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Structure and composition of silicon nitride and silicon carbon nitride coatings for joint replacements

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Abstract

SiN_x and SiC_xN_y coatings were fabricated with high power impulse magnetron sputtering (HiPIMS). The coatings microstructure, growth pattern, surface morphology, composition, and bonding structure were investigated by AFM, SEM, GIXRD, TEM, EDS as well as XPS, and related to the deposition parameters target powers and substrate temperature. Cross-sections of SiC_xN_y coatings showed either dense and laminar, or columnar structures. These coatings varied in roughness (Ra between 0.2 and 3.8 nm) and contained up to 35 at.% C. All

coatings were substoichiometric (with an N/Si ratio from 0.27 to 0.65) and contained incorporated particles (so called droplets). The SiN_x coatings, in particular those deposited at the lower power on the silicon target, demonstrated a dense microstructure and low surface roughness (Ra between 0.2 and 0.3 nm). They were dominated by an (X-ray) amorphous structure and consisted mainly of Si-N bonds. The usefulness of these coatings is discussed for bearing surfaces for hip joint arthroplasty in order to prolong their life-time. The long-term aim is to obtain a coating that reduces wear and metal ion release, that is biocompatible, and with wear debris that can dissolve *in vivo*.

Keywords: Silicon nitride coating; Silicon carbon nitride coating; High power impulse magnetron sputtering (HIPIMS); Total joint replacements; Microstructure.

1. Introduction

Although total hip arthroplasty (THA) is considered a successful treatment and has been called the main surgical procedure in orthopedics [1], there is a significant amount of research on-going in order to increase the longevity of the implants. A high success rate of artificial hip joints is reported at 10 to 15 years [2], and commonly it is not the implant itself that wears out; it is the biological response to the wear debris that is the limiting factor [3]. Today, THA commonly has a metal-on-polymer bearing contact, with a cobalt chromium alloy (CoCr) head and an ultra-high molecular weight polyethylene (UHMWPE) acetabular cup. However, UHMWPE wear debris may lead to inflammation, bone resorption, aseptic loosening [3-5], and later revision surgery.

As a consequence, alternative bearing contacts such as metal-on-metal, ceramic-on-ceramic and, ceramic-on-metal have been further developed. For metal-on-metal bearings, a small number of patients have experienced serious problems, such as soft tissue necrosis caused by wear debris, causing the governmental Medicines and Healthcare products Regulatory Agency (MHRA) in the UK to announce a first medical device alert on the subject 2010. Alumina (Al_2O_3) is the most widely used ceramic material for the bearing contact in THA and has shown promising results *in vivo* [6, 7], although brittle fracture is still a concern [8, 9]. Silicon nitride (Si_3N_4) has been used for more than 50 years in extreme conditions in industrial applications, such as ball bearings and engines, due to its high fracture toughness, wear resistance, low density as well as chemical and thermal stability [10]. In water, silicon nitride can form a tribofilm that gives low friction and wear rates [11-13]. Silicon nitride is currently being introduced as a biomaterial [14-22]. A product based on silicon nitride got Food and Drug Administration (FDA) approval for use as spinal implants in 2006 and the first silicon nitride femoral head was implanted in early 2011 [23]. Silicon nitride has shown to be

biocompatible [19] and recent studies have also shown better antibacterial and osteoinductive properties compared to titanium and polyether ether ketone (PEEK) [21, 22]. In an earlier publication by the authors [24], *in vitro* studies of blood plasma and antibody adsorption onto commercial silicon nitride surfaces were performed. Adsorption of blood plasma proteins indicated a good acceptance of silicon nitride in the body and a relatively low activity of the immune response compared to both titanium and zirconia (ZrO_2) [24]. Further, silicon nitride particles (~ 90 nm) have been shown to dissolve in aqueous medium [25, 26], which suggests that wear debris can dissolve *in vivo*. This shows a potential to reduce the negative body response to any wear debris and possibly increase the longevity of the implant. Silicon nitride coatings have also been found to dissolve in an *in vivo* study in rats, with dissolution rates from 0.33 to 2.0 nm/day [27]. Hence, relatively thick coatings of several μm are likely required to withstand slow dissolution and this range of thicknesses is also recommended to provide sufficient wear life of ceramic coatings on hip implants [28-30].

