Research Journal of Engineering Technology and Medical Sciences (ISSN: 2582-6212), Special Issue 2 (2020)
Available at www.rjetm.in/

Mechanical and Tribological Behaviour of Silicon Nitride and Silicon Carbon Nitride Coatings

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* Corresponding Author: Author Name Manuscript Received: Manuscript Accepted:

Abstract: A wear resistant configuration with wear particles that resorb in vivo can potentially increase the lifetime of an implant. In this study, silicon nitride (SixNy) and silicon carbon nitride (SixCyNz) coatings were produced for this purpose using reactive high power impulse magnetron sputtering (HiPIMS). The coatings are intended for hard bearing surfaces on implants. Hardness and elastic modulus of the coatings were evaluated by nanoindentation, cohesive, and adhesive properties were assessed by micro scratching and the tribological performance was investigated in a ball-on-disc setup run in a serum solution. The majority of the SixNy coatings showed a hardness close to that of sintered silicon nitride (~18 GPa), and an elastic modulus close to that of cobalt chromium (~200 GPa). Furthermore, all except one of the SixNy coatings offered a wear resistance similar to that of bulk silicon nitride and significantly higher than that of cobalt chromium. In contrast, the SixCyNz coatings did not show as high level of wear resistance.

Keywords: silicon nitride, silicon carbon nitride, coatings, total joint replacements, biotribology.

1. Introduction The metal-on-polymer bearing is the most common configuration, using cobalt chromium alloy (CoCr) on ultra-high molecular weight polyethylene (UHMWPE). However, wear particles from UHMWPE may induce an inflammatory reaction, which may lead to bone resorption and loosening of the implant (Ingham and Fisher, 2005). The release of metal ions is also a reason for concern due to toxicity (Sargeant and Goswami, 2007). Furthermore, a risk of catastrophic failure arises when bulk ceramics are used, due to their brittleness. In order to avoid this, the ceramic can be used as a coating on a more ductile (metal) substrate. Advantages with coatings can include reduced wear rates and an increased corrosion resistance (Lappalainen and Santavirta, 2005). A reduced amount of metal ion release would naturally be of great interest. Different surface treatments and coatings have been investigated for the bearing surfaces between the femoral head and the acetabular cup in hip implants, such as TiN (Harman et al., 1997; Pappas et al., 1995; Teresa Raimondi and Pietrabissa, 2000), diamond-like carbon (Affatato et al., 2000; Fisher et al., 2002; Lappalainen et al., 1998), CrN (Fisher et al., (2002), CrCN (Fisher et al., 2002), ZrO2 (Yen et al., 2001), and Al2O3 (Yen and Hsu, 2001). However, insufficient adhesion and coating artifacts, such as droplets, have been reported as major concerns for these coatings. During the last decades silicon nitride has been investigated for and introduced into the biomedical field. Traditionally, it has been used in engines, cutting tools, and ball bearings for its high mechanical performance (Riley, 2000). Today, silicon nitride is used for spinal implants and in early 2011 the first silicon nitride femoral head was implanted in USA. The choice of silicon nitride as an implant material is motivated by its excellent biocompatibility, low wear rates as well as relatively high fracture toughness and strength (Mazzocchi and Bellosi, 2008; Mazzocchi et al., 2008; Sonny Bal et al., 2008, 2009). 3 Furthermore, silicon nitride particles dissolve in aqueous media (Laarz et al., 2000). This, in turn, suggests that wear particles can dissolve in vivo, which may reduce the negative body response from the debris, and potentially increase the longevity of the implant. Additionally, density functional theory (DFT) calculations have shown that small amounts of substitutionally-bonded carbon can destabilize crystalline Si3N4, indicating the possibility to tune the dissolution rate (Olofsson et al., 2012). To this date, there have only been a few publications on silicon nitride (SixNy) and silicon carbon nitride (SixCyNz) coatings for joint implants (Olofsson et al., 2012; Shi et al., 2011, 2012). Olofsson et al. (2012)

