# Evaluation of silicon nitride as a wear resistant and resorbable alternative for total hip joint replacement

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Many of the failures of total joint replacements are related to tribology, i.e., wear of the cup, head and liner. Accumulation of wear particles at the implants can be linked to osteolysis which leads to bone loss and in the end aseptic implant loosening. Therefore it is highly desirable to reduce the generation of wear particles from the implant surfaces.

Silicon nitride  $(Si_3N_4)$  has shown to be biocompatible and have a low wear rate when sliding against itself and is therefore a good candidate as a hip joint material. Furthermore, wear particles of  $Si_3N_4$  are predicted to slowly dissolve in polar liquids and they therefore have the potential to be resorbed in vivo, potentially reducing the risk for aseptic loosening.

In this study, it was shown that  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>-powder dissolves in PBS. Adsorption of blood plasma indicated a good acceptance of Si<sub>3</sub>N<sub>4</sub> in the body with relatively low immune response. Si<sub>3</sub>N<sub>4</sub> sliding against Si<sub>3</sub>N<sub>4</sub> showed low wear rates both in bovine serum and PBS compared with the other tested wear couples. Tribofilms were built up on the Si<sub>3</sub>N<sub>4</sub> surfaces both in PBS and in bovine serum, controlling the friction and wear characteristics.

# Introduction

Total hip joint replacement is one of the most commonly performed orthopedic operations.<sup>1</sup> A total hip joint replacement has an average life span of about 15 years.<sup>2</sup> Implant failures can be due to several factors but one of the most critical is release of wear particles from the bearing surface of the implant. Accumulation of wear particles at the implant has been linked to osteolysis which leads to bone loss and eventually aseptic implant loosening.<sup>2,3</sup> The chemistry and particle size have been found to be of high importance to the inflammation response.<sup>2,4</sup> Therefore, it is highly desirable to reduce the generation of wear particles from the implant surfaces. One strategy to overcome the problem is to develop a material combining wear resistance, biocompatibility and biodegradability. Ideally, such material would release very few and very small wear particles, which would readily resorb without being detrimental to the tissue or even stimulate bone formation. This paper describes a first step toward such a material strategy and pin points some important future steps.

A commonly used material in the acetabular cup is ultra-high molecular weight polyethylene (UHMWPE), often combined with a femoral head of cobalt-chromium (CoCr). UHMWPE against either a metal or a ceramic material has exhibited a relatively low coefficient of friction but the UHMWPE liner often gets worn and produces a relatively large amount of wear particles.<sup>5,6</sup> CoCr based materials have been shown to have adequate properties for use as load-bearing implants. Experiments have however shown that CoCr particles released due to wear and corrosion could restrain the bone growth similar to UHMWPE.<sup>7</sup>

Titanium alloys and stainless steels have also been frequently used in joint implants.<sup>2</sup> The main risk with metal alloy implants is the release of metal ions due to corrosion and wear and the potential negative effect of these ions.<sup>4</sup> Alumina (Al<sub>2</sub>O<sub>3</sub>) and zirconia (ZrO<sub>2</sub>) ceramics have been used due to their high wear and corrosion resistance.<sup>6,8,9</sup> In general, bulk ceramic materials have a poor fracture toughness and e.g., alumina components in joint replacements have been shown to release wear particles due to this short coming.<sup>10</sup> However, the ceramic wear particles may be less bioreactive than those of UHMWPE.<sup>10</sup> Other interesting ceramic materials include silicon nitride  $(Si_3N_4)$  that has a higher fracture toughness and is more resistant to micro crack propagation than alumina.<sup>10-12</sup> The most common crystalline forms of Si<sub>3</sub>N<sub>4</sub> are the  $\alpha$ -phase and  $\beta$ -phase. The  $\beta$ -phase has longer grains, tougher and softer than the  $\alpha$ -phase.<sup>13</sup> Silicon nitride sliding against itself in a water based lubricated environment has shown a very low coefficient of friction and also low wear.<sup>14</sup> It has been reported that the wear of silicon nitride in water occurs by tribochemical dissolution of the material without release of any solid wear particles.<sup>15</sup> Others claim that the wear particles that are produced when Si<sub>3</sub>N<sub>4</sub> slides against Si<sub>3</sub>N<sub>4</sub> in water often consists of silica (SiO<sub>2</sub>) and are mainly amorphous.<sup>14</sup> Silicon nitride as a bulk material has been shown to be bioinert and having good biocompatibility.<sup>10,16,17</sup> Guedes e Siliva et al. found small contents of Si<sup>4+</sup> ions in extracts after solubility tests of Si<sub>3</sub>N<sub>4</sub>.<sup>17</sup> Other investigations have shown that mesoporous silica degrades in phosphate buffered saline (PBS),18 and that Si ions can be incorporated into bone tissue (or even stimulate new bone formation).<sup>19</sup> Moreover, Boshitskaya et al.<sup>20</sup> have shown that