A ceramic coating on a metal substrate could give a better implant performance in comparison to a bulk ceramic or metal, benefiting from the biocompatibility and wear resistance of the ceramic together with the toughness of the metal substrate. Furthermore, a ceramic coating can improve corrosion resistance and minimize metal ion release. A number of different coating compositions and deposition techniques have been studied for hip implants, the most common are titanium nitride (TiN), diamond-like carbon (DLC), zirconium oxide (ZrO_2), and chromium nitride (CrN) deposited by physical vapor deposition (PVD) or chemical vapor deposition (CVD) [29, 31-33]. However, the recently introduced coating systems SiN_x and SiC_xN_y are not yet well investigated for joint applications, in particular when produced by high power impulse magnetron sputtering (HiPIMS). This deposition method has been reported to form dense and smooth coatings on complex-shaped substrates [34]. In addition HiPIMS can be used to accomplish a good adhesion between coating and substrate, as well as

to tailor the coating microstructure through the use of guided highly ionized plasma species [35-37]. One drawback for some material systems is the lower deposition rate of HiPIMS compared to conventional magnetron sputtering. Pusch et al. showed a significant difference in the structural properties of SiC_xN_y coatings when comparing the deposition techniques radio frequency magnetron sputtering (RFMS), direct current magnetron sputtering (DCMS) and HiPIMS. Moreover, the hardness and elastic modulus of these coatings deposited by HiPIMS varied strongly depending on the carbon source[38].

In an earlier study by the authors, density functional theory (DFT) calculations showed that small amounts of substitutional carbon can destabilize crystalline silicon nitride, which indicates a possibility of tuning the dissolution rate [39]. Different carbon concentrations were therefore used in the current study with an aim of understanding how the addition of carbon would affect the microstructure and composition of silicon nitride coatings.

The aim of the present study is to relate the deposition parameters of HiPIMS deposited SiN_x and SiC_xN_y coatings to their structure and composition. A parallel study investigated the effect on the mechanical and tribological properties of the coatings [40]. The long term aim is to apply the coatings on CoCr alloys for medical implants. As inferred from above, potential advantages of silicon nitride include low wear rates and less wear particles, with a potential of slow dissolution *in vivo*. In this paper we refer mostly to hip implants, but the coating could be applicable to all joint replacements, such as knee, elbow, and extremities as well as to other parts of the implant such as the taper region etc.

The coatings were examined regarding morphology and surface roughness on the nanoscale using atomic force microscopy (AFM). Surface roughness is an important parameter as smooth surfaces can minimize later production steps. Also, smooth surfaces are generally

required to obtain low wear rates and possibly full film lubrication. The growth pattern and morphology were studied by scanning electron microscopy (SEM) on cross-sections of the coatings. To evaluate the crystallinity of the coatings, grazing incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM) were employed. Energy dispersive spectroscopy (EDS) was used to determine the chemical composition of the coatings and X-ray photoelectron spectroscopy (XPS) for the bonding configuration.

2. Materials and methods

2.1. Coating deposition

Depositions were performed using an industrial coating system (CemeCon CC800/9 ML, Germany), using the same processes as described in [40]. The vacuum chamber of the industrial deposition system is equipped with four rectangular magnetron sputtering cathodes (50×8.8 cm) facing a substrate holder in the center, where two of the cathodes can be run in HiPIMS mode. The pulse frequency was set to 300 Hz, with a pulse width of 200 μ s. Two of the magnetrons were used for the two types of depositions in this study; SiN_x and SiC_xN_y coatings. A Si target (purity 99.999%) was used for all depositions, and for the latter depositions, a C target (purity 99.5%) was also used for co-deposition. The two targets were positioned at a distance of 6 cm from the rotating substrate holder. For the SiN_x coatings, the substrate had a stationary position, perpendicular to the Si target (later referred to as ‘stationary’), and for the SiC_xN_y coatings the substrates were rotated (‘dynamic’). A pulsed bias voltage of – 100 V was applied to the substrates, synchronized with the cathode pulses. Two different substrate temperatures were used, 110 °C and 430 °C, later referred to as low (*l*) and high (*h*). The coatings were sputtered in an Ar-N₂ atmosphere with a nitrogen fraction of 0.16. The power on the Si target was varied from 1 kW to 4 kW and the C target power from 0 to 1.4 kW. The coatings are hereafter named after these deposition parameters, for example coating SiCN (4/0.7/*h*) is a SiC_xN_y coating deposited with an Si target power of 4 kW and C

target power of 0.7 kW at a substrate temperature of 430 °C while coating SiN (1/-/I) is a SiN_x coating deposited with an Si target power of 1 kW, stationary without employing the C target and at 110 °C.

