Silicon nitride for total hip replacements

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Dissertation presented at Uppsala University to be publicly examined in Häggsalen, Ångströmslaboratoriet, Lägerhyddsvägen 1, Uppsala, Friday, 22 May 2015 at 13:30 for the degree of Doctor of Philosophy. The examination will be conducted in English. Faculty examiner: Professor Kenneth Holmberg (VTT Technical Research Centre of Finland).

Abstract

For more than 50 years total hip replacements have been a common and successful procedure to increase patient mobility and quality of life. The 10-year implant survival rate is 97.8%. However, for longer implantation times there are limitations linked to the negative biological response to wear and corrosion products from the currently used biomaterials.

In this thesis silicon nitride (SiNₐ) coatings were evaluated for use in total hip replacements, on the articulating bearing surface and modular taper connections. Homogeneous, dense SiNₐ coatings were deposited using reactive high power impulse magnetron sputtering (HiPIMS) up to a thickness of 8 µm. The N/Si atomic ratios ranged from 0.3 to 1.1 and the coatings showed a low surface roughness. The wear rate of a SiNₐ coated cobalt chromium molybdenum alloy (CoCrMo) was similar to that of bulk Si₃N₄, and less than one 46th of uncoated CoCrMo, an alloy that is commonly used in joint replacements. Wear debris generated from SiNₐ coatings was round in shape, with a mean size of 40 nm, and ranged between 10 and 500 nm. Model particles, similar in size and shape as the wear debris, were soluble in simulated body fluid. The dissolution rate was higher than the expected rate of debris generation. Along with the size of the debris, which is not in the critical range for macrophage activation, this dissolution may limit negative biological reactions. The SiNₐ coatings also dissolved in simulated body fluid. The coating with the highest N/Si ratio exhibited the lowest dissolution rate, of 0.2 to 0.4 nm/day, while CoCrMo under the same condition dissolved at a rate of 0.7 to 1.2 nm/day. SiNₐ-coated CoCrMo exhibited a reduced release of Co, Cr and Mo ions into the solution by two orders of magnitude, compared to uncoated CoCrMo. Si₃N₄ evaluated under micro-displacement in a corrosive environment, replicating the modular taper, showed a lower corrosion current compared to common biomedical alloys. SiNₐ coatings may also act beneficially to reduce issues associated with this type of contact.

SiNₐ coatings have shown several properties in a laboratory environment that are hypothesised to increase the longevity of joint replacements. The promising results encourage further evaluation closer to the clinical application of total hip replacements, in particular in the articulating bearing surface and in modular tapers.

Keywords: SiNx, Si₃N₄, coatings, CoCr, Ti, alloy, tribology, wear, corrosion, dissolution, debris, hip, arthroplasty

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ISSN 1651-6214
urn:nbn:se:uu:diva-247800 (http://urn.kb.se/resolve?urn=nbn:se:uu:diva-247800)
To curiosity
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


IV  Pettersson, M., Skjödebrand, C., Engqvist, H., Persson, C. Morphology and dissolution rate of wear debris from silicon nitride coatings—a laboratory investigation. Submitted

V  Pettersson, M., Bryant, M., Schmidt, S., Engqvist, H., Hall, R., Neville, A., Persson, C. Dissolution behaviour of silicon nitride coatings for joint replacements. *Manuscript*

VI  Pettersson, M., Oladokun, A., Bryant, M., Engqvist, H., Hall, R., Persson, C., Neville, A. Fretting behaviour of silicon nitride against biomedical alloys for joint replacements. *Manuscript*

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My contributions to the papers included in this thesis are:

**Paper I:** Part of planning, experimental work (excluding deposition and TEM analysis), part of evaluation and writing.

**Paper II:** Major part of planning, experimental work (excluding deposition, AFM and TEM analysis), major part of evaluation and writing.

**Paper III:** Major part of planning, experimental work (excluding deposition and micro-scratching), major part of evaluation and writing.

**Paper IV:** Major part of planning, experimental work (excluding ICP analysis), major part of evaluation and writing.

**Paper V:** Major part of planning, experimental work (excluding deposition, ICP analysis), major part of evaluation and writing.

**Paper VI:** Major part of planning, experimental work, evaluation and writing.
Related work


Vuong, V., Pettersson, M., Persson, C., Larsson, S., Grandfield, K., Engqvist, H. **Surface and subsurface analyses of metal-on-polyethylene total hip replacement retrievals.** *Submitted*

Hedberg, Y. S., Pettersson, M., Pradhan, S., Odnevall Wallinder, I., Rutland, M., Persson, C. **Do cobalt and chromium ions have the potential to increase friction in a joint prosthesis?** *Manuscript*
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Abbreviations

CoC  ceramic-on-ceramic
CoCrMo  cobalt chromium molybdenum alloy (Co-28Cr-6Mo)
CoM  ceramic-on-metal
CVD  chemical vapour deposition
EDS  energy-dispersive x-ray spectroscopy
GI-XRD  grazing incidence x-ray diffraction
HiPIMS  high power impulse magnetron sputtering
HXLPE  highly cross-linked UHMWPE (see below)
ICP-AES  inductively coupled plasma atomic emission spectroscopy
ICP-MS  inductively coupled plasma mass spectrometry
LPR  linear polarisation scan
MoM  metal-on-metal
MoP  metal-on-polymer
OCP  open circuit potential
PECVD  plasma-enhanced CVD (see above)
PBS  phosphate-buffered saline solution
PVD  physical vapour deposition
RF-PVD  radio frequency PVD (see above)
SAED  selected area electron diffraction
SEM  scanning electron microscope
SiNx  silicon nitride coating (amorphous)
Si3N4  silicon nitride, bulk (stokiometric)
TEM  transmission electron microscopy
TiAlV  titanium aluminium vanadium alloy (Ti-6Al-4V)
UHMWPE  ultra-high molecular weight polyethylene
VSI  vertical scanning interferometry
XPS  x-ray photoelectron spectroscopy
XRD  x-ray diffraction
1 Introduction

Total hip replacements have increased the quality of life for people for more than six decades. It has often been referred to as the most successful orthopaedic procedure. In Sweden, the success rate between 2011 and 2013 at 10 years after implantation was 97.8\%\(^1\). At longer implantation times there are limitations related to the commercially available materials used today.

This thesis aims to evaluate whether silicon nitride have specific qualities that could increase the longevity of hip joint replacements, with a focus on development and investigation of silicon nitride coatings. The hypothesis is that certain qualities that silicon nitride possesses, namely high wear and corrosion resistance, a certain degree of solubility in aqueous solutions as well as a potentially higher biocompatibility, can be transferred into coatings, which may give an advantage in the application of total joint replacement, and can further increase the longevity of the replacements.

The first objective of this work was to select a deposition technique and parameters that could produce high-quality coatings (in this context, meaning coatings with a dense and homogeneous silicon nitride structure and a low surface roughness) and understand the correlation between the deposition parameters and the coating adhesion to the substrate as well as the coating hardness, covered in papers I, II, and III. 

Secondly, the objective was to evaluate the wear behaviour of silicon nitride in a sliding contact, in terms of wear resistance (in paper I and III) and wear debris (in paper IV), as well as subjected to micro-motions in corrosive environment (in paper VI).

Finally, the objective was to understand the dissolution properties of silicon nitride, how wear debris and coatings dissolve, and if the coating has the ability to act as a barrier and to enable metal ion release from the substrate (covered in papers IV and V).

This summary aims to provide a background for the reader and to put the papers into context, especially if the reader does not have a background in the field. After reading this thesis, the reader should have an understanding of the current materials-related challenges in total hip replacements, and the possibilities and limitations that silicon nitride may have in the application.
2 Background

The first known hip replacement, reported by Themistocles Gluck in the 1890s, was made of carved ivory. Following this introduction, the development of hip replacements took several important steps forward (as with the introduction of Co-alloys as early as 1939), although it was not until the 1950s that the hip replacement procedure had started to become simple and reliable enough to be practiced by the average surgeon. Two major contributions to the development were made around that time, first by Austin Moore, who introduced the long stem prosthesis in the 1950s, and then in 1962 when John Charnley introduced a new design using highly cross-linked polyethylene on a metal femoral head and stem and the use of bone cement. This type of implant became so reliable that it is still in use today. The materials have been further modernised since then, introducing ever more advanced ceramic materials, metal alloys, and polymers.

Today it is estimated that around one million patients undergo surgery for total hip replacements every year around the world. The number of primary total hip replacements (the first implantation) in Sweden increased from six in 1967 to more than 16,000 in 2013. In the United States, Kurtz et al. predict that primary hip arthroplasty procedures will more than double between 2010 and 2030. The patients who undergo total hip replacement surgery are typically over 40 years (>95%), and 84% are between 60 and 89 years of age. The most common reason for implanting a total hip replacement is due to primary osteoarthritis, which is associated with aging. A natural hip is shown in Figure 1. Primary osteoarthritis is caused by the breakdown of cartilage, which leads to stiff joints and pain in the hip. Other reasons for undergoing a total replacement surgery may be fracture or trauma, where a total hip replacement may give back mobility and reduce pain for the patient.

The cost of a total hip replacement procedure and for the implant itself varies depending on country and region. For example, in the United Kingdom the procedure, including the implant, costs around 6,000 GBP (9,300 USD), and in Sweden typically 100,000 SEK (12,000 USD), while in the United States the cost is around 22,500 USD, this includes the cost of the implant, which costs around 8,000 USD. The implant costs vary between designs and materials; an implant with ceramic articulating parts and a coated stem is almost twice the price (8,000 USD) of a standard metal-on-polymer (MoP) implant with uncoated stem (5,000 USD), with an average selling price from 2010.
There are several reasons for primary revision (reoperation) of the prosthesis. In Sweden in 2013 (the date for the most recent data available), the main reason for revision was aseptic loosening (~40%), with the largest risk for failure after >4 years of implantation. After aseptic loosening, the most common reasons were deep infection (~24%), fracture (~12%), and dislocation (~12%). The risk for dislocation and deep infection is higher during the first years (<3 years), while the risk for fracture is almost constant during the time of implantation.  