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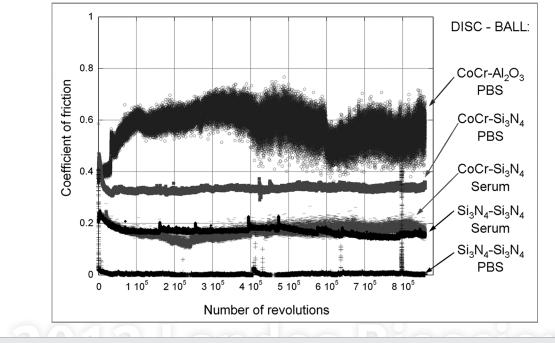


Figure 1. Coefficient of friction as a function of number of revolutions in the pin-on-disc test, with either PBS or a serum solution as lubricant.

 $Si_3N_4$ -powders dissolve in blood serum, gastric juice and a synthetic biochemical media at pH 7.4. This suggests that the use of  $Si_3N_4$  in hip implants may give less wear particles and those produced would be biocompatible and biodegradable. The less detrimental biological response may give a reduced number of revisions as an end result. However, whereas the wear and tribofilm formation of  $Si_3N_4$  sliding against itself in water have been investigated,  $^{10,11,14,15,21}$  there is a lack of knowledge on the wear and tribofilm formation in PBS and bovine serum and also regarding the solubility of the wear particles.

The purpose of this work is to examine the friction, wear and chemical properties of silicon nitride as well as the solubility of silicon nitride particles in a simulated physiological fluid. In addition, the materials response of the material to blood coagulation and immune complement activation has been studied in vitro.

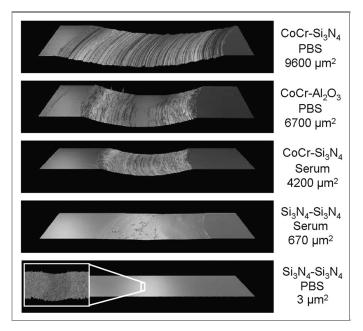
# Results

Tribological testing and analysis. The friction curves varied dramatically between the different tests with respect to both the friction level and the fluctuations, see Figure 1. All the tests lubricated with PBS started with a coefficient of friction of approximately 0.4, whereas those lubricated with serum solution started at approximately 0.2. For the Si<sub>3</sub>N<sub>4</sub>-disc sliding against a Si<sub>3</sub>N<sub>4</sub>-ball in PBS the friction rapidly fell to around 0.01. The friction curve here shows a few peaks lasting around 7,000 revolutions, which probably are connected to the refilling of water.

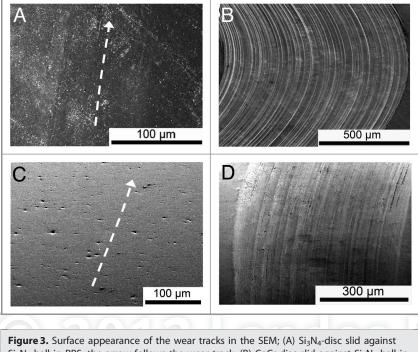
The tests lubricated with the serum solution demonstrated much less friction difference between the different material combinations. Both combinations had mean value of  $\mu = 0.17$ . However, the CoCr-Si<sub>3</sub>N<sub>4</sub> combination demonstrated a slightly

more fluctuating curve. The  $\rm Si_3N_4\text{-}Si_3N_4$  friction curve had a few peaks which all occurred in connection with the water refilling.