All coatings were deposited on silicon wafers (001), to facilitate analysis after deposition. Substrates were individually cleaned ultrasonically in acetone and ethanol, in 5 min sequences, and dried in dry N₂ gas before being introduced into the chamber. No pre-sputtering of the substrate surfaces was performed. The Si target power, the C target power and the substrate temperature were varied according to Table 1 (column 1) in order to vary the composition as well as the microstructure of the coatings.

2.2. Structure and composition

The morphology of the coatings was studied with AFM (Dimension 3100, Veeco Instruments, USA) operating in tapping mode and equipped with a Si tip delivered with a tip radius curvature less than 10 nm and a cone angle of 22° (tip stiffness: 10-130 N/m, Nanosensors, Switzerland). Root mean square (rms) roughness and average roughness (Ra) were evaluated from 1x1 µm scans. Microstructure and thickness were examined by SEM (Leo 1550 FEG SEM Gemini, Carl Zeiss, Germany) on cross-sections of the coatings from a fracture of the Si (001). The cross-sections were either covered with a thin layer of Pt (~10 nm) or mounted on adhesive Cu tape to prevent charging. The amorphous (or crystal) structure was evaluated using GIXRD (Siemens D5000, Germany) at 1° incidence angle. One coating was further examined using TEM (FEI Tecnai F30 ST, USA). The sample was prepared with a focused ion beam (FIB, FEI Strata DB235, USA) with an *in-situ* lift-out method. In order to assess the microstructure high resolution TEM (HRTEM) was performed along with selected area electron diffraction (SAED) using an energy filter (Gatan Imaging Filter (GIF) 2002, USA). EDS (EDAX Microanalysis, Netherlands) was employed in an SEM, with an acceleration

voltage of 5 kV, to study the coating composition as well as investigating possible contaminations. The chemical bonding was examined using XPS (Physical Electronics (Phi) Quantum 2000, USA) with a monochromatic Al-K α source applying electron and ion neutralizer during measurements. Before the XPS measurements the samples were sputter-etched with Ar⁺ ions for 45 min at 200 eV over 1x1 mm. Core level spectra were analyzed using the software XPS Peak and Gaussian curve shapes were fitted after Shirley background correction.

3. Results

3.1. Structure

Representative surface plots from AFM measurements are shown for selected SiN_x and SiC_xN_y coatings in Fig. 1. The surface plots show similar morphologies. However, smoother surfaces, with rms values ranging from 0.2 to 0.3 nm, were revealed for SiC_xN_y coatings deposited at the higher temperature using a high Si target power, and all SiN_x coatings. Two examples of smooth surfaces are seen in Fig. 1a and 1f. Note that Fig. 1a is plotted with a smaller z-range in order to show that the smoother coatings had a similar morphology to the other coatings, but on a smaller scale. The remaining SiC_xN_y coatings exhibited a rougher surface with rms values between 1.4 and 4.8 nm, see Table 1. The highest rms values were found for SiC_xN_y coatings deposited at low temperature using a low Si target power, Fig. 1b and 1d, Table 1. Varying amounts of incorporated particles were observed in the AFM measurements, one example can be seen in Fig. 1e. The roughness values from the AFM measurements presented in Table 1 were calculated in areas without droplets.

Fractured cross-sections, viewed in SEM, revealed a variation in surface morphology and microstructure of the coatings, Fig. 2. All SiN_x coatings appeared smooth and showed a *dense*, homogeneous microstructure without indications of columnar growth, both at low and high

temperatures. The thickness of these coatings varied between 1.2 and 4.4 μm , as presented in Table 1. For SiC_xN_y coatings the power of the Si targets influenced the microstructure. SiC_xN_y coatings deposited at lower Si target power (1 kW) exhibited a *columnar* microstructure, whereas an increased power (4 kW), generated a dense homogeneous microstructure with a superimposed *laminar* contrast. The thickness of the SiC_xN_y coatings varied between 0.4 and 0.9 μm , see Table 1. The surface morphology of SiN_x and SiC_xN_y coatings, determined by SEM, were divided into three groups in Table 1. The coatings had a *smooth* appearance for all SiN_x coatings and SiC_xN_y coatings deposited at higher deposition temperatures combined with a high power of the Si target, SiCN (4/0.5-1.4/h), Fig. 2a and 2d. With the lower deposition temperature, SiCN (4/0.5-1.4/l), spherically shaped *small nodules* were observed on the surfaces, 20-50 nm in size. A similar morphology but with *larger nodules*, 50-100 nm, was observed on coatings grown at low Si target power, regardless of temperature for the SiC_xN_y coatings, SiCN (1/0.7-1.4/l) and SiCN (1/0.7-1.0/h), Fig. 2b-c. These groups correlate to AFM surface plots in Fig. 1, where smooth is represented by Fig. 1a and 1f, small nodules by Fig. 1e and large nodules by Fig. 1b-d.