2.1 Materials in hip joint replacements

For a total hip replacement, damaged bone and cartilage are removed from the natural hip and replaced with implant components (see Figure 2). The natural femoral head is removed and a metal stem (cobalt chromium molybdenum alloys (CoCrMo), Ti-alloys, or stainless steel) is inserted into the femur. This is attached either by bone cement (the most common method in Sweden), or press-fitted, often with a coating on the stem surface to increase bone ingrowth. On top of the stem, an implant femoral head is either integrated with the stem as a monoblock or press-fitted as a module on a taper. There may also be two-way modular neck junctions between the head and the stem (not shown in the figure). The femoral head is commonly composed of a metal alloys (CoCrMo or stainless steel) or a ceramic (commonly alumina, zirconia, or a combination of the two). Mating with the femoral head, on the pelvis side, is a cup made either as a single component or as a shell.
with an insert. The whole cup or the insert are in most cases made of a polymer (mainly ultra-high molecular weight polyethylene (UHMWPE)), but may also be made of a metal alloy (CoCrMo) or a ceramic. A cup made of only polymer can be attached by bone cement to the pelvis, whereas metallic shells (titanium, stainless steel, or CoCrMo) can be press-fitted.

![Diagram of total hip replacement](image)

**Figure 2.** A schematic sketch of a typical total hip replacement. Tribological challenges in the articulating surface between the head and the cup, as well as in the taper junction are noted to the right.

There are several material combinations for the articulating surface between the head and the cup. The combinations vary for patient groups and with the surgical and healthcare environment. In Sweden, the most commonly used combination in 2013 was the aforementioned metal-on-polymer (MoP), with ~84%; the second most common combination is ceramic-on-polymer (CoP), with ~15%; these are distantly followed by ceramic-on-ceramic (CoC, 0.5%) and metal-on-metal (MoM, 0.4%)\(^1\). The modular taper junction often combines similar or dissimilar metals, or, in the case of ceramic femoral heads, ceramic with metal.
2.1.1 Metals

The three main groups of biomedical alloys used for the articulating surface, taper and stem are cobalt chromium alloys, titanium alloys, and stainless steel.

Austenitic stainless steel, such as 316L, was an early metal of choice in joint replacements. Even if the material itself is economical, its use is limited by its relatively low resistance to crevice corrosion and for commonly using Ni as an alloying element.\(^2\)

Cobalt chromium molybdenum (CoCrMo) alloys are widely used today in hip replacements. CoCrMo is valued for its corrosion resistance along with its high strength and fatigue- and wear resistance. The metal debris and ions that originate from CoCrMo can however cause adverse biological reactions, especially in MoM couplings.\(^8,9\) Since the issues associated with MoM articulations were discovered, their use has significantly decreased. In Sweden their use decreased from 4.2% in 2007 to 0.4% in 2013\(^1\).

Another common alloy used, mainly for the stem, is Ti-6Al-4V (TiAlV), valued for its corrosion resistance and its biocompatibility. TiAlV has a lower stiffness than CoCrMo, so it is more suited as a stem, as there is a smaller difference in stiffness between the alloy and the bone. At the same time, its tribological properties are relatively poor, which excludes their use in femoral heads or pelvic bearing parts.\(^2\) (The field of tribology, or the properties of parts moving in relation to each other, is discussed in more detail in Section 2.3.)

2.1.2 Polymers

UHMWPE has been the most common material used in acetabular cups since the material’s introduction by Charnley. Although conventional UHMWPE has been performing well for decades, it has been a limiting factor for total joint replacements. It creates a sufficient volume of wear debris in a critical sub-micron size range that triggers macrophage activity, which eventually may lead to loosening of the implant; this is believed to be the main cause of late aseptic loosening.\(^10,11\) Since the 1990s, UHMWPE has undergone structural development introducing the more wear-resistant highly cross-linked UHMWPE (HXLPE). From 2005 to 2013 the use of HXLPE increased from 1% to 70% in Sweden\(^1\). Recent in vivo reports have been promising in terms of decreased revision rates and a reduced risk of osteolysis compared to conventional UHMWPE.\(^1,12,13\)

2.1.3 Ceramics

Alumina (Al\(_2\)O\(_3\)) and zirconia (ZrO\(_2\)) ceramics have been used in orthopaedics for more than 30 years. Advantages with these ceramics include low
wear rates, chemical stability and bio inertness. Ceramic components are often recommended for younger patients or metal sensitive patients. Early stage development of ceramics witnessed fractures and catastrophic failures, however large improvements in their composition and structure has led to enhanced mechanical properties. 

2.1.4 Coatings

Today the most common coatings in commercial use related to joint replacements are hydroxyapatite coatings, which can increase bone ingrowth on the stem or the metal backing of the cup. This thesis does not cover these coatings or surfaces; instead, it covers coatings for the articulating surface and for modular junctions.

One advantage of using coatings is that properties from both the coatings and the substrate have practical importance, so a coating can provide beneficial surface properties (such as corrosion or wear resistance) while the bulk of the component can contribute with (for example) elasticity. This dual function is also what encourages the use of coatings in total hip replacements.

Coated articulating components have been used in joint replacements for more than a decade. Today there are several commercially available coatings or coated components, for example physical vapour deposition (PVD) or plasma-enhanced chemical vapour deposition (PECVD) deposited coatings such as TiN, TiAlN, AlTiN, TiNbN, CrN, ZrN (also with a multi-layered structure underneath), and diamond-like carbon (DLC). Another type of coating is based on a metallic zirconium bulk with an oxidised zirconia surface. Coated surfaces are generally recommended for patients who are at risk for metal sensitivity.

The reports of in vivo use of bearing coatings are still limited. Studies on TiN coatings have however reported high wear, caused by inadequate adhesion and detached fragments from the coating. Detachment has also been observed following dislocation of a prosthesis for oxidised zirconia.

2.2 Coating deposition

Coated surfaces have played an important role in industry; they have made an enormous impact on manufactured materials’ life expectancy, reduced manufacturing costs (by the use of coated cutting tools), increased the efficiency in engines, and decreased corrosion of components in tough environments.

The materials and deposition techniques available today are virtually endless. Two common groups of deposition methods applying gaseous states are the aforementioned chemical vapour deposition (CVD) and physical vapour
deposition (PVD). CVD methods introduce gaseous reactants into the deposition chamber, which condense on the substrate and form a coating. As the CVD process is thermally activated, high temperatures are used (typically 800°C to 1200°C), which limits its substrates.20

The PVD processes use atomised or evaporated material from a solid in the deposition chamber, to build up a coating on the substrate. In the process known as sputtering, a solid material called a target is used to form the coating. Atoms (ions or molecules) are removed from the target by bombarding it with ions from the plasma of an inert gas (commonly Ar). The collision of ions on the target releases material, which is guided to the substrate by a potential difference. A schematic drawing of such a deposition process is shown in Figure 3.

Figure 3. Schematic drawing of a sputtering deposition process.

Two sputter deposition techniques are used in this thesis: radio frequency PVD (RF-PVD) and high power impulse magnetron sputtering (HiPIMS). RF-PVD uses an oscillating power source to generate plasma from the inert gas20. HiPIMS is a magnetron sputtering technique, where magnetrons are used to trap the electron in a track on the target and increase the ionisation, and thus the deposition rate. In addition, HiPIMS uses a high impulse power. By applying higher powers than other PVD methods (in the range of kW instead of W), and in short pulses (in μs), it generates denser plasma, which further increases ionisation. Normally there are kinetic restrictions of the compounds and structures that can be built in a coating. In HiPIMS the process can occur outside of thermodynamic equilibrium, which allows the opportunity to exceed conventional limitations and allows for tailoring of the coating properties. HiPIMS can also generate dense and smooth coatings on more complex substrates21.

The coating composition will be determined by the solid target materials along with the gases present. By using a reactive gas in the chamber mixed
with the inert gas, a wider range of materials can be built. For example, a Si target with \( \text{N}_2 \) as a reactive gas and \( \text{Ar} \) as an inert gas can be used to produce a \( \text{SiN}_x \) coating.

Not only will the deposition technique influence the growth and the properties of the coating, but several deposition parameters can be adjusted to control and fine-tune the coating’s properties. Common parameters to adjust are, primarily, the materials and their origins (targets and gases). Other parameters are the substrate temperature, the pressure in the chamber, and the power applied on the target. In general, for slower deposition and higher temperatures, atoms have the possibility of moving around and finding energetically favourable positions during the growth of the coatings. For example, a higher deposition temperature may result in broader and larger grains or columns in the microstructure\(^{22}\).

2.3 Tribological contacts

Tribology is the science and engineering of surfaces’ interaction in relative motion, including terms such as wear, friction, and lubrication. For two surfaces that are in contact, the real contact area will be considerably smaller than it appears. Every surface has a roughness, with peaks and valleys, and only a few of the highest peaks will be in contact. As they move relative to one another, the peaks may deform plastically, break, or plough the counter surface. The motion will in this way involve microscopic deformation or even wear of material. The force required to perform this relative movement is the friction force. The friction coefficient, or the ratio between the friction force and the normal force, is often used to describe the resulting friction. This is not a parameter specific to one material. The friction is a system parameter, and can be affected by lubrication, humidity, surface roughness, material removal mechanisms, and so forth. In a lubricated contact the surfaces can be more (or less) separated at low loads, high speed, and high viscosity of the lubricant, resulting in low wear and friction, called fluid film lubrication. Lubricated surfaces can also be partly in contact, often resulting in higher wear and friction, called boundary lubrication. It can also be a mix of the two, called mixed lubrication.

In the case of a total hip replacement, the wear and the wear products are critical parameters for its longevity. In most cases wear will lead to loss of material for the softer material. A way to compare wear between materials under determined tribological conditions is to calculate the ‘specific wear rate’. The specific wear rate is defined as the wear volume divided by the load and sliding distance; it is based on a wear equation put forth by Holm in 1946 and by Archard in 1953. One should however be cautious when comparing wear rates between studies, as more parameters than those included in the equation can affect the wear rate. Just as in the case of the coefficient of
friction, the specific wear rate is far from a materials parameter, but very sensitive to the whole system in which it was measured.

In a total hip replacement there are several tribological contacts; the most obvious is that between the femoral head and the acetabular cup (see Figure 2). During each stride, this interface slides in the range of mm to cm and is lubricated with a synovial fluid (found inside the synovial joints). The contact is conformal, with contact pressures typically from 9 MPa for MoP up to 90 MPa for CoC.

The variations in wear volume, determined from simulator studies and summarised by Hallab and Jacobs, show the importance of materials and material combinations. For MoP, using conventional UHMWPE, a wear rate of ~80 mm³/year was obtained, while with HXLPE it was about half, ~40 mm³/year. By using a ceramic on the conventional UHMWPE (CoP), the wear volume was halved again to ~20 mm³/year. MoM and CoC showed the lowest wear rates: ~1 mm³/year and ~0.04 mm³/year, respectively.

Another contact in total hip replacement that is subject to wear (and corrosion) is modular junctions, which most commonly connects the neck taper and the femoral head (see Figure 2), but may also connect the neck and the stem. The modular implants allow the surgeon flexibility to design an implant specifically for the patient at a late stage. The modular junctions experiences micro-motions, and may fail in the long term due to fretting corrosion or fatigue. The modular junctions are further challenged by the tough acidic chemical environment created in the crevice.