CoCr sliding against  $Al_2O_3$  in PBS showed the highest friction. However, the CoCr disc that slid against  $Si_3N_4$  showed most wear. This wear track had a cross-section area of 9,600  $\mu$ m<sup>2</sup>, Figure 2. While the other CoCr discs also had wear scar in



**Figure 2.** Optical profile images of worn discs and the calculated cross-section areas of the wear tracks. All the images have the same magnification. The width of the analyzed area is 1.1 mm, except for the enlarged area of the  $Si_3N_4$  disc that slid against a  $Si_3N_4$ -ball in PBS.



 $Si_3N_4$ -ball in PBS, the arrow follows the wear track; (B) CoCr-disc slid against  $Si_3N_4$ -ball in PBS; (C)  $Si_3N_4$ -disc slid against  $Si_3N_4$ -ball in bovine serum, the arrow follows the wear track; (D) CoCr-disc slid against  $Si_3N_4$ -ball in bovine serum.

the same order of magnitude, the Si<sub>3</sub>N<sub>4</sub> disc that slid against Si<sub>3</sub>N<sub>4</sub>-ball in PBS had a significantly smaller wear track, with a width of 150  $\mu$ m, depth of 30 nm and a cross-sectional area of 3  $\mu$ m<sup>2</sup>. The Si<sub>3</sub>N<sub>4</sub> disc that slid against a Si<sub>3</sub>N<sub>4</sub>-ball in the serum solution had a lager wear track, with a width of 600  $\mu$ m, a depth of about 1.4  $\mu$ m and a cross sectional area of 670  $\mu$ m<sup>2</sup>.

The  $Si_3N_4$  discs did not show any clear wear marks irrespective of lubricant, whereas the wear marks on the CoCr discs appeared distinctly for both lubricants, Figure 3. The CoCr-disc tested in PBS had a more distinct scratch pattern when tested in bovine serum. The widths of the wear marks on the balls were about the same magnitude as the widths of the wear scars on the discs.

The original surface hardness for CoCr was lower than the hardness in the wear track, **Table 1**. The opposite trend was observed for  $Si_3N_4$  both tested in PBS and in bovine serum. The hardness differences between the two unworn CoCr samples could be due to deformation hardening induced by small differences in the surface preparation process.

The XPS depth profiles of the CoCr samples showed that the atomic concentration has reached the bulk alloy values after about

Table 1. Nano hardness values (and standard error) at indentation depth of 30 nm

Disc material	Unworn surface	Wear track (PBS)	Wear track (serum)
CoCr	9.1 ± 0.5 GPa	10.4 $\pm$ 0.3 GPa	
CoCr	8.1 ± 0.3 GPa		8.5 ± 0.3 GPa
Si <sub>3</sub> N <sub>4</sub>	23.1 ± 0.6 GPa	21.3 ± 0.9 GPa	
Si <sub>3</sub> N <sub>4</sub>	23.8 ± 0.9 GPa		22.0 ± 0.7 GPa

2 min of sputtering for both the reference surface immersed in PBS and the unworn surface from the serum test, Figure 4A and B. Both surfaces consist mainly of Cr-oxide. The depth profile of the wear track from the serum test is quite different, Figure 4C. Here the affected layer of carbon and oxygen extends down to a sputter time of 30 min, i.e., 15 times longer than outside the wear track. This carbon and oxygen has been introduced into the bulk by the friction induced shear deformation of the surface layers.

The Cr 2p spectra obtained from the passivated and bovine serum lubricated surfaces recorded in, and outside the wear track are shown in Figure 5A. The vertical lines mark the CoCr position of the following components in the  $2p_{3/2}$  level: bulk metal,  $Cr^{3+}$  oxide (shifted 2.2 eV relative to the bulk<sup>22</sup>) and  $Cr^{3+}$  hydroxide (shifted 3.4 eV relative to the bulk<sup>22</sup>).

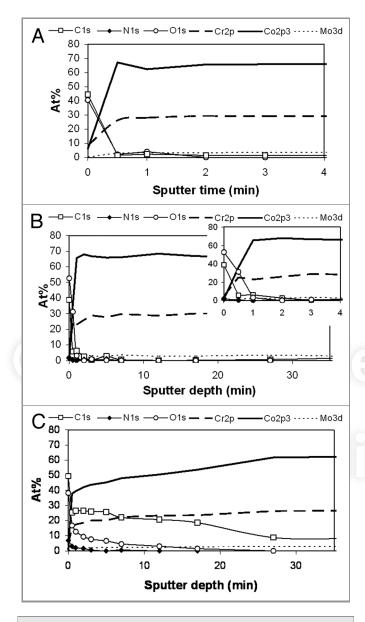
It is in general difficult to separate the two ionic contributions from each other since they are internally broad and overlap. On the original surface of the PBS immersed sample, the two ionic contributions are fitted with one broad structure. After 60 sec of sputtering all structure related to the surface modification is removed