Both SEM and AFM studies showed varying amounts of droplets, with a size of 10 nm to 1 μm , on the surfaces. Observations of SiN_x coatings indicated that for higher Si target power more droplets had formed. The SiC_xN_y coatings deposited at low Si target power showed a more *limited* amount of droplets, Fig. 3a. However, SiCN (1/0.7/h), grown using the lowest powers of all coatings, still showed droplets. In Fig. 3b, a coating with a larger number of droplets is presented (denoted *yes* in Table 1, ‘Droplets’ column). Here, the molten nature of the droplets upon impact on the growing coating surface can be observed. The power on the C target did not seem to influence the amount of droplets.

GIXRD analysis showed that all coatings were X-ray amorphous, although low intensity signals were obtained around 28 and 50° for SiN (4/-/l), SiN (2/-/h) and SiN (3/-/h). In addition, both HRTEM and SAED pattern of coating SiN (1/-/l) indicated an amorphous to nanocrystalline structure, see Fig. 4.

3.2. Coating composition

EDS analysis of the coating composition showed N/Si ratios between 0.27 and 0.65, see Table 1. The N/Si ratio decreased with increased Si target power and deposition temperature. In the SiN_x coatings small amounts of C were also detected, within the margin of error. For the SiC_xN_y coatings the C content is summarized in Table 1. The C content increased from 6 at.% to 35 at.% with increasing C target power as well as decreased Si target power. Traces of contaminating elements Ar, O (and C for SiN_x coatings) were detected in all coatings.

XPS analysis of the Si2p core level spectra demonstrated Si-N (~101.0 eV, [38, 41]) as a dominant bond in all coatings, Fig. 5a. For coatings deposited with a higher Si target power, the Si2p peaks were broader, indicating contributions from the Si-Si bond (~ 99.5 eV, [42]) see Fig. 5a. Presumably the component assigned to Si-C bonds (~100.3 eV) is concealed within the intense signals from Si-N and Si-Si bonds and can therefore not be resolved for the SiC_xN_y coatings. The Si-N bonds were confirmed by photo electron peaks for N1s (~ 397.4 eV, [38]), Fig. 5b. Coatings deposited at higher Si target power contained more Si and also a higher intensity component assigned Si-Si bonds. There was no signal obtained from Si-O bonds, see Fig. 5a.

In the C1s core level spectra the SiC_xN_y coatings with higher C content (over 10 at. % in Table 1) showed C-Si bonds (~ 282.8 eV, [38, 41]), Fig. 5c. For coatings with the highest C content, SiCN (1/1.0-1.4/l) and SiCN (1/1.0/h), a possible double peak was recorded. The two

peaks were likely formed from a large C-Si peak along with a C-C peak (~ 284.5 eV, [38, 41]). At an intermediate C content, samples SiCN (1/0.7/*l* and *h*) and SiCN (4/1.4/*l* and *h*), distinct C-Si bonds were found, while the contributions from C-C bonds were small or non-detectable. A higher ratio of C-Si bonds (and less C-C bonds) was formed at higher temperature and lower C target power, while the Si target power has no significant impact on the intensity of the component assigned to these bonds. The intensity of the C peaks in the XPS correlates to the C signal from the EDS analysis. Coatings with a low C content (less than 10 at. % in Table 1) showed no distinct C peak for C1s and was for that reason not included in Fig. 5c. Small amounts of contaminating elements (O and Ar) were detected in all coatings, which were also detected with EDS. An overview of how the structure and composition changed with the deposition parameters is displayed in Fig. 6 and 7, for SiN_x and SiC_xN_y coatings, respectively.