2.3.1 Wear debris

The negative biological reactions limiting the longevity of total hip replacements are not only linked to wear volume; they are also related to the chemistry and size distribution of the debris. In the case of conventional UHMWPE a large enough volume of debris, in a critical size range of 0.1 to 1 μm, is believed to be the main cause for late aseptic loosening. The metal and ceramic debris is commonly smaller, between 10 and 100 nm; metal debris is typically round to oval in shape, while ceramic debris is round or angular in shape. The corrosion products from the debris can cause negative biological reactions, especially for metals. High metal ion levels in the blood, metallosis, hypersensitivity, and pseudotumours have occasionally been reported for metallic implants, especially MoM. Ceramic wear products have not been associated with limited longevity in the same way that metal ions and debris or UHMWPE debris has. Ceramic debris has however caused concerns after revision, acting as abrasives in the next implant leading to toxic levels of cobalt. The majority of debris generated from CrN, TiN, and DLC-coated implants in simulators were 30 to 50 nm in diameter, with a few larger shards, 50 to 200 nm in diameter.
2.3.2 Fretting

Fretting is a wear mechanism that occurs due to relative oscillating motion in the μm range between two surfaces. Part of the contact may deform elastically while another part may deform plastically. In a more elastic contact, the counter surfaces stick to one another, referred to as the ‘stick regime’. The stick regime is often associated with low damage levels but it may lead to fatigue in the long term. In a ‘gross-slip regime’ there is more sliding in the contact, and the wear and debris formation is more severe. Due to the short displacement, oxidised wear debris may be trapped in the contact and contribute to abrasive wear. With a high number of cycles, or motions between the components, the failure modes might first be found as cracking in the material and then as fretting fatigue. The fretting situation may be further challenged in a corrosive environment, especially in the taper junction.

2.4 Corrosion and dissolution

An implant’s biocompatibility will depend on the type and amount of wear and corrosion it is subjected to. These two processes can have a strong synergistic effect: the corrosion process may increase wear, and the wear process may increase corrosion. Even without the presence of wear, all metallic surfaces in the body will corrode to some extent. The process includes reactions from a higher energy state to a lower state, where a metal forms a metal oxide. It typically involves a transfer of electrons where an anodic reaction forms metal oxides (releasing electrons), and a reduction of oxygen or hydrogen at the cathode (uptake of electrons).

The corrosion process results in degradation of the material, for example, structural changes and the release of ions. This degradation may occur uniformly over the surface (general corrosion), in a shielded environment (crevice corrosion), or locally (pitting corrosion). In turn, the corrosion process can be affected by its geometry (e.g. for a crevice), the structures of the material’s surfaces (e.g. local defects may be starting points for pitting), mechanical stress (e.g. leading to cracks and reduced corrosion resistance), and the surrounding chemical environment (e.g. solution and temperature it is immersed in). Common biomedical alloys like CoCrMo and TiAlV have been selected for biomedical applications partly for their ability to form passivating surface oxides. These oxides can form spontaneously in air and thus protect the material from further corrosion. When a surface is worn, these oxides may be removed and thus expose the bulk alloy, which can increase both wear and corrosion; this will in turn lead to debris and ion release.

The point at which the anodic and cathodic reactions are in balance is called the open circuit potential (OCP). Measuring the OCP over time can describe changes in the anodic or cathode reactions in a semi-quantitative
way, as when surface oxides form or are removed. OCP is measured as the potential between the working electrode (the sample) and a reference electrode (commonly Ag/AgCl).

While the corrosion current \( (I_{\text{corr}}) \), which is the current at OCP, is a useful parameter for determining the corrosion rate, it cannot be measured directly. Rather, it needs to be estimated by forcing the electrochemical potential away from OCP and forcing the system out of balance. Potential changes in a small range (tens of mV) around OCP, along with recording the current, can help to determine the resistance to polarisation \((R_p)\); this is called a linear polarisation scan (LPR). \( I_{\text{corr}} \) can then be estimated by using the Stern-Geary equation: \( I_{\text{corr}} = \frac{(\beta_a \cdot \beta_c)}{(2.3 \cdot R_p (\beta_a + \beta_c))} \). The anodic and cathodic Tafel constants \((\beta_a \text{ and } \beta_c)\) can be determined from a Tafel plot, or simply estimated. Further, the mass loss due to oxidation can be projected by using Faraday’s law: \( m = \frac{(Q \cdot M)}{(F \cdot z)} \), where \( m \) is the mass loss of the corroded material, \( Q \) is the charge transfer, \( M \) is the atomic mass, \( F \) is the Faraday constant and \( z \) is the number of electrons in each anodic half-cell reaction. \( m \) and \( z \) can be set by assuming half-cell reactions on the corroded material, and \( Q \) by integrating the \( I_{\text{corr}} \). These are common electrochemical techniques, and calculations can be applied to further understand the materials’ corrosion evolution during tests.

### 2.5 Requirements for materials

A background to and current limitations of materials used in the articulating and taper contacts have been presented. To increase the longevity of total hip replacements through the use of new materials an increased performance is required. A list of requirements for the materials and their performance is presented in Table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
</tr>
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| Biocompatibility| non-toxic surface and bulk  
non-negative response to debris  
non-toxic corrosion products (ions) |
| Fracture toughness| high \( \rightarrow \) reduce chipping and risk of catastrophic failure |
| Wear resistance | high in sliding contacts (head/cup) \( \rightarrow \) reduce volume and number of wear debris and ions  
high in fretting contacts (taper) \( \rightarrow \) reduce wear-induced corrosion |
| Corrosion resistance | high \( \rightarrow \) reduce amount of ions released  
\( \rightarrow \) reduce corrosion-enhanced wear |
2.6 Silicon nitride and joint replacements

With the aim to accomplish the target profile described in Table 1, SiN coatings are evaluated.

2.6.1 Bulk silicon nitride

Commercial interest and early industrial adoption of Si$_3$N$_4$ started in the 1950s. Today the material has many uses in demanding applications such as high-speed ball bearings and turbine components. Properties such as low density, chemical stability, high fracture toughness, and high wear resistance, properties that are also valid at high temperatures, have been the main reasons for its use. As a biomaterial, Si$_3$N$_4$ was introduced in spinal fusion devices in 2006, and the first Si$_3$N$_4$ femoral heads were implanted in 2011.

The principal reason for using Si$_3$N$_4$ as a biomaterial is based on its biologically accepted elements. N is a natural component of the human body and Si ion release has been shown to contribute to osteoblast formation and to inhibit osteoclast activity. Studies on Si$_3$N$_4$ have shown no cytotoxicity, decreased bacteria activity compared to titanium and polyether ether ketone (PEEK), and no inhibited bone growth around an implant. Si$_3$N$_4$ nanoparticles have however, along with ZrO$_2$ nanoparticles, been found to activate osteoblast and macrophage-like cells. An additional point of assessment for bulk Si$_3$N$_4$ is the sintering aids used for the manufacturing of silicon nitride ceramics. In industry these are commonly yttria (Y$_2$O$_3$), alumina (Al$_2$O$_3$), or magnesia (MgO). An alternative in biomedical applications may be to select alternative biocompatible sintering aids, such as Ca or Sr.

Even if Si$_3$N$_4$ is often selected in industry for its inertness, slow dissolution still occurs. Si$_3$N$_4$ in water often dissolves through formation of silicon oxide on the surface ($\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{SiO}_2 + 4\text{NH}_3$). In a tribological water-lubricated contact, further reactions that form tribochemical layers (for example through $\text{SiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4$) can be beneficial, and can result in even lower friction and wear for Si$_3$N$_4$.

Silicon nitride tested in hip simulators has shown low wear rates, which gives a potential advantage for use in total hip replacements. In addition, particles of Si$_3$N$_4$ have also been shown to dissolve in water and phosphate-buffered saline solution (PBS). The dissolution of wear debris from a Si$_3$N$_4$ joint replacement could potentially reduce any negative biological responses related to the wear debris.
2.6.2 Silicon nitride coatings

SiN\textsubscript{x} and SiN\textsubscript{x}C\textsubscript{y} coatings have been produced by deposition techniques such as CVD and PECVD\textsuperscript{44-48}, direct current PVD and RF PVD\textsuperscript{49-51}, and HIPIMS\textsuperscript{52}. SiN\textsubscript{x} coatings are generally amorphous when deposited under normal deposition rates and temperatures (<800°C)\textsuperscript{29,51}. The majority of publications to date on SiN\textsubscript{x} and SiN\textsubscript{x}C\textsubscript{y} coatings have been produced for the field of semi-conductors. SiN\textsubscript{x} coatings have also been evaluated as a biomaterial for joint replacements\textsuperscript{49,50}, in parallel with the papers presented in this thesis.

The use of SiN\textsubscript{x} coatings may provide the same advantages as bulk Si\textsubscript{3}N\textsubscript{4} as already noted, but could also draw on the advantages of using the more ductile bulk material underneath.

2.6.3 Potential benefits with SiN\textsubscript{x} coatings in a total hip replacement

The potential benefits with using SiN\textsubscript{x} coatings are summarised in Table 2. An understanding and proof of possible advantages, or disadvantages, are still lacking. First, what is a good way to manufacture high-quality SiN\textsubscript{x} coatings? Can a SiN\textsubscript{x} coating have the same low wear rate as the bulk material? Can the coating act as a barrier and hinder metal ions from being released from the substrate? What does the wear debris look like? If the particles dissolve at an adequate rate will the dissolution of the coating then be an issue?

Table 2. Potential benefits with SiN\textsubscript{x} coatings.

<table>
<thead>
<tr>
<th>Benefit</th>
<th>Current proof</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good biocompatibility</td>
<td>non-toxic surface and bulk non-negative response to debris non-toxic ions for Si\textsubscript{3}N\textsubscript{4}\textsuperscript{33,35,36} nm Si\textsubscript{3}N\textsubscript{4} \textit{in vitro} cell activation\textsuperscript{37} for N (natural), and Si-ions\textsuperscript{32}</td>
</tr>
<tr>
<td>High fracture toughness</td>
<td>reduce risk of catastrophic failure due to ductile metal bulk -</td>
</tr>
<tr>
<td>High wear resistance</td>
<td>in sliding contacts (head/cup) in fretting contacts (taper) for Si\textsubscript{3}N\textsubscript{4} in simulator\textsuperscript{41} -</td>
</tr>
<tr>
<td>Dissolution of debris</td>
<td>reduce risk of inflammatory or toxic effects Si\textsubscript{3}N\textsubscript{4} particles dissolve in water\textsuperscript{38,39} and PBS\textsuperscript{36}</td>
</tr>
<tr>
<td>High corrosion resistance</td>
<td>increased coating lifetime -</td>
</tr>
<tr>
<td>Reduced metal ion release</td>
<td>coating prevents release of metal ions from the bulk -</td>
</tr>
</tbody>
</table>
3 Results and discussion

This section covers the work in studying and developing SiNₓ and SiCₓNy coatings for total hip joint replacement materials. On occasion, bulk Si₃N₄ and manufactured model Si₃N₄ particles are used instead of coatings, debris from coatings or as a reference. This is to understand the general potential of silicon nitride in the application, but also due to the easier access of these commercially available materials.