and only the contribution from the bulk remains. The outermost part of the oxidized layer on the bovine lubricated surfaces is terminated by a Cr hydroxide. After 30 sec of sputtering the hydroxide decreases in intensity and the surface is now terminated by  $Cr^{3+}$  oxide with trace of hydroxide still left.

C 1s spectra from the bovine lubricated surfaces are displayed in **Figure 5B**. Spectra from the outermost surface obtained in and outside the wear track are decomposed into four and three peaks, respectively. The main peak at 284.5 (C1) can be associated to C–C and C–H bonds, the C2 peak shifted 1.5 eV is associated to C–O bonds, and the C3 component shifted 3.7 eV to N-C = O bonds.<sup>22,23</sup> These structures are observed in the spectrum recorded in and outside the wear track of the original surfaces and after sputtering for 30 sec in the wear track. The C4 component shifted 6.4 eV relative to the main line is only observed in the spectrum from the wear track and is assigned to O = C-O bonds.<sup>24</sup> The C4 structure shows that the normal peptide bonds have been partly oxidized in the wear track.

Figure 5C shows the N 1s spectra from the bovine lubricated CoCr surface. The main peak is situated at 399.9 eV. The peak on the high energy side shifted 2.5 eV to higher energies is only observed in the spectra from the wear track.

Si 2p spectra from  $Si_3N_4$  samples lubricated with PBS solution and bovine serum are shown in Figure 6A. All spectra were recorded in un-sputtered condition and have similar appearance with one bulk related component (Si<sub>B</sub>) at 101.3 eV and one surface related component Si<sub>S</sub> shifted 1.3 eV. The Si<sub>S</sub> component is associated with SiO<sub>2</sub>/SiO<sub>x</sub>-OH<sub>y</sub>. The binding energy value for the Si<sub>B</sub> component is lower than the values reported in the literature (102 eV<sup>25,26</sup>) while the energy shift to the oxide



**Figure 4.** Depth distribution of different elements in the CoCr samples; (A) Surface immersed in PBS, (B) Surface exposed to bovine serum, outside the wear track; (C) Surface exposed to bovine serum in the wear track.

component is in line with earlier reported values for the SiO\_2/ SiO\_x-OH\_y. ^{26,27}

The N 1s spectra are recorded from the wear track on samples that have been lubricated with either PBS solution or bovine serum, **Figure 6**. In the case of PBS solution the spectrum can be fitted with one component and in the case of bovine serum the spectrum is composed of two distinct components. During sputtering of the bovine lubricated surface the N2 component diminish after around 60 sec (not shown). The N1 component at a binding energy of 397 eV is associated to the bulk material and the N2 component shifted 2.6 eV to the peptide containing tribosurface. Also here the binding energy of the bulk component is somewhat lower than the values reported in the literature.<sup>28</sup>

Figure 6C shows the C 1s spectrum from the wear track of the  $Si_3N_4$  bovine lubricated surface. The C 1s peak can be fitted with three components labeled C1, C2, and C3. The interpretations of the different structures are the same as for those observed on the CoCr surface (i.e., C1, C–C and C–H, C2, C–O, and C3 N-C = O bonds). The X-ray diffractograms demonstrated that the disc and the ball were of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>, Figure 7.

Solubility test. The concentration of free Si in the filtered solutions indicates that some of the powder has been dissolved The concentration of Si in the filtered PBS solutions was about 75 mg/l for all pH variations and also approximately the same for the different incubation periods, see Figure 8. This would correspond to a dissolution of  $Si_3N_4$  powder of 1.87%. All samples of PBS solutions without any addition of powder showed Si concentrations of less than 0.5 mg/l.

