Si₃N₄ have been found to agglomerate in MG63 human osteoblast-like cells³⁸. It has however been found that nanometer sized alumina particles (23 nm), agglomerating to submicron sizes (0.62 μm), give a better cell response (increased osteoblastic viability) than bigger particles (0.18 μm agglomerating to 5.83 μm)⁴², which suggests that the current study results are promising, since the SiN_x wear debris found here is of similar

size to the former particles. However, as bulk Si_3N_4 is a relatively new material in orthopaedics and SiN_x coatings are currently being studied in bench tests, the behaviour of the debris is yet to be evaluated *in vitro*, in simulators, and *in vivo*. This work can be seen as a first estimate of the size and behaviour that could be expected. It does not cover a quantitative evaluation of the total amount of debris that can be generated during an implant's lifetime nor the wear of the same. Further studies focussing on the biological response to the particles are of course of utmost importance.

Silicon nitride model particles, with a similar mean and median size as the SiN_x wear debris particles (Table 1, Figure 4), showed a steady dissolution in simulated body fluid over the 30 days investigated and remained under the saturation concentration for oxidised silicon nitride and silica³³. The observed pH increase, starting only after a few days, cannot be an effect of the dissolution of the particles alone, as it was observed also for the controls not containing particles. The absence of a verifiable pH increase in comparison to the control is positive for an eventual clinical application, since it has been found that at pH 7.8 and higher, osteoblastic activity decreases⁴³. The dissolution rate seen in this study was higher than what was reported by Zhmud et. al.³² in water, possibly due to the smaller particles used here, nm compared to μm , giving a larger surface area. Laarz et. al.³³ evaluated particles ~ 90 nm in size at different temperatures, estimating a higher dissolution rate than that seen in this study. There may be several reasons for this: the original concentration of particles is estimated to be higher than in this study (in fact the dissolution appeared to reach saturation after less than 5 days) and also a magnetic stirrer was used, possibly increasing the dissolution rate.

The dissolution rate seen here, of 38.8 mg/l Si after 30 days, would correspond to 64.6 mg/l of Si_3N_4 (assuming the molar masses for stoichiometric Si_3N_4), or 65 wt.% of the initial particle amount. If we further assume that a SiN_x on SiN_x articulating contact in a hip joint has a wear rate of $0.04 \text{ mm}^3/\text{year}$ ⁴⁴ and a SiN_x density of 3.2 g/cm^3 ⁴⁵, the mass of the SiN_x wear debris per year would be 0.13 mg. A hip joint capsule contains a few ml⁴⁶⁻⁴⁷ of synovial fluid, which can be assumed to be exchanged at least every

week. Saturation of the synovial fluid is not considered a risk *in vivo*, and the dissolution rate of the particles is higher than the estimated wear rate of a ceramic hip replacement.

Conclusions

In this study, an Al_2O_3 ball was used to generate SiN_x coating debris in a ball-on-disc setup in simulated body fluid. The study results can be used as a preliminary prediction of what wear debris from SiN_x coatings may look like and how they may behave in future *in vitro*, simulator or *in vivo* studies. In summary, the following main points can be extracted from the results of the current study:

- Debris from UHMWPE was round to fibril shaped with a median size of $0.29\text{ }\mu\text{m}$, ranging between 0.11 and $7.2\text{ }\mu\text{m}$, in accordance with previous studies.
- Debris from SiN_x coatings was round with a median size of 40 nm , ranging between 10 and 500 nm , and forming agglomerates up to $3.2\text{ }\mu\text{m}$ in size, with a majority in the sub-micron size range (median $0.59\text{ }\mu\text{m}$).
- SiN_x model particles, similar in size and shape to the SiN_x debris, dissolved in a simulated body fluid, following the equation: $c(t) = 39.45 [1 - \exp(-1.11 \cdot 10^{-6}t)]$, with the dissolution concentration given in mg/l and the time in s . This dissolution rate was estimated to be higher than the wear rate of the final implant.
- No increase in pH could be confirmed during particle dissolution.

All of the above points related to SiN_x debris were interpreted as encouraging for further evaluation of SiN_x coatings for joint replacements.

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Table of contents graphic

Morphology and dissolution rate of wear debris from silicon nitride coatings

Maria Pettersson, Charlotte Skjöldebrand, Luimar Filho, Håkan Engqvist, and Cecilia Persson

Micron-sized SiN_x wear debris agglomerates consisting of nanometer-sized individual particles.

Table 1. Sizes of individual particles and/or their agglomerates, for debris generated in the test as well as for model silicon nitride particles.

	Number analyzed, <i>n</i>	Median (μm)	Range (μm)
Screening: UHMWPE debris	70	0.29	[0.11-7.24]
Screening: SiN _x debris/agglomerates	62	0.29	[0.08-3.25]
High-res.: SiN _x agglomerates	15	0.59	[0.15-1.96]
High-res.: SiN _x debris	345	0.04	[0.01-0.50]
High-res.: SiN _x model particles	200	0.04	[0.02-0.08]
High-res.: SiN _x agglomerated model particles	264	0.17	[0.05-0.51]

Figure 1. A) SiNx coating deposited on CoCr (Ø 30 mm), and B) a fractured cross section of a featureless SiNx coating deposited on a Si wafer.
49x26mm (300 x 300 DPI)

Figure 2. Illustration of the ball-on-disc setup used to generate the wear debris. The heated bath holding the flat sample and the solution is not shown.
35x12mm (300 x 300 DPI)

Figure 3. SEM images from the screening method of A) UHMWPE, B) SiNx debris on a Si wafer, and in C) an example of the size evaluation.
52x15mm (300 x 300 DPI)

Figure 4. Size distributions of debris and agglomerates, for A) UHMWPE according to the screening, B) SiNx according to screening and high resolution analysis, C and D) SiNx with both screening and high resolution analysis at different size ranges, E) SiNx model particles and F) SiNx agglomerated model particles according to the high resolution analysis.

871x1015mm (96 x 96 DPI)

Figure 5. EDS spectra confirmed elements from the debris, C and Si, respectively, and the absence of other elements, where A) shows EDS spectra from a debris of UHMWPE in B), and an SiNx agglomerate in C). The arrows indicate where the EDS point analysis was made.
60x20mm (300 x 300 DPI)

Figure 6. High-resolution evaluation of SiNx wear debris agglomerates in the sub-micron to micron range in A) and B), where the individual debris in the nm range can be seen in more detail in C).
49x13mm (300 x 300 DPI)

Figure 7. Model SiNx particles, with similar size and morphology to the wear debris in A). B) shows a close-up of one of the agglomerates.
49x18mm (300 x 300 DPI)

Figure 8. The dissolution of particles in 25 vol. % serum solution over 30 days. In A), the Si concentration measured using ICP is shown, and in B) the pH of the solution after the dissolution is shown, the initial pH is marked with a dashed line.
70x27mm (300 x 300 DPI)