To evaluate the potential benefits of using SiNₓ coatings stated in Table 2, a high-quality coating needs to be developed. First, suitable deposition techniques and coating properties—such as structure, composition, hardness, and adhesion—are evaluated and described in Section 3.1; they are based on papers I, II, III, IV, and V. Second, the tribological properties, wear in a sliding contact, wear debris, and fretting corrosion are evaluated in Section 3.2; this material is based on papers I, III, IV, and VI. Finally, the corrosion and dissolution properties of the SiNₓ coatings and model SiNₓ particles without a tribological contact are evaluated in Section 3.3; this is based on papers IV, and V. An overview and descriptions of methods and analytical techniques used in this section can be found in the Appendix, while detailed settings and parameters can be found in the individual papers.

3.1 Coating deposition and coating properties

Papers: I, II, III, IV, and V. This section focuses on the following questions:

- Can high-quality SiNₓ and SiCₓNy coatings be deposited using RF-PVD or HiPIMS?
- How do the deposition parameters (target power, deposition temperature, and gas flow) affect the coating properties (structure, composition, hardness, and adhesion)?

3.1.1 Deposition parameters’ effects on structure and composition

SiNₓ and SiNₓCᵧ coatings were deposited using RF-PVD (paper I) and HiPIMS (paper II, III, IV, and V); the deposition parameters varied in the ranges
noted in Table 3. SiN\textsubscript{x}C\textsubscript{y} coatings were evaluated, along with the SiN\textsubscript{x} coatings, as density functional theory (DFT) calculations showed that even small amounts of substitutional C in the structure (<5 atomic %) could increase the surface’s reactivity, which in turn could increase the dissolution rate (paper I). Coatings were deposited on Si wafers to facilitate evaluation, and on cast or wrought CoCrMo. Coating thicknesses between 0.4 to and 8.0 μm were deposited.

### Table 3. Deposition techniques and parameter ranges.

<table>
<thead>
<tr>
<th>Deposition technique</th>
<th>Target power [W]</th>
<th>Deposition temp. [°C]</th>
<th>N/Ar flow ratio</th>
<th>C incorporation</th>
<th>Thickness [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF-PVD</td>
<td>150–300</td>
<td>25–280</td>
<td>0.5–3</td>
<td>ethylene gas (C\textsubscript{2}H\textsubscript{4})</td>
<td>0.6–1.7</td>
</tr>
<tr>
<td>HiPIMS</td>
<td>600–4,000</td>
<td>110–430</td>
<td>0.06–0.31</td>
<td>C target:</td>
<td>0.4–8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5–1.4 kW</td>
<td></td>
</tr>
</tbody>
</table>

For RF-PVD, two different target powers (150 W and 300 W) were applied; imaged cross-sections of the coatings using scanning electron microscopy (SEM) are shown in Figure 4a-c (paper I). At 300 W, the coatings had a columnar structure (Figure 4a). A lower power, 150 W, resulted in a finer columnar structure and a decreased deposition rate (Figure 4b). While a columnar microstructure was seen using a deposition temperature of 280°C, when deposited at 25°C a patch-like structure was seen. The patches resulted in a high average surface roughness (R<sub>a</sub>=250 nm, compared to 10 nm for the other coatings), which was likely due to the cyclic deposition process in combination with low mobility. The RF-PVD coatings with N/Ar gas flow ratios between 0.5 to 3 resulted in a high N/Si ratio, about 1.5 (±0.3), whereas stoichiometric Si\textsubscript{3}N\textsubscript{4} has a N/Si ratio of 1.33. The introduction of C\textsubscript{2}H\textsubscript{4} to incorporate C into the coating disrupted the columnar growth and formed a coarser structure (Figure 4c). Even if the C\textsubscript{2}H\textsubscript{4} gas disrupted the growth of the coating, no C increase was observed compared to the other coatings, which also had a small atomic % of C.

Deposition using HiPIMS and applying Si-target powers between 1,000 and 4,000 W, and deposition temperatures of 110°C or 430°C, resulted in a homogeneous and dense structure, as shown in Figure 4d (paper II). This dense structure, in turn, exhibited a low surface roughness. Even so, defects like droplets were observed on all coatings, although there were fewer for the lower target power (1,000 W) than the higher (4,000 W) target power. These coatings showed an N/Si atomic ratio of around 0.3 to 0.4. After further deposition development, N/Si atomic ratios between 0.3 and 1.1 were obtained (paper V). This was done by using a lower target power (600 W) and applying a N/Ar gas flow ratio between 0.06 and 0.31, in contrast to the ratio of 0.16, which was used for coatings in papers II, III, and IV. The incorporation of C in the HiPIMS process was made with the use of a C target, which required the use of rotation in the chamber for the samples to pass...
both the Si- and the C-targets. By using rotation and two target materials, the coating’s microstructure was altered. With a Si-target power of 1,000 W, and C-target power between 700 W and 1,400 W, a columnar structure was revealed (Figure 4e). The columnar structure resulted in a rougher surface, with a slightly lower surface roughness at the higher deposition temperature. When using a higher Si-target power of 4,000 W, and C-target powers between 500 W and 1,400 W, a dense and laminar microstructure emerged (Figure 4f). This dense, laminar microstructure resulted in a low surface roughness. At the higher deposition temperature (430°C), the surface roughness was as low as the SiNₓ coatings. With the use of the C-target the composition in these coatings could be tuned to between 6 and 35 atomic %.

Several SiNₓ and SiCₓNᵧ coatings were evaluated for their crystalline properties using grazing incidence x-ray diffraction (GI-XRD, papers I and II), and all were shown to be x-ray amorphous. One RF-PVD coating evaluated us-
ing transmission electron microscopy (TEM) and selected area electron dif-
fraction (SAED) showed a nanocrystalline structure (paper I), while one
HiPIMS coating showed an amorphous to nanocrystalline structure (paper II).

The bonding structure in the coatings, evaluated using x-ray photoelec-
tron spectroscopy (XPS), has mainly shown two types of bonds for Si2p:
either Si-N (for Si$_3$N$_4$) bonds (~101 eV\textsuperscript{52, 53}) or Si-Si (~99.5 eV\textsuperscript{54}). In paper II, coatings deposited at the target power of 4,000 W showed a larger propor-
tion of bindings around 99.5 eV assigned to Si-Si bonds. For coatings depos-
ited at 1,000 W, a large peak was seen around 101 eV assigned to Si-N
bonds. Different N/Ar gas flow ratios influence the Si bonding structure
(paper V). At flow ratios of 0.16 and 0.31, the dominant peak was around
101 eV, associated with Si-N bindings. For the flow ratio 0.06, the dominant
peak was seen at 99.6 eV, associated with Si-Si bonds. Both by varying the
Si target power and the N/Ar-flow ratio, the ratio between available Si and N
in the deposition chamber was shifted, which sometimes resulted in a change
in the bonding structure in the coating.

A homogeneous structure and a low surface roughness may reduce wear
and make the material more corrosion resistant. A coating with columnar
structure in general has a higher surface roughness compared to a homoge-
neous and dense coating (also shown in paper II). A rough articulating coa-
ting risks abrading its opposing surface, causing increased wear and debris,
and may need further processing. In addition, a columnar structure may be
less chemically and mechanically stable between the columns. When there is
poor cohesion between the columns, or poor cohesion between layers in the
coating, this can increase the wear rate (paper III). Because any region that
is different from its surroundings—such as spaces between columns, grain
boundaries, or other defects, such as droplets—may be a starting point for
corrosion, this can be a cause for concern. Pitting can slowly penetrate the
coating into the substrate, causing delamination\textsuperscript{15}. For this reason, a mini-
mum number of defects such as droplets are desired (also for dense coat-
ings), not only to reduce wear, but also to reduce the risk of localised corro-
sion. In the same manner, an amorphous or in theory a single crystalline
structure in the coating could be more resistant to localised corrosion. Even
so, there may be many differences between amorphous and crystalline struc-
tures. They may affect other mechanical or chemical properties such as wear
or dissolution, which will be further studied for the coatings in the coming
sections. Yet there is no known optimal composition or bonding structure for
these coatings. The knowledge of the bonding structure and chemical com-
position can, however, be used to interpret the mechanical, tribological, and
corrosion properties of the materials.
3.1.2 Hardness and adhesion

The SiNx coatings deposited using either RF-PVD or HiPIMS (papers I and III) showed nanohardnesses between 17 and 24 GPa. There was no apparent dependence on the deposition temperature for any coating, nor for Si-target power on the RF-PVD coatings. A trend of increased hardness was observed with decreased target power for HiPIMS SiNₓ coatings (from 17 to 21 GPa). Overall, the coating hardness of the SiCₓNᵧ coatings varied in a similar range as the SiNₓ coatings, i.e. between 14 to 20 GPa, with the exception of coatings with columnar structure (target power 1,000 W, deposited at 110°C). These coatings with columnar structure showed a significantly lower hardness of between 10 and 11 GPa. The lower hardness could either be related to easily deforming columns in the structure, or it is a measurement artefact as a consequence of the rough surface (see Figure 4e) in relation to the shallow indent (40 nm).

The adhesion was found to be a concern for the RF-PVD coatings (paper I). A scratch test was used to obtain an estimation of the coatings’ adhesion to the substrate. Several coatings showed such poor adhesion that they delaminated where the diamond tip first touched the surface, or even before testing. Only a small number of coatings could withstand any progressive load on the diamond tip, and all failed before a load of 10 N.

The HiPIMS coatings (deposited on Si wafers) were evaluated for their cohesive properties using a scratch test on the micro scale (paper III), with a finer tip and lower loads than in the above-mentioned scratch test. The SiNₓ coatings showed no obvious cohesive failures, but in some cases large chipping was noted and in other cases no failure for the evaluated loads was noted. The thinner SiCₓNᵧ coatings showed cohesive failure related to the microstructure; for the columnar structure (Figure 4e), cohesive failures were noted perpendicular to the surface, while for the laminar structure (Figure 4f), flaking parallel to the surface was noted.