4. Discussion

4.1. Structure

The coating thickness differed between individual coatings due to the variation in deposition time and deposition rate. The deposition rate increased with the Si target power. The substrate temperature did not influence the deposition rate to a great extent. A difference in deposition rate was seen between coatings deposited in a stationary or dynamic (rotation) mode. The deposition rate varied from similar to up to 25 times higher for stationary deposition. This is attributed to the fact that during depositions employing sample rotation, the samples faced the cathodes only a fraction of the time compared to depositions where they were stationary. Compared to r.f. sputtered SiN_x coatings [39], the HiPIMS deposited SiN_x coatings had up to 10 times higher deposition rate. The SiC_xN_y coatings deposited with rotation had a similar rate as the r.f. sputtered. Even though a low deposition rate can be a concern for HiPIMS, it was not found to be a major issue in this study. In order to increase the deposition rate further,

more targets can be used or deposition parameters such as target power or pulse frequencies could be tuned.

Low Ra and rms values of coatings deposited on Si are promising for joint bearing applications [32, 43-45]. However, when deposited on CoCr substrates, which are rougher than Si-wafers, the surface roughness of the coating will also increase. For the SiN_x coatings none of the deposition parameters appeared to influence the surface roughness. However, for the SiC_xN_y coatings, which showed a generally higher roughness, two of the deposition parameters - Si target power and substrate temperature - appeared to have an effect on the roughness. At a higher Si target power and/or a higher temperature, smoother surfaces were obtained. According to Thornton's zone model a higher deposition temperature results in lower surface roughness and denser structure, since it enables atoms or ions to find more energetically favorable positions on the surface [46], including filling surface vacancies and cusps.

Different types of microstructures were formed in the SiC_xN_y coatings depending on the Si target power: at the lower power a columnar microstructure was formed, and at the higher power a laminar microstructure was found. In comparison to r.f. sputtered SiN_x coatings [39], all HiPIMS deposited SiN_x coatings were more homogeneously dense and did not have a pronounced columnar growth pattern. However, HiPIMS deposited SiC_xN_y appeared more porous in cross-section than the r.f. sputtered SiN_x coatings. Droplet formation is a concern since the droplets could contribute to coating failure by acting as corrosion paths, giving rise to local stresses and an increased fracture risk under loading, or an increase in wear. Generally droplets are not a major issue for HiPIMS, but can emerge due to dust particles or molten splashes when a conductive target has been covered with an insulating layer [47]. A possibility to limit droplet formation could be to use shorter pulses during deposition, which

can prevent glow-to-arc transition [47-49]. Droplets on the SiN_x coatings indicate that higher Si target power causes the formation of more droplets. Our current assumption is that a higher Si target power causes increased arcing, which leads to local target melting and ejection of particles that are incorporated into the growing coatings. Still, SiCN (1/0.7/h), grown using the lowest Si target power, showed droplets. Only SiN (1/-/l) showed a very limited amount of droplets.

When changing the deposition from stationary (SiN_x coatings), to dynamic (SiC_xN_y coatings) and introducing the C target, the microstructure changed. For the SiN_x coatings, no notable difference in microstructure was observed for different power and/or temperature settings, all cross-sections showed dense coatings. On the other hand, for SiC_xN_y coatings, a lower Si target power resulted in columnar and more porous structures, whereas a higher Si power caused a denser structure without pronounced columns. It was also found that an increased deposition temperature resulted in a slightly denser structure for columnar structures, seen in Fig. 2b-c. A distinct laminar structure due to the substrate rotation and direction dependent deposition flux, could be observed for SiC_xN_y coatings deposited at a Si target power of 4 kW, but not for those with the lower Si target power of 1 kW. At 1 kW, it is possible that a laminar structure is present, but is simply not resolved in the SEM.

All coatings were X-ray amorphous. Coating SiN (1/-/l), studied in TEM, showed an amorphous to nanocrystalline structure. Nanocrystals possibly occur, especially for SiN_x coatings that show slight signals in the XRD spectra. These coatings were deposited at a higher temperature and/or at a higher Si target power. This is in agreement with literature, as it suggests higher deposition temperatures and nitrogen fractions for the formation of a crystalline (or polycrystalline) Si_3N_4 structure [10, 50, 51]. For implant applications, an amorphous structure may be an advantage compared to a polycrystalline structure, as an

amorphous structure generally is more uniform with less corrosion paths such as grain boundaries [32]. The X-ray amorphous structure in these coatings has shown a similar wear rate to crystalline Si_3N_4 , however a higher coefficient of friction was noted [40].