Blood plasma incubations. Surface mass densities on  $Si_3N_4$ , CoCr and Ti references resulting from exposure to human blood plasma and subsequent antibody incubations are plotted in Figure 9 for antibodies of factor C3c, HMWK and Fib. Results from adsorption experiments on  $ZrO_2$  surfaces, a material commonly assumed to be compatible with soft as well as hard tissues, are included in the plot.<sup>29</sup> Some variations of the adsorbed amounts of plasma (lower part of bars) among the samples can be observed, mainly due to a variation in surface roughness. The lower values of adsorbed plasma on  $ZrO_2$  can be explained by a shorter incubation time. The results from exposure to antibody solutions probes the composition of the layer adsorbed from plasma.

# Discussion

The tribological tests performed in this study showed that the coefficient of friction does not directly correlate to the wear of the components. The highest friction was achieved with CoCr disc against an Al<sub>2</sub>O<sub>3</sub> ball in PBS. However, this disc showed lower wear than the CoCr disc slid against the Si<sub>3</sub>N<sub>4</sub> ball in PBS, which had a lower coefficient of friction, Figures 1 and 2. Further, in the bovine serum solution both material combinations exhibited similar friction, while the CoCr disc was substantially more worn than the Si<sub>3</sub>N<sub>4</sub> disc. The similarity in friction could be explained by the presence of the same type of tribofilm: the XPS results showed that both the CoCr and Si<sub>3</sub>N<sub>4</sub> discs have tribosurfaces consisting of metal oxide/hydroxide mixed with fragments from the serum proteins. The amount of protein fragments is highest in the wear track even if the areas outside the wear track also show traces of these fragments. The hardness measurements of the Si<sub>3</sub>N<sub>4</sub> discs indicated that the surfaces became slightly softer with the deposited layer. The thin deposited layers are probably much softer than the measured values where the contribution form the bulk is significant. It was further noticed that the CoCr discs were hardened by wear. The CoCr disc tested in bovine serum exhibited less wear, had a smoother wear track and less hardness increase than the CoCr disc tested in PBS.

The XPS data from the C 1s and N 1s show that samples lubricated with bovine serum contain traces of peptide fragments, which stem from the proteins in the serum. The absorption of

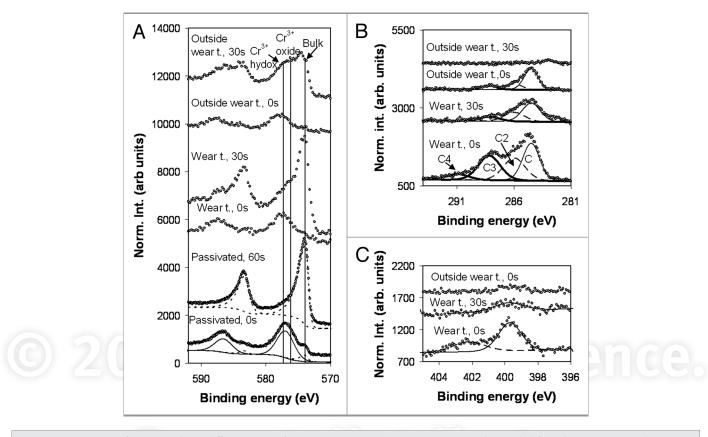


Figure 5. XPS spectra of CoCr samples at different times of sputtering (0, 30 and 60 sec); (A) Cr 2p peak recorded from the CoCr immersed in PBS (passivated); (B); C 1s-peak for CoCr in bovine serum, both in and outside wear track; (C) N 1s-peak for CoCr in bovine serum, both in and outside wear track.