The hardness presented for the SiNₓ and SiCₓNᵧ coatings in papers I and III were slightly lower than Si₃N₄ (24.5 GPa, paper III), and were in a similar range as coatings described in the literature. Pusch et al. reported hardnesses between 12 and 25 GPa for SiCₓNᵧ coatings deposited using different PVD techniques (DC, RF, and HiPIMS) ⁵². Taylor compared PE-CVD and CVD coatings with different N/Si ratios, showing hardnesses between 16 and 23 GPa, with increasing hardness with increasing N/Si ratio⁴⁷.

A higher hardness is not necessarily optimal for hip joint applications. The hardness needs to be balanced with elastic properties, and related to the tribological and biological system as a whole. Hardness, can however be used as a tool for interpreting the coating’s mechanical performance, and will be further discussed in Section 3.2.

Even if delamination of a coating would not be as catastrophic as a brittle fracture of a ceramic hip, due to the ductile metal substrate underneath, ad-
hesion is central for coatings in joint replacements. To adopt the use of SiN<sub>x</sub> or SiC<sub>x</sub>N<sub>y</sub> coatings in joint replacements, an adequate adhesion is required to withstand not only articulations, but also micro-separation (which may occur when the hip is flexed, as when rising from a chair or climbing high steps) and the impact forces applied during implantation and subsequent use. For the earlier papers (*I and III*), poor adhesion limited the mechanical testing, whereas by selecting better adhering coatings combined with further deposition optimisation in the latter papers (*IV and V*), further mechanical testing could be conducted. Future simulator studies, a natural next step in the development of SiN<sub>x</sub> coatings for hip replacements, should include micro-separation<sup>55</sup> to further elucidate whether adhesion could be an issue.

3.1.3 Concluding remarks on this section

SiN<sub>x</sub> coatings, amorphous to nanocrystalline, were deposited on CoCrMo using RF-PVD and HiPIMS with a N/Si atomic ratio ranging between 0.3 and 1.5. RF-PVD coatings had, in most cases, a columnar microstructure and insufficient adhesion. For HiPIMS coatings, the N/Si ratio and the proportion of Si-N bonds increased either by using a lower target power or by increasing the N/Ar gas flow ratio. The SiN<sub>x</sub> coatings had a homogenous and dense microstructure along with a low surface roughness. A trend of higher hardness and fewer defects in the coatings was seen for lower Si-target powers, along with chipping or no cohesive failure during scratch testing.

Although an attempt was made to manufacture SiC<sub>x</sub>N<sub>y</sub> coatings using RF-PVD, with the ethylene gas introduced during deposition, no elemental C increase was seen afterwards; in addition, one coating flaked off even before testing. The HiPIMS SiC<sub>x</sub>N<sub>y</sub> coatings resulted in either a columnar or lamellar microstructure, reflected in their cohesive failure in the scratch test. Mainly due to poor adhesion or problems with homogeneous incorporation of C, the RF-PVD coatings and the HiPIMS SiC<sub>x</sub>N<sub>y</sub> were evaluated for wear resistance but no further studies were performed.

The HiPIMS SiN<sub>x</sub> coatings showed a low surface roughness and a dense microstructure; these coatings were further evaluated in *papers III, IV, and V* with a focus on coatings deposited at low target power (≤1,000 W) due to fewer defects, higher N/Si ratio, and a higher proportion of Si-N bonds.

3.2 Wear and debris

Papers: I, III, IV, and VI. The following questions are addressed in this section:

- Can SiN<sub>x</sub> and SiC<sub>x</sub>N<sub>y</sub> coatings reduce the wear rate compared to CoCrMo in a sliding contact?
• What can be expected of the wear debris from SiN\textsubscript{x} coatings regarding the debris size and shape?
• How does Si\textsubscript{3}N\textsubscript{4} perform in a fretting corrosive contact with biomedical metal alloys?

3.2.1 Sliding wear

The materials to be used in an articulating surface, exposed to sliding wear (Figure 2), were replicated by the simplified geometry of a ball-on-disc. As a consequence of the selected geometry, the wear test was accelerated by a high contact pressure. The wear behaviour SiN\textsubscript{x} and SiC\textsubscript{y}N\textsubscript{x} coatings against a Si\textsubscript{3}N\textsubscript{4} ball were evaluated in a simulated body. Several RF-PVD SiN\textsubscript{x} and SiC\textsubscript{y}N\textsubscript{x} coatings (paper I) and HiPIMS SiC\textsubscript{y}N\textsubscript{x} coatings (paper III) could not be evaluated for wear resistance, as the coatings detached from the substrate before or during the wear test.

Those coatings with sufficient adhesion to endure the wear test showed specific wear rates similar to that of bulk Si\textsubscript{3}N\textsubscript{4} (1.0·10\textsuperscript{-7} mm\textsuperscript{3}/Nm). The RF-PVD coatings (paper I) showed wear rates between 2.7·10\textsuperscript{-7} mm\textsuperscript{3}/Nm and 3.2·10\textsuperscript{-7} mm\textsuperscript{3}/Nm, without any evident influence from the deposition parameters (target powers 150 or 300 W; process pressure 0.5 or 1.0 Pa; N/Ar ratios 1 or 3). The HiPIMS coatings (paper III) showed wear rates between 1.3·10\textsuperscript{-7} mm\textsuperscript{3}/Nm and 240·10\textsuperscript{-7} mm\textsuperscript{3}/Nm, with all coatings except one in the range between 1.3·10\textsuperscript{-7} mm\textsuperscript{3}/Nm and 4.8·10\textsuperscript{-7} mm\textsuperscript{3}/Nm. For the SiN\textsubscript{x} coatings there was a trend of lower wear rates for depositions with lower target power; this was also in line with the trend of higher hardness. All SiN\textsubscript{x} coatings, except one, showed lower wear rates than CoCrMo (60·10\textsuperscript{-7} mm\textsuperscript{3}/Nm).

A smoothing effect with few abrasive marks was seen in the wear tracks for SiN\textsubscript{x} coatings and Si\textsubscript{3}N\textsubscript{4}, while the softer CoCrMo was severely abraded, which caused high material loss. Sections of representative wear tracks are shown in Figure 5. The coefficient of friction was overall stable and entered a steady state after the running-in period. One coating (SiN\textsubscript{x} deposited at 4,000 W at 110°C, paper III) showed a friction increase in the start, in addition to a high wear rate, as mentioned previously in the paragraph.

An accelerated wear test was applied as a first step to evaluate if a wear rate similar to that of Si\textsubscript{3}N\textsubscript{4} and substantially lower than that of CoCrMo could be obtained from the SiN\textsubscript{x} coatings. This was shown to be the case. The study was limited to evaluating CoC and ceramic-on-metal (CoM), excluding common configurations such as MoP or CoP and with a contact pressure substantially higher than typical hip joint replacements. In papers I and III an initial maximal Hertzian contact pressure of 0.77 GPa for CoM and 0.86 GPa for CoC was used, compared to an implant where 0.09 GPa could be expected in the CoC case\textsuperscript{23}. With the higher contact pressure, the lubrication can be expected to be in the boundary lubrication regime (or the mixed regime), rather than the full film and mixed regimes often present in
CoC hip replacements\textsuperscript{56}. With this high contact pressure used, higher friction and wear than \textit{in vivo} can be expected. Even so, and along with difficulties comparing wear rates between setups, the levels of wear for the SiN\textsubscript{x} coatings were comparable to CrN-on-CrN (coatings) and CrCN-on-CrCN (coatings) but lower than TiN-on-TiN (coatings) or CoCrMo-on-CoCrMo\textsuperscript{26}.

Figure 5. Sections of representative wear tracks for SiN\textsubscript{x} coatings deposited using RF-PVD and HiPIMS along with the reference materials Si\textsubscript{3}N\textsubscript{4} and CoCrMo. The figures were obtained from vertical scanning interferometry (VSI). The squares are approximately 360 by 450 μm, with a strongly exaggerated thickness of 3 μm.

3.2.2 Wear debris

Wear debris from SiN\textsubscript{x} coatings was produced by wearing the coatings against an Al\textsubscript{2}O\textsubscript{3} ball in a simulated body fluid (paper IV). In this setup an initial contact pressure of 0.41 GPa was used. A coarse screening evaluation, semi-automatically determining the debris size, showed a size distribution between 0.08 and 3.2 μm, with a mean size of 0.44 (±0.50) μm. The evaluation was complemented by a high-resolution imaging with SEM and chemical evaluation, using energy-dispersive x-ray spectroscopy (EDS). The high-resolution imaging revealed that the coarser method mainly showed agglomerates. The high-resolution method showed agglomerates ranging between 0.15 and 2.0 μm with a mean size of 0.7 (±0.47) μm (Figure 6a and c). The round debris (in the agglomerates) ranged between 10 and 500 nm, with a mean size of 40 (±30) nm (Figure 6b and d). Chemical evaluation, using EDS, showed mainly O, C, and Si in the debris. No N signal was detected in most cases, which may be due to SiN\textsubscript{x} dissolving by first forming SiO\textsubscript{2} on
the surface (paper V), in combination with the difficulties in detecting light elements with EDS, especially in low amounts.

The biological reactions in the body depend on the concentration of debris and their size. A large amount of debris in the sub-μm to μm range has been shown to cause negative biological reactions leading to loosening of the implant. There is a risk that the cells interpret tightly bonded agglomerates as larger debris. This is likely only an issue if the wear rate is as high as for conventional UHMWPE, which there have been no indications of. The debris itself should be too small to trigger the negative macrophage activation and the subsequent loosening. Small debris has a large surface area, enabling a high chemical reactivity and solubility of the debris. Future cell studies using agglomerated SiNx debris are encouraged to improve the understanding of their biological impact.

![Figure 6. Wear debris from a SiNₓ coating produced in a ball-on-disc test. Showing an agglomerate of debris in a) and to distinguish individual particles the agglomerate in higher resolution in b). The sizes of the agglomerates are summarized in c) and the size of the debris in d).](image)

### 3.2.3 Fretting corrosion

The potential of reducing the risk of fretting corrosion by the use of Si₃N₄ in modular taper junctions (Figure 2) was evaluated in paper VI. In a simplified reciprocating geometry, a Si₃N₄ ball (representing the femoral head) was run
against the commonly used biomedical alloys CoCrMo, TiAlV and against a Si3N4 disc. The test was performed at 37°C in a simulated body fluid with the same initial contact pressure of 1 GPa for all material combinations. During the test OCP and LPR was monitored to evaluate the fretting-corrosion.