4.2. Coating composition

The coatings had a low N/Si ratio (0.29 to 0.65) compared to stoichiometric Si_3N_4 (1.33). For higher Si target power and higher substrate temperature, more Si was detected in the coating. In order to obtain information from the coating and not from the substrate, a low acceleration voltage (5 kV) was used for the EDS analysis. An electron flight simulation based on a Monte Carlo model at this voltage estimates an information depth in Si_3N_4 of 0.3 μm . This elemental analysis should be used for comparison between samples in this study and not as absolute quantitative values, as no references were used and signals from light elements such as C and N can be difficult to detect.

By varying deposition parameters, the C content could be tuned up to approximately 35 at. %. According to earlier DFT calculations [39], the surface reactivity – and consequently also the dissolution rate – of crystalline Si_3N_4 can be increased by the addition of small amounts (1, 3, and 4 at. %) of substitutional C. Tuning of the dissolution rate may be required in order to make it fast enough to avoid negative effects from the wear debris, and slow enough to ensure an adequate longevity of the coating. The calculations apply to C bonded to Si, and not C-C. XPS measurements in this work showed C-Si bonds if a lower C target power and/or a higher Si target power along with a higher deposition temperature were used. The calculations made in the previous study were made on stoichiometric, crystalline Si_3N_4 , in contrast to the (X-ray) amorphous coatings with another N/Si-ratio, which may affect the dissolution rate.

There are two possible Ar contamination sources, both from the deposition process and/or pre-sputtering in the XPS analysis. However, since Ar was also detected in EDS, the deposition definitely is one of them. O, but also N and C, are likely to originate from ambient contamination. The risk of sputter damage was minimized as far as possible for the XPS analysis through the use of low ion energy. [52]

The SiN_x coatings showed little dependence on deposition parameters such as contaminating elements, morphology, microstructure, N-Si bonds, or surface roughness. Neither did the varying coating thickness appear to affect the chemical and structural analysis.

4.2. Effect on mechanical properties

For SiN_x coatings, the mechanical properties and the chemistry can be related to the Si target power. At lower Si target power, a higher N/Si ratio as well as a higher quota of Si-N bonds and lower of Si-Si bonds was obtained, which possibly explains the slight increase from 17 to 21 GPa in coating hardness [40]. The hardness effect is likely to be related to the chemistry since structural properties such as the surface roughness and cross-section microstructure were similar for all SiN_x coatings.

The high surface roughness, for coatings SiCN (1/0.7-1.4/l) compared to the other SiC_xN_y could possibly explain the lower hardness (10-11 GPa vs. 15-21 GPa) and elastic modulus (140-150 GPa vs. 170-220 GPa) measured on these coatings [40]. The hardness measurements were made at a maximum depth of 40 nm, where the high surface roughness could have affected the measurement (Fig. 1b and 1d).

In general it was found that the deposition parameters, such as target power and the combination of different targets, strongly affected the structure and composition of the coating,

and in turn the mechanical properties. As for the specific wear rate it appears that the dense structure obtained for SiN_x coatings can give a better performance than the less dense structures found for SiC_xN_y coatings [40]. This also motivates more in depth investigation on the N content along with the microstructure, and hence the mechanical properties.

5. Conclusions

SiN_x and SiC_xN_y coatings were fabricated using HiPIMS for joint bearing surfaces. The coatings were examined for their microstructure, surface appearance and composition. SiN_x coatings were smooth and showed a dense, homogeneous microstructure with thicknesses between 1.2 and 4.4 μm . SiC_xN_y coatings varied in roughness, where higher deposition temperature and lower Si target power resulted in smoother coatings. The thickness of the coatings ranged between 0.4 and 0.9 μm . SiC_xN_y coatings exhibited two types of microstructure: columnar (deposited at Si target power 1 kW) and dense/layered (deposited at Si target power 4 kW). All coatings contained droplets on the surface, the amount of droplets increased with higher Si target power.

The coatings were (X-ray) amorphous and had a low N/Si ratio, from 0.27 to 0.65. The ratio decreased with increased Si target power and deposition temperature. The Si-N bond was the most dominant bonding type for Si in all coatings but when a higher power was used on the Si target, an increasing amount of Si-Si bonds were formed. For SiN_x coatings, no notable difference was found for coatings deposited at different temperatures. SiC_xN_y coatings with up to 35 at.% C were produced. An increased power on the Si target and an increased deposition temperature resulted in more Si-C bonds (less C-C bonds), and vice versa.