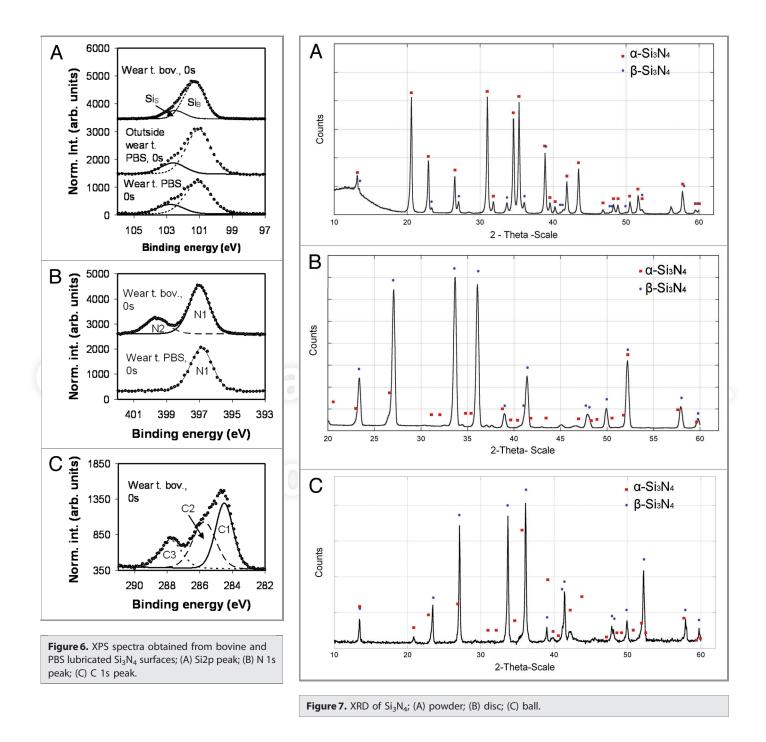
proteins occurs both in and outside the wear track, even if the thickness of the peptide containing layer is thicker in the wear track than outside. In the ceramic on metal contact there is, besides wear, a component of mechanical mixing that occurs in the sub surface layer. This effect is clearest distinguished on the CoCr-Si3N4 system lubricated with bovine serum were the carbon profile extend into the material in a manner that can described as mechanical mixing (Fig. 4C). For the CoCr-CoCr system it has been shown that the mechanical mixing can be described as a formation of a nano-crystalline layer by rotation of clusters of atoms. In this process denatured proteins from the solution is incorporated into the metal.<sup>30</sup> This is in line with the data shown in Figure 4C. The underlying reason for the binding energy being lower for the Si and N bulk levels compared with other studies could be found in the shielding of the final state. It is likely that the bulk material in the present measurement contains higher number of defects/doping states that act as free charges that can shield the final state, which may result in a lower binding energy.

The tribofilm present on the  $Si_3N_4$  disc tested in PBS contributed to an extremely low coefficient of friction. However, that tribofilm was found to be very sensitive and after it had been broken, it took approximately 600 revolutions until it was reformed and the coefficient of friction reached a value of 0.02. The occasional high friction periods could be connected to the

refilling of deionized water. The friction sensor was never touched but the tribofilm might have been disturbed due to fluctuation and foaming of the PBS liquid. These high friction periods were not just instant peaks, the highest lasted for about 1,000 revolutions. The peaks show that this tribofilm is very sensitive to external disturbance. These results are in agreement with Xu and Kato,<sup>14</sup> who suggested that the silica tribofilm is dispersed when it reaches a certain thickness and replaced by a new film which forms on the surface.

The XRD measurement shows that the tested discs and balls contain predominantly  $\beta$ -Si<sub>3</sub>N<sub>4</sub>. As previously mentioned,  $\beta$ -Si<sub>3</sub>N<sub>4</sub> is advantageous due to its higher wear resistance and higher toughness than the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> phase. However, the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> phase is harder than  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.  $^{13,31}$  According to Zhu and Sakka<sup>13</sup> the  $\alpha$ -phase is less chemically stable since the  $\alpha$ -phase transforms into the  $\beta$ -phase at high temperatures when a liquid phase is present.

The solubility tests showed that  $Si_3N_4$ -powder, which was mainly of  $\alpha$ -phase, was soluble in PBS at 37°C, which is in accordance with Boshitskaya et al.<sup>20</sup> These authors have shown that  $Si_3N_4$ -powders dissolve in blood serum, gastric juice and a synthetic biochemical media at pH 7.4. The solubility tests in the present investigation showed no difference in the amount of Si-ions between 35 and 75 d or between the different pH values. This may be due to a saturation of the solutions at an early stage,



in accordance with a previous study.<sup>32</sup> Future studies will focus on lower concentrations of Si<sub>3</sub>N<sub>4</sub>-powder as well as powders of different phases, as sintered silicon nitride commonly consists mainly of  $\beta$ -phase. However, if the silicon nitride is to be realized as a coating on a metal substrate, it may be of an amorphous nature, and such particles will hence also be of interest. Ultimately, wear particles from tribological tests of the final material will need to be tested in vivo.