Short fretting displacements (relative motions of 10 μm) between the Si3N4 ball and CoCrMo or TiAlV kept the system in the stick regime, characterised by low wear (Figure 7), no wear-induced depassivation, and a contact dominated by elastic deformation. For Si3N4-on-Si3N4 the stick regime prevailed at both 10 μm and 25 μm displacement. However, the wear was too low to be determined with the technique used. For TiAlV, also increased displacements (25 and 50 μm) occurred in the stick regime. Despite this, a higher wear volume and wear-induced depassivation was seen at 50 μm.

CoCrMo entered the gross-slip regime at 25 μm displacement, with an increased proportion of sliding in the contact, but still showed a low wear volume. At further increased displacement (50 μm), sliding was dominant in the contact, resulting in wear-induced depassivation and several times higher volume loss due to wear and corrosion. The highest wear volume was seen for Si3N4-on-Si3N4 at the longest displacement (50 μm) in the gross-slip regime.

The volume loss caused by oxidation for CoCrMo, calculated from LPR scans and I_{corr}, followed the wear volume trend for the metal plate (Figure 7). At short displacements TiAlV showed a high volume loss caused by oxidation and a low wear volume, while at long displacements a lower volume loss caused by oxidation was seen, along with higher wear volume.
On the outermost surface (in the order of nm) outside the wear scar, a thin biofilm, containing N, O, and C, had formed by adsorption from the solution. Below this adsorbed layer, metal oxides that commonly form in ambient air were observed. Cr-oxides/hydroxides were detected on CoCrMo, and TiO₂ and small amounts of Al₂O₃ on TiAlV. Schematic drawings of the adsorbed biofilms, tribofilms, and oxide films are shown in Figure 8a and b.

![Schematic drawings of CoCrMo and TiAlV](image)

**Figure 8. Schematic drawings and actual appearance (SEM) of the various films formed on CoCrMo and TiAlV in the fretting corrosion tests. Left column shows CoCrMo, and the right column TiAlV.**

In the fretted wear scar on CoCrMo, a tribofilm containing Cr-oxides and transferred Si had formed in patches, for all displacements, see Figure 8c. Although patches of tribofilm formed on the Si₃N₄ ball at the shorter displacements (10 and 25 μm), they did not form at the longer (50 μm), where higher wear was observed.

For TiAlV, a shift of wear mechanism could be distinguished when increasing the displacement from 25 μm to 50 μm. At the shorter displacements (10 and 25 μm), a tribofilm containing TiO₂ and transferred Si formed in the contact. The formation of this oxidised tribofilm may be the reason the high ‘volume loss’ due to corrosion (Figure 7). The tribofilm patches had a thickness in the sub-μm to μm range, and were several μm long and wide, as shown in Figure 8d. This can be compared to a retrieval study of failed stem-neck junctions, where a mixed titanium oxide tribofilm was observed to be ~20 μm thick. In the retrieval study, the formation of the tribofilm and oxygen reduction was hypothesised to have caused a pH of 2 to 3 in the contact, leading to an even more severe corrosive environment. At the longer displacement (50 μm), as more sliding occurred, no tribofilm formed. The
Si$_3$N$_4$ ball also showed a tribofilm build-up, which increased in area and thickness with displacement (10 to 50 $\mu$m).

Compared to MoM contacts investigated under the same conditions in a parallel study$^{61}$, the CoM contacts investigated in paper VI showed lower corrosion currents, which may reduce the risk of taper failures caused by crevice corrosion. The wear volume for CoCrMo-on-TiAlV was similar to that of the combination Si$_3$N$_4$-on-TiAlV, whereas CoCrMo-on-CoCrMo had more than twice as high a wear volume as the material combination of Si$_3$N$_4$-on-CoCrMo.

3.2.4 Concluding remarks on this section

In an accelerated sliding wear test, SiN$_x$ coatings, deposited both by RF-PVD and HiPIMS, showed low wear, similar to that of Si$_3$N$_4$ and up to 46 times lower than the CoCrMo reference. HiPIMS SiN$_x$ coatings showed a trend of higher wear resistance at lower target power (along with a trend of higher hardness and increased proportion of Si-N bond). Several coatings could not be evaluated for their wear resistance due to insufficient adhesion. SiC$_x$N$_y$ coatings deposited with HiPIMS were excluded from further evaluation, as they either failed during the wear test or showed a wear rate higher than that of CoCrMo.

Further, wear debris originating from HiPIMS SiN$_x$ coatings were round and in the nm range, and formed agglomerates in the sub-$\mu$m range. Nanometre-sized debris may be an advantage in joint replacements, as small debris does not generally trigger macrophage activity to the same extent as particles in the sub-$\mu$m to $\mu$m range do. The biological response to these particles however needs to be evaluated, as well as whether agglomeration has an effect on the outcome.

Under the same initial contact pressure, the fretting corrosion behaviour varied between Si$_3$N$_4$-on-CoCrMo, Si$_3$N$_4$-on-TiAlV, and Si$_3$N$_4$-on-Si$_3$N$_4$. Si$_3$N$_4$-on-CoCrMo entered the gross-slip regime already at 25 $\mu$m displacement, where depassivation was seen, and the wear rate and oxidation volume loss increased at the longest displacement. Si$_3$N$_4$-on-TiAlV stayed in the stick regime at all displacements investigated. At the shorter displacements a patch-like tribofilm was seen, believed to cause a high oxidation volume loss (corrosion current). This effect needs to be further evaluated, along with pH and ion release, to understand if the oxidation may have an effect the biocompatibility. Si$_3$N$_4$-on-Si$_3$N$_4$ is more inert than the alternative metals and showed a wear rate too low to quantify at short displacements, however it showed a considerable increase in the wear volume in the gross-slip regime.
3.3 Corrosion and dissolution properties

Papers: IV, V, and VI. The following questions are addressed in this section:

- Can SiNx particles dissolve in simulated body fluid, and if so, how fast?
- How fast do SiNx coatings dissolve?
- Can a SiNx coating reduce the metal ion release?

3.3.1 Particle dissolution

If wear debris dissolves in the body, releasing no adverse elements and ions, it may reduce the negative biological response as well as reduce the risk of acting as abrasive particles, and thus increase the longevity of joint replacements. Due to the difficulty in generating large amounts of SiNx wear debris, model particles were evaluated in the dissolution studies in paper IV. The model particles used (Figure 9) were selected due to their similarity to the wear debris generated from the SiNx coatings shown in Figure 6 (paper IV). The model particles were amorphous, round in shape, and less than 50 nm in diameter, and they appeared in agglomerates.

The model SiNx particles were shown to dissolve in a simulated body fluid. The Si concentration in the solution was determined over 30 days combining inductively coupled plasma mass spectroscopy (ICP-MS) and ICP atomic emission spectroscopy (ICP-AES, Figure 9). The dissolution rates were fitted according to Zhmud and Bergström’s equation\(^{43}\), \(c(t) = c_s \cdot [1 - \exp(-kt)]\), where \(c(t)\) is the dissolved concentration as a function of time, \(c_s\) is the saturation concentration, and \(k\) is the dissolution rate constant. The best fit parameters were: \(c_s=39.44\ \text{mg/l}\), \(k=1.11 \cdot 10^{-6} \ \text{s}^{-1}\) (\(R^2 = 0.992\)).

![Figure 9. SEM image of model SiNx particles used in the dissolution study in a), and the dissolution rate of Si over 30 days in a simulated body fluid in b).](image)
The dissolution of Si₃N₄ particles in water studied by Zhmud and Bergström⁴³ at room temperature (RT) showed a lower dissolution rate, probably due to the larger particles used in their study. The dissolution rate in another study, by Laarz et al.⁴², showed higher dissolution rates, although a too-high particle concentration was used, as saturation was reached in less than five days.

The concentration of Si after 30 days was 38.8 mg/l of Si, corresponding to 64.6 mg/l Si₃N₄. In paper IV it was estimated that 2.58 mg or 65% of stoichiometric SiNₓ particles (as Si₃N₄) had dissolved after 30 days. A CoCr implant in hip simulators typically generates 0.04 mm³/year⁶². Assuming the same wear rate for a Si₃N₄-on-Si₃N₄ contact and the density 3.2 g/cm³⁵¹, it would result in a wear volume of 0.13 mg/year. Furthermore, if we assume that a hip joint capsule contains 4 ml of synovial fluid⁶³,⁶⁴, and that if it is naturally exchanged every week (probably an underestimation of the exchange rate for a healthy hip joint), 0.21 l of fluid would pass through a hip joint in a year. The dissolution rate appears to be higher than the wear rate, and has the potential to reduce possible negative biological responses.

### 3.3.2 Coating dissolution

Even though a high dissolution rate may be advantageous for the debris, a low dissolution rate is desired for a long lasting coating. The dissolution rate of SiNₓ coatings without mechanical loading was evaluated in paper V, using a holder designed specifically for the purpose. The holder enabled evaluation of OCP and LPR over time, tested on several areas on a coated sample simultaneously. A holder is displayed in Figure 10.

![Figure 10. Holder used for dissolution tests of SiNₓ coatings and CoCrMo. A top view of the top and bottom ends of the holder is shown in a) and a side view in b) of an assembled holder without solution. The working electrode (WE), the reference electrodes (RE) and the counter electrodes (CE) are marked in the figure.](image)

The dissolution rate of the coating was evaluated using three different methods, first by evaluating the corrosion current throughout the test and calculating the oxidation mass loss, then by post-analysis determining the step height on the edge of the dissolution area using VSI, and finally by evaluat-
ing the Co, Cr, and Mo ions in the solution using ICP-MS. Four types of coatings were evaluated; one of them, called SiN$_{0.8\text{(std)}}$, based on previous studies, had an N/Si atomic ratio of 0.8. The other three coatings, after further deposition development, were evaluated due to the difference in their nitrogen content: SiN$_{0.3}$, SiN$_{0.8}$, and SiN$_{1.1}$.

The dissolution rate for the SiN$_{0.8\text{(std)}}$ coating was initially slower, around 0.3 nm/day at the third day, to later stabilise around 0.5 nm/day (Figure 11a) evaluated using the corrosion current, and around 1.2 nm/day evaluated using VSI. The dissolution rate decreased with an increased N/Si ratio, from between 0.4 and 1.2 nm/day for SiN$_{0.3}$, to between 0.2 and 0.4 nm/day for SiN$_{1.1}$, see Figure 11b. CoCrMo had a dissolution (corrosion) rate in a similar range as some of the coatings, between 0.7 and 1.2 nm/day.