Findings in this paper support further development of these coatings for surfaces in joint replacements. Especially the SiN_x coatings are of interest since they have shown to be dense

with low surface roughness, in particular coatings grown at lower Si target power for a minimized amount of droplets. Future research will focus on investigating the dissolution rates of wear particles and coatings together with biological reactions. Also, further development in terms of thicker coatings and improved adhesion is needed, as well as an increased understanding of the influence of N concentration and the N bonding structure.

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Table 1. Summary of observations by SEM (thickness, microstructure, morphology and droplets), AFM (average and root mean square roughness) and EDS (composition).

Coating Name (Si-target power [kW]/ C-target power [kW]/ Temp.)	Thickness [μm]	Deposition rate [nm/s]	Ra [nm]	Rms [nm]	Morphology	Droplets	Microstructure	N/Si-ratio [at. %]	C content [at. %]
SiN (1/-/l)	1.2	0.7	0.3	0.3	smooth	very limited	dense	0.42	1
SiN (2/-/l)	2.8	1.6	0.2	0.3	smooth	limited	dense	0.32	2
SiN (3/-/l)	4.3	2.4	0.2	0.2	smooth	yes	dense	0.31	1
SiN (4/-/l)	4.4	2.4	0.3	0.3	smooth	yes, a lot	dense	0.29	0
SiN (2/-/h)	2.5	1.4	0.2	0.2	smooth	yes	dense	0.31	1
SiN (3/-/h)	3.8	2.1	0.2	0.3	smooth	yes	dense	0.27	1
SiCN (4/0.5/l)	0.50	0.33	1.3	1.6	small nodules	yes	dense/laminar	0.37	6
SiCN (4/0.7/l)	0.65	0.50	1.4	1.7	small nodules	yes	dense/laminar	0.38	9
SiCN (4/1.4/l)	0.55	0.42	1.1	1.4	small nodules	yes	dense/laminar	0.35	14
SiCN (1/0.7/l)	0.55	0.14	3.3	4.2	nodules	limited	columnar	0.57	23
SiCN (1/1.0/l)	0.40	0.10	3.4	4.3	nodules	limited	columnar	0.65	30
SiCN (1/1.4/l)	0.85	0.22	3.8	4.8	nodules	limited	columnar	0.65	35
SiCN (4/0.5/h)	0.80	0.35	0.2	0.3	smooth	yes	dense/laminar	0.34	6
SiCN (4/0.7/h)	0.90	0.39	0.2	0.2	smooth	yes	dense/laminar	0.27	9
SiCN (4/1.4/h)	0.70	0.33	0.2	0.2	smooth	yes	dense/laminar	0.27	15
SiCN (1/0.7/h)	0.70	0.13	1.7	2.1	nodules	yes	columnar	0.53	22
SiCN (1/1.0/h)	0.70	0.13	2.3	2.9	nodules	limited	columnar	0.57	29

Fig. 1. AFM surface plots (1x1 μm) of representative coatings with a z-scale of 5 nm (a) and 25 nm (b-f) per division. The images represent smooth surfaces (a and f), with small nodules (e) and with nodules (b-d). A surface with droplets is shown in (e).

Fig. 2. Fractured cross-sections viewed in SEM where a) represent a dense homogeneous microstructure, SiN (2/-/h), b-d) a columnar microstructure, in SiCN (1/1.0/l) and SiCN (1/1.0/h), while d) represents a laminar microstructure, in SiCN (4/0.5/h).

Fig. 3. Droplets studied in SEM are described as a) a surface with limited amount of droplets and in b) surfaces with droplets to a higher extent.

Fig. 4. HRTEM image of coating SiN(1/-/l) obtained at defocus near the coating surface (a), and a SAED pattern, confirming an amorphous to nanocrystalline structure (b).

Fig. 5. XPS core level spectra of a) Si2p, b) N1s and c) C1s for selected SiN_x and SiC_xN_y coatings with varying deposition parameters, where the thick gray lines show the measured data and the thin black lines shows fitted peaks.

Fig. 6. Overview of structures and compositions of SiN_x coatings depending on the target power and substrate temperature.

Fig. 7. Overview of structures and compositions of SiC_xN_y coatings depending on the target power and substrate temperature. When marked ' $\propto T$ ' or ' $\propto Si$ ', temperature or Si-target power also affect this property.