Large amounts of HMWK adsorbed on the Si<sub>3</sub>N<sub>4</sub> surfaces indicate that the intrinsic pathway of coagulation is activated,<sup>33</sup> probably due to the negative charge of the surfaces. Negatively charged surfaces tend to denature proteins at the surface to a lower

extent. Low binding of complement (C3c) was found on Si<sub>3</sub>N<sub>4</sub>, as compared with both Ti and ZrO<sub>2</sub>, indicating less immune activation. The adsorption results on CoCr surfaces are comparable to results of Wälivaara.<sup>34</sup> The small amounts of HMWK and the large amounts of Fib indicate a hydrophobic surface. The high levels of adsorption of Fib indicate binding and activation of platelets and thereby clotting.<sup>35</sup> The small amounts of Fib on Si<sub>3</sub>N<sub>4</sub> indicate the opposite, i.e., less activation of platelets and less clotting.

The results from this study indicate that  $Si_3N_4$  fulfil the initial profile set-out to find a wear resistant low-friction material that also has the potential to give resorbable wear particles in vivo.

Biomatter

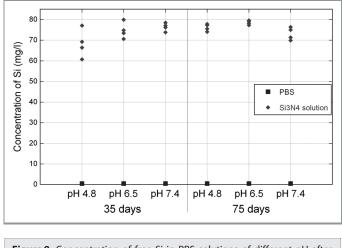
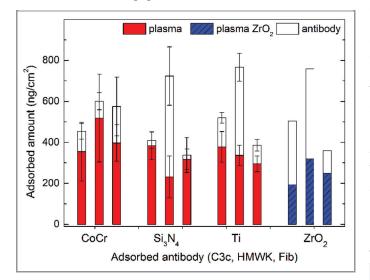


Figure 8. Concentration of free Si in PBS solutions of different pH after 35 and 75 d.

Future work will focus on developing a deposition method for coatings on metals with the same properties as the bulk material, as well as confirming the solubility of produced wear particles.

# **Materials and Methods**

**Tribological testing and analysis.** The tribological tests were performed with ball-on-disc equipment, where a stationary ball was pressed against a rotating disc and the friction force was continuously measured.<sup>36</sup> The balls had a diameter of 6 mm, the sliding speed was 0.05 m/s, the radius of the rotation was 3.2 mm and the normal load was 1 N. The sliding speed and the radius of the rotation are in accordance with the ASTM standard test.<sup>37</sup> However, due to the small ball radius and the limitation of the lowest load for the equipment, the maximum hertzian contact



**Figure 9.** Adsorbed amounts of blood plasma and antibodies onto surfaces of CoCr,  $Si_3N_4$  and reference surfaces of titanium. The lower part of the bar represents adsorbed plasma and the upper part represents adsorbed antibody. Results from adsorption experiments on zirconia surfaces<sup>29</sup> are also included.

pressure is about 0.8 GPa. This pressure corresponds to a normal load of 400 kN for a Si<sub>3</sub>N<sub>4</sub> head of 28 mm in diameter against a cup of  $Si_3N_4$  with a radial clearance of 100  $\mu$ m. The tests were performed for approximately 900,000 revolutions. The tests were performed with commercial balls of Si<sub>3</sub>N<sub>4</sub> or Al<sub>2</sub>O<sub>3</sub> (Spekuma), sliding against discs of commercial sintered silicon nitride (Keranova AB) or commercial CoCr (ASTM F75, Sandvik AB). CoCr and Al<sub>2</sub>O<sub>3</sub> were included in the tests as references since both materials are commonly used in hip joint implants. The discs were mounted in a steel cup. The tests were performed in PBS (Sigma-Aldrich) or in bovine serum diluted with deionized water according to the ASTM standard.37 The cup was refilled with deionized water once or twice a day to make up for evaporation losses. Before the tests, the discs were polished to a surface roughness (Ra) of 5-15 nm and subsequently cleaned in an ultrasonic bath with acetone and then ethanol. The balls had a surface roughness of approximately 50 nm. As a reference, a CoCr sample was immersed in PBS for 90 d. The surface appearance of the wear tracks of the discs was analyzed using scanning electron microscopy (SEM), the surface roughness and volume loss was studied using an optical profiler based on white light interference (OP). The chemical composition of the wear tracks and unworn reference surfaces was analyzed with XPS (X-ray photoelectronic spectroscopy, PHI Quantum 200). XRD (X-ray diffraction, Siemens P5000) was used in order to analyze the phase composition of the  $Si_3N_4$  discs and powder.