The SiN$_x$ coatings showed a lower average $I_{\text{corr}}$ and charge (Q) passing through the samples than CoCrMo, where SiN$_{1.1}$ showed the lowest values of the coatings, with average values of OCP at -0.27, $I_{\text{corr}}$ at 4 nA, and Q at 0.2 mC per day. ICP-MS analysis after three weeks of testing showed that SiN$_x$ coatings on CoCrMo reduced the release of Co, Cr, and Mo ions into the solution by two orders of magnitude, from $\sim$10 μg for a CoCrMo to $\sim$0.1 μg for a SiN$_x$-coated CoCrMo substrate.

![Figure 11](image.png)

**Figure 11.** The dissolution rate over time in a), and the effect of N/Si atomic ratio in the coating on the dissolution rate compared to CoCrMo in b), determined using the corrosion current ($I_{\text{corr}}$), the step height on the edge of the dissolution area using VSI, and using ICP-MS for determining the concentration of the ions Co, Cr, and Mo.

The SiN$_x$ coatings with $x \leq 0.8$ showed Si-N and Si-Si bonds in the bulk, and formation of Si-O bonds on the general surface and on the surface that had been in contact with the solution. The SiN$_{1.1}$ coating, which contained more nitrogen, contained a higher proportion of the more stable Si-N bonds, and not such evident formation of Si-O bonds on the surface; this is assumed to be correlated to the lower dissolution rate of this coating. A schematic sketch
of the structure and dissolution of SiN\textsubscript{x} coatings and CoCrMo is displayed in Figure 12.

Similar dissolution rates as those shown in this study have been found in animal studies for CVD silicon nitride coatings, with dissolution rates between 0.33 and 2.0 nm/day\textsuperscript{46}, or <0.56 nm/day\textsuperscript{65}. Assuming a constant and homogeneous dissolution rate of 0.4 nm/day, no wear, and a 7.5 μm-thick coating, it would take more than 50 years for the coating to fully dissolve. Although a suitable dissolution rate of the coating will depend on the wear rate and the time of implantation, this investigation shows that the dissolution rate can be tuned, with the N/Ar flow ratio as an important parameter, and the low dissolution rates of between 0.2 and 0.4 nm/day obtained for SiN\textsubscript{1.1} are promising.

![Figure 12. Schematic sketch of the elemental bonding structure in the bulk and on the surface of a coated SiN\textsubscript{0.8(std)}-coated CoCrMo substrate in a), and an uncoated CoCrMo plate in b) in air and in contact with a simulated body solution with the elements of the adsorbed biofilm and the ions released into the solution.](image)

### 3.3.3 Concluding remarks on this section

Model SiN\textsubscript{x} particles, round and with a size of 20 to 50 nm, were shown to dissolve in a simulated body fluid of 25 vol. % serum. The dissolution rate obtained was higher than the estimated wear rate in a Si\textsubscript{3}N\textsubscript{4}-on-Si\textsubscript{3}N\textsubscript{4} hip joint.

The dissolution rate of the SiN\textsubscript{x} coatings decreased with a higher N/Si ratio: the lowest rate was obtained for the N/Si ratio 1.1 with 0.2 to 0.4 nm/day. The lower dissolution rate is believed to be related to the higher proportion of the stronger Si-N bonds, compared to Si-Si seen at higher proportion for the coatings with a lower N/Si ratio. Uncoated CoCrMo had a dissolution rate between 0.7 and 1.2 nm/day, in line with the faster dissolving coatings and higher than the slowest dissolving.
4 The goal, achievements and future work

4.1. Goal

The general goal of this thesis has been to contribute to the development of new materials for joint replacements through improved properties with respect to wear rate, corrosion rate, and biocompatibility. To achieve this, the possibility of introducing SiN\textsubscript{x} coatings for the bearing surfaces and the taper of joint replacements has been investigated. This selection was based on initial hypotheses (summarized in Table 2) that such coatings could offer a beneficial combination of general biocompatibility, good fracture toughness, low wear rates, reduced metal ion release, low coating corrosion rate, and few and small wear particles that can dissolve, hence avoiding a negative biological response.

The work has focused on proving some of these early hypotheses of possible advantages or disadvantages of SiN\textsubscript{x} coatings and bulk Si\textsubscript{3}N\textsubscript{4}. Being early-stage material development, several test methods were simplified in order to clearly distinguish specific properties and to make it possible to test such wide-ranging hypotheses.

4.2. Achievements

The major achievements towards the general goal can be summarized as below (with reference to the relevant papers).

**Deposition of high-quality SiN\textsubscript{x} coatings \rightarrow HiPIMS**

- SiN\textsubscript{x} and SiC\textsubscript{y}N\textsubscript{y} coatings, amorphous to nanocrystalline, were deposited using RF-PVD or HiPIMS. Out of the evaluated coatings, the highest-quality coating was a SiN\textsubscript{x} coating deposited using HiPIMS with a Si-target power of 1 kW, showing a dense and homogeneous microstructure, few defects, low surface roughness, no cohesive failure during scratch testing, higher N/Si ratio, and higher proportion of Si-N bonds (and less Si-Si). *(Papers I, II, and III)*

**Wear resistance \rightarrow up to 46 times lower than CoCrMo**

- A reduced wear rate of up to 46 times compared to CoCrMo was displayed from several RF-PVD and HiPIMS SiN\textsubscript{x} and SiC\textsubscript{y}N\textsubscript{y} coatings,
tested in a sliding ball-on-disc contact against Si$_3$N$_4$ in a simulated body fluid.  
(Papers I and III)

**Wear debris size and shape**  \(\rightarrow \approx 40\) nm, round
- Wear debris from SiN$_x$ coatings was round, with a mean size of 40 nm, ranging between 10 nm and 500 nm. The debris tended to form agglomerates between 0.15 \(\mu\)m and 2.0 \(\mu\)m in size.  
(Paper IV)

**Fretting-corrosion resistance**  \(\rightarrow\) decreased corrosion and wear
- The corrosion current in a fretting corrosive environment was lower for CoM compared to MoM. A lower wear rate was also seen for CoCrMo plates in the CoM contact compared to MoM, although there was no difference for TiAlV discs. The Si$_3$N$_4$-on-Si$_3$N$_4$ contact was advantageous for the shortest displacements due to its inerntness and low wear, although in the gross-slip regime the wear rate was substantially higher.  
(Paper VI)

**Particle dissolution rate**  \(\rightarrow c(t) = 39.44[1-exp(-1.11 \cdot 10^{-6} \cdot t)]\)
- Model SiN$_x$ particles, 20 to 50 nm in diameter, dissolved in simulated body fluid. The dissolution rate of Si, analysed using ICP techniques, can be described as:  
\[c(t) = 39.44[1-exp (-1.11 \cdot 10^{-6} \cdot t)]\], with the dissolution concentration given in mg/l and the time in s.  
(Paper IV)

**Coating dissolution rate**  \(\rightarrow 0.2\text{-}0.4\) nm/day
- The dissolution rate of SiN$_x$ coatings was lower for higher N/Si ratios. For SiN$_{1.1}$ two different techniques gave a dissolution rate of 0.2 and 0.4 nm/day, which was lower than what was observed for the CoCrMo with a dissolution rates between 0.7 and 1.2 nm/day.  
(Paper V)

**Metal ion release**  \(\rightarrow\) reduced by two orders of magnitude
- SiN$_x$ coatings deposited on CoCrMo gave a two orders of magnitude lower Co, Cr, and Mo ion concentration in the solution than uncoated CoCrMo.  
(Paper V)

4.3. Future work
In order to reach the main goal of introducing a SiN$_x$ coating as an alternative material in joint replacements, a number of challenges remain. The natural progression is to confirm the wear rate, debris characteristics, dissolution and corrosion of the SiN$_x$ coatings in simulator studies, along with an evaluation of its biocompatibility in *in vitro* and *in vivo* studies. The results in this thesis should be a useful tool in designing and assessing such studies.
Verify hypotheses in hip simulators

- Si₃N₄ and SiNx coatings should be further evaluated under conditions closer to their application. Hip simulator studies on SiNx coated implant components, both for the bearing surface and the modular taper junctions, should be performed for wear rate, dissolution rate, wear debris, and ion release.

- When introducing coatings to joint replacements, their adhesive properties are central and should be investigated under conditions closer to their application. In order to evaluate if the adhesion is adequate for the application, simulator studies could include micro-separation.

- As the N/Ar ratio has been shown to affect the dissolution rate, this variable would be of interest to evaluate further.

Biocompatibility of coatings, wear debris, and ion release

- Further, it is important to complement the current literature on the biocompatibility of Si₃N₄ with the in vitro and in vivo biocompatibility of SiNx coatings, ion release, and debris. An evaluation of biocompatibility was not part of the scope of this thesis, it is however central to a successful introduction of SiNx to total joint replacements.
Summary in Swedish – Kiselnitrid i höftproteser

Höftproteser har sedan 1950-talet gett många patienter en möjlighet till ökad rörlighet och livskvalitet. Idag anses detta ortopediska ingrepp vara ett av de mest lyckade. Efter 10 år är protesöverlevnaden, dvs. de proteser som inte omopererats, 97.8% för primära proteser i Sverige. Tyvärr minskar protesöverlevnaden i längre tidsperspektiv, delvis på grund av att kroppen reagerar negativt på nötningsprodukter som partiklar och joner som bildas från proteserna.

En typisk höftprotes har en stam som fästs i lärbenet. Högst på stammen sitter en kon på vilken det i sin tur fästs en kula, se Figur 13. På höftbenet ersätts den naturliga ledytan med en kopp. Kulan, typiskt en metalllegering som koboltkrommolybden (CoCrMo) eller en keram som aluminiumoxid, glider mot koppen, som utgörs av en till hög grad tvärbunden polyeten (UHMWPE), CoCrMo eller en keram. Nötningspartiklarna från UHMWPE förmodas ha varit en av huvudsakerna till s.k. aseptisk lossning, vilket är en av de vanligaste anledningarna till omoperation. En annan begränsning är de nötningspartiklar och joner som CoCrMo avger, vilka kan leda till höga koncentrationer av metalljoner i blodet, metallos, och pseudotumörer. Denna avhandling undersöker kiselnitrid som ett potentiellt material för att förlänga protesöverlevnaden för höftproteser. Kiselnitrid undersöks primärt som en beläggning för kulan av CoCrMo eller i den koniska kontakten där kulan passas. Möjliga fördelar med kiselnitrid som potentiellt kan öka protesöverlevnaden är minskat utsläpp av metalljoner i kroppen, långsam nötning, samt att de nötningspartiklar som ändå bildas kan lösas upp, vilket skulle hindra inflammation och efterföljande aseptisk lossning.