The superficial hardness of the unworn discs and the wear tracks was measured with an ultra nano hardness tester (UNHT, CSM) using a Berkovich indenter. The hardness was measured at an indentation depth of 30 nm. The indents were analyzed in accordance with the Oliver-Pharr method.<sup>38</sup>

Solubility test. Since actual wear particles of silicon nitride were inaccessible due to the very low wear in the tribological tests, a commercial silicon nitride powder (P95H, Akzo Nobel) was used for a preliminary solubility study. This powder was reported to contain 98.5+% Si<sub>3</sub>N<sub>4</sub>, with a minimum of 90% alfa-Si3N4,  $d10 = 0.23 \ \mu m$ ,  $d50 = 0.77 \ \mu m$ ,  $d90 = 4.0 \ \mu m$ , corresponding to BET surface area  $9 \pm 3 \text{ m}^2/\text{g}$ . The average grain size of the powder was confirmed to be approximately 1 µm (measured with SEM and optical microscopy). The powder was mixed with PBS using three different pH values: 4.8, 6.5 and 7.4. It has been shown that the pH value in the vicinity of the implant can vary between 4.4-7.7.39 PBS has a natural pH of 7.4 and hydrochloric acid was added to decrease the value. The mixture was stored in plastic tubes with plastic lids. The tubes were placed on a rocking platform shaker and stored at 37°C during 35 and 75 d respectively, (Table 2). One hundred milligrams of silicon nitride

Table 2. Solubility test: number of samples per pH and time point

	100 mg Si₃N₄-powder			PBS without powder		
рН	4.8	6.5	7.4	4.8	6.5	7.4
Time (days)						
35	4	4	4	1	1	1
75	4	4	4	1	1	1

powder was mixed with 15 ml PBS. After the storage time, the mixture was filtered through a 0.2  $\mu$ m PTFE membrane using a syringe. Dynamic light scattering analysis (Malvern Zetasizer NanoZS, Malvern Instruments, Nordic AB) did not detect any particles smaller than 200 nm (diameter in the original powder. Subsequently to the filtration, ICP-MS (inductively coupled plasma mass spectrometry) was used to determine the silicon ion content of the solutions.

**Blood plasma incubations.** The adsorption experiments with blood plasma and antibodies were performed and measured in situ using a null ellipsometer. The experiment started with incubation in human blood plasma for 20 min and after measurement of adsorbed protein thicknesses the samples were incubated in three antibodies [of complement 3c (C3c), high molecular weight kininogen (HMWK) and fibrinogen (Fib)] for 30 min. Details on the experimental setup can be found elsewhere.<sup>40</sup>

# Conclusions

Friction, wear and chemical properties of  $Si_3N_4$  as a potential joint implant material have been studied. Pin-on-disc wear tests have been performed with  $Si_3N_4$  and CoCr discs sliding against  $Si_3N_4$  or  $Al_2O_3$  balls in PBS and bovine serum solutions. Subsequently the surface appearance, wear volume and chemical compositions of the wear were analyzed. Furthermore, a preliminary study on the solubility of  $Si_3N_4$ -powder in PBS was analyzed. In addition, responses to immune complement activation and blood coagulation have been reported. The

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following main conclusions were drawn: (1)  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>-powder dissolves in PBS. Further studies are needed to confirm the solubility of other phases as well as the in vivo solubility of wear particles from the final material. (2) Antibody adsorbtion indicated that the Si<sub>3</sub>N<sub>4</sub>-surface has relatively low immune activation and tends to denature proteins to a low extent at the surface which might be an indication of an improved acceptance of the body. (3) Si<sub>3</sub>N<sub>4</sub> sliding against Si<sub>3</sub>N<sub>4</sub> showed low wear rate in both bovine serum and PBS. (4) Tribofilms were built-up on the Si<sub>3</sub>N<sub>4</sub> surfaces in both PBS and in bovine serum which contributed to a decrease in friction. (5) The build-up of tribofilm and the type of tribofilm strongly affects the coefficient of friction. However, the material combination is of high importance for the total amount of wear. Si<sub>3</sub>N<sub>4</sub> against Si<sub>3</sub>N<sub>4</sub> was shown to be a material combination with a good performance for hip joints, possibly realized as a coating on CoCr.

### Disclosure of Potential Conflicts of Interest

No potential conflicts of interest were disclosed.

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