Undersökningarna började med att optimera beläggningsmetoder för att framställa kompaka och slätta kiselnitridbeläggningar innehållande varierande mängder kväve. Utvalda beläggningar undersöks för sitt nötningsmotstånd. Nötningsstaken för dessa beläggningar visade sig kunna reduceras upp till 46 gånger i jämförelse med CoCrMo, och liknade den för solid kiselnitrid. De nötningspartiklar som genererades från beläggningarna var runda med en medeldiameter på 40 nm, med en spridning mellan 10 och 500 nm. För att sätta detta i perspektiv, om protesens kula (28 mm i diameter) var lika stor som arenan Globen i Stockholm, skulle en beläggning (7.5 μm)
vara 3 cm tjock och en partikel (40 nm) vore med sina 0.16 mm i diameter nätt och jämnt synbart för ögat.

Modellpartiklar med samma form och storlek som nötningspartiklarna, löstes upp i simulerad ledvätska, i en takt som var högre än den uppskattade nötningstakten. Kombinationen av de riktigt små nötningspartiklarna och deras relativt höga löslighet skulle kunna minska risken för negativa reaktioner i kroppen, vilket skulle öka implantatöverlevnaden jämfört med idag.


Då dessa partiklar löser upp sig är det även intressant att veta i vilken takt själva beläggningen löser upp sig. Detta visade sig bero på hur hög halt kväve som finns i beläggningen, den högsta halten (N/Si=1.1) visade den lägsta upplösningstakten (0.2 till 0.4 nm/dag). Med denna takt (0.4 nm/dag) och en 7.5 μm tjock beläggning skulle det hypotetiskt ta mer än 50 år för beläggningen att lösa upp sig om den inte utsätts för nötning. Under samma förhållanden löstes CoCrMo i en takt av 0.7 till 1.2 nm/dag. Dessutom bekräftades hypotesen om minskat jonutsläpp; att täcka CoCrMo-metallen med den keramiska kiselnitriderbeläggningen minskade frigörandet av metalljoner (Co, Cr och Mo) till mindre än en hundradel. Möjligheten att använda beläggningen i konkontakten undersöktes med hjälp av solid kiselnitrider. Det visade sig att korrosionsströmmen var lägre när kiselnitrider användes än för de vanliga metalliska legeringar som används idag. Detta kan eventuellt
minska risken för frigörande av metalljoner från kontakten och därmed kroppens negativa reaktioner på dessa.

Denna avhandling har bekräftat flera hypoteser om vilka fördelar och eventuella nackdelar kiselnitrid kan ha i höftproteser. De lovande resultaten uppmuntrar till fortsatta och mer applikationsnära studier, för att på sikt kunna ge patienter möjlighet till bättre material i sina höfter.
Acknowledgements

First, I would like to acknowledge the work my supervisors have done with and for me:

Cecilia, for the hard work, your enthusiasm, and for lifting everything to the next level. I have really enjoyed working more closely with you over the last year.

Staffan, for showing me a new way of thinking and the intriguing world of tribology. I am grateful that your door is always open and for your ability to ask the right questions, and for holding back with the right answers.

Håkan, for showing the bigger picture and for the unlimited trust that you put in us, which has let me grow.

Johanna O and Charlotte, I have enjoyed all the discussions and work we have done together. Mike, Anne, Abi, Chun, thank you for making my stay at the University of Leeds both productive and fun. Thanks also to all other collaborators at universities around the world contributing to the research, from UU, LiU, KTH, Leeds and McMasters. Sara, Bagge, Janne, Fredrik, and Ingrid, thank you for being experts in your field and for doing it in an enjoyable way.

To all my present and former colleagues in Tribo and MiM, thank you for all the discussions, the company in the labs, the travel companionship, and for making these years very enjoyable. Thank you all in applied materials science for fikas and lunches that have taught me so much more than research. Also, Merlin and Mombasa, thank you for the fun times. A special thanks to Janna: you have given me great scientific advice, support as a friend, and much laughter. I wish I could bring you with me to my next office.

Thanks to MS²E and to Life Long Joints for the financial support to conduct this research. Thanks to Nationella Forskarskolan i Tribologi, stiftelsen Axel Hultgrens fond, Anna Maria Lundins stipendienämnd, GradAM, and Innovationsstyrelsen for the scholarships that allowed me to experience an exchange, courses, and conferences, and allowed me to learn how to kitesurf.

Appendix: Methods and analytical techniques

This appendix gives a brief description of the most frequently used techniques and analyses in the thesis. Further details on the experiments and analyses can be found in the individual papers.

Solutions and solution analysis
Synovial joint fluid was simulated in the tests by 25 vol.% fetal bovine serum (FBS) in water. The addition of 20 mM of ethylenediaminetetraacetic acid (EDTA) is added to reduce the precipitation of calcium phosphate on the surface. The addition of 0.2 to 0.3 % sodium azide (SA) can be used as an antibacterial agent. This recipe is based on ASTM International (formerly the American Society for Testing and Materials) standard F 732-00. When investigating the corrosive and degradation process, in the studies that included electrochemical evaluation, the salt solution phosphate buffered saline (PBS) solution was used instead of water to ensure that the ion concentration was closer to that of the biological environment. The solutions used in each paper are summarised in Table 4.

The dissolution of Si, Co, Cr, and Mo into the solution was evaluated using inductively coupled plasma–mass spectrometry (ICP-MS) and inductively coupled plasma–atomic emission spectrometry (ICP-AES). In ICP-AES, an ICP is produced to excite electrons to a higher energy state; as decay occurs, a photon with a characteristic energy for the element is emitted and monitored. The use of ICP-MS quantifies concentrations by a mass spectrometer, separating isotopes based on their mass-to-charge ratio. ICP-MS has a higher sensitivity, but is less accurate at high concentrations compared to ICP-AES.

Structural and chemical analysis
The surface appearance, roughness, wear, and dissolution volumes were evaluated using vertical scanning interferometry (VSI), which is an optical technique that evaluates the difference in light from the sample surface and compares it to light hitting a reference mirror. The light is then combined, and the path difference gives the interference. By scanning the z-axis, a reso-
olution down to the nm range may be obtained, while the lateral resolution is the same as with an optical microscope, limited by the wavelength of light (sub-μm range).

The hardness and elastic moduli of the coatings was evaluated using nanoindentation. A diamond tip was used to make an indent on the surface and the indent depth and force were continuously measured during loading and unloading. The hardness was determined, and the elastic modulus calculated (assuming a Poisson’s ratio) by a method developed by Oliver and Pharr. Nanoindentation enables surface-sensitive evaluation, so the hardness of the coating without contributions from the substrate can be evaluated.

Crystalline phases can be evaluated using x-ray diffraction (XRD), where an incoming x-ray hits the surface, and depending on the distance between the ordered atoms (lattice planes), the outgoing beam will be diffracted to different angles. For a material with short-range ordering or a fully amorphous structure, it will not give the increased intensity at specific angles. To obtain information closer to the surface, such as for coatings, a low angle of incoming x-rays can be used; this technique is called grazing incidence XRD (GI-XRD).

Scanning electron microscopy (SEM) is an imaging technique that scans the surface with electrons and records how the emitted electrons have interacted with the surface. Depending on the energy of the incoming electrons and the detection of the emitted electrons, elemental and topological information from both the surface and subsurface (sub-μm to μm) can be obtained.

For even higher resolution imaging, down to the level of atoms, transmission electron microscopy (TEM) may be used. An electron-transparent sample is used, requiring thin samples (typically <100 nm) and more advanced sample preparation. Due to the high-resolution, TEM can give information on the atomic ordering and on the level of crystallinity in a sample with imaging or selected area electron diffraction (SAED).

Both SEM and TEM can use integrated energy-dispersive x-ray spectroscopy (EDS or EDX), allowing elemental analysis. As incoming electrons may excite an electron in the material analysed, an electron from a higher energy may decay, emitting a characteristic x-ray from the element and electron shell.

Chemical composition and bonding structures can be determined by x-ray photoelectron spectroscopy (XPS), also commonly referred to as electron spectroscopy for chemical analysis (ESCA). The sample is irradiated with x-rays to excite photoelectrons, with characteristic kinetic energy related to its composition and its binding energy to neighbouring elements. The photo electrons have a low energy and can only excite the top few nanometres of the sample, resulting in a surface-sensitive technique. In order to evaluate the chemistry deeper within the sample, the area can be sputter cleaned by bom-
bonding it with Ar ions. The last four analytical methods described—SEM, TEM, EDS, and XPS—are all run under vacuum.

Tribological evaluation

The following is an overview of the tribological experimental setups used for papers I, III, IV, and VI. The parameters used were adopted for the applications, with sliding wear replicating the motion between the femoral head and the cup; for generating wear debris, a lower contact pressure but higher speed was used; and for the fretting corrosion experiments replicating the taper connection, higher loads and shorter displacements were used.

Table 4. A summary of the test parameters, with the solutions and temperatures used during the test, the calculated initial Herzen contact pressure; and the tribological setup, including the motion, speed or frequency, radius (r) or length of the wear track, and the number of cycles.

<table>
<thead>
<tr>
<th></th>
<th>Sliding wear</th>
<th>Wear debris</th>
<th>Fretting corrosion</th>
<th>Dissolution particles</th>
<th>Dissolution coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution</td>
<td>25 vol.% FBS (EDTA, SA)</td>
<td>25 vol.% FBS (EDTA, SA)</td>
<td>25 vol.% FBS in PBS (SA)</td>
<td>25 vol.% FBS (EDTA, SA)</td>
<td>25 vol.% FBS in PBS (SA)</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>RT</td>
<td>37</td>
<td>37</td>
<td>37</td>
<td>37</td>
</tr>
<tr>
<td>Contact pressure [GPa]</td>
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<td>CoC: 0.41</td>
<td>1</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Motion</td>
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<td>reciprocating</td>
<td>reciprocating</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Speed/freq.</td>
<td>0.04 m/s</td>
<td>3 Hz</td>
<td>1 Hz</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Wear track</td>
<td>2.5 mm (r)</td>
<td>10 mm</td>
<td>10; 25; 50 μm</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Cycles</td>
<td>10,000</td>
<td>21,600</td>
<td>6,000</td>
<td>n/a</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Electrochemical evaluation

To evaluate the electrochemical process of a material, such as the open circuit potential (OCP), the sample was connected as a working electrode to a potentiostat. The potential was recorded in relation to a reference electrode (commonly Ag/AgCl) that was inserted close to the sample in the solution. In order to perform linear polarisation scans (as a current is expected to flow), a third electrode—a counter electrode—was needed. The counter electrode then acted as a cathode if the working electrode worked as an anode, and vice versa. Often the counter electrode is integrated in the reference electrode.
References


A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)