used reactive radio frequency (r.f.) sputtering to produce SixNy and SixCyNz coatings that showed a potential for high wear resistance, but issues with coating defects and poor adhesion leading to flaking off of the coatings were reported. Shi et al. (2011) also used different magnetron sputtering methods for fabricating SixNy and SixCyNz coatings; r.f., direct current and unbalanced magnetron sputtering. However, adhesive properties of the coating were not reported. In this study, SixNy and SixCyNz coatings were deposited using high power impulse magnetron sputtering (HiPIMS). Owing to high plasma densities and increased ionization probabilities, HiPIMS has been reported to produce dense coatings on complex structures (Alami et al., 2005). In addition, HiPIMS can be used to obtain increased adhesion between coating and its substrate (Sarakinos et al., 2010). In order to assess the mechanical properties and the durability of the coatings, hardness and elastic modulus were studied by nanoindentation, while cohesive and adhesive failure were investigated with micro scratching. The tribological properties, friction and wear resistance were studied in a ball-on-disc setup.

2. Materials and Methods

2.1. Coating deposition

Conventional P-doped Si (001) (Semiconductor Wafer, Inc) was used as substrate material for all coatings, due to its availability and the preliminary nature of the study. Additionally, three of the coatings were deposited on cobalt chromium (CoCr, ASTM F75, Sandvik AB, Sweden). The substrates were cleaned in 5 min sequences, first in acetone then in ethanol, and dried in N2 gas before 4 depositions. The coatings were deposited using the industrial coating system CC800/9 ML (CemeCon, Germany) with rectangular targets (50 × 8.8 cm). The deposition process took place in power controlled HiPIMS mode using a pulse width of 200 µs, at a frequency of 300 Hz. The reactive sputter process was carried out with an Ar/N2-flow ratio of 0.16. For the SixNy coatings, a silicon target (purity 99.999%) was used. During the deposition process the substrates faced the target at a distance of 6 cm. SixCyNz coatings were produced by co-sputtering from a silicon target and a graphite target (purity 99.5%). Here, the samples were rotated to pass both targets at the same target-to-substrate distance as for the SixNy coatings. This sample rotation causes the formation of Si- and C-monolayers with a thickness below 10 nm. A negative bias voltage of -100 V was applied during the deposition. No pre-sputtering of the substrate was performed before the coating deposition. In order to alter the composition of the coatings, the following parameters were varied; the substrate temperature (110 ºC, hereinafter denoted ‘l’ for low, and 430 ºC, denoted ‘h’ for high), the Si target power (1-4 kW), Ctarget power (0-1.4 kW or absent for SixNy coatings), as well as a stationary deposition for SixNy coatings and sample rotation for SixCyNz coatings. Hence, the coatings are referred to using these variations, for example SiCN (4/0.5/h) intend a SixCyNz coating deposited with a Si target power of 4 kW, a C target power of 0.5 kW and a substrate temperature of 430ºC. which is a SixNy coating deposited at a silicon target power of 1 kW, with no C-target and a substrate temperature of 110ºC. The C content was estimated by energy dispersive spectroscopy analysis (EDS, EDAX Microanalysis, Netherlands) integrated in a scanning electron microscopy (SEM), at an acceleration voltage of 5 kV to obtain a surface sensitive measurement. The stationary deposited SixNy coatings were thicker (1.2-4.4 µm) than the SixCyNz coatings (0.4-0.9 µm).

2.2. Mechanical characterization

Two bulk materials were used as references: CoCr (ASTM F75, Sandvik AB, Sweden, Ra ~8 nm) and Si3N4 (Keranova AB, Sweden, Ra ~15 nm). Hardness and elastic modulus of the reference materials and the coatings were obtained using a commercial nanoindenter (CSM Instruments UNHT, Switzerland) with a Berkovich tip. A total of 30 indents per sample were completed varying the 5 maximum loads to obtain an approximate indentation depth of 40 nm. Hardness and elastic modulus were calculated using the Oliver-Pharr method (Oliver and Pharr, 1992). The elastic modulus was determined for the coatings and for the reference Si3N4 using a Poisson’s ratio of 0.25 (Walmsley et al., 2007), whereas for CoCr a Poisson’s ratio of 0.3 was assumed. Scratch tests were performed using a micro scratcher (CSM Instruments UNHT, Switzerland) with a sphero-conical stylus (apex 90°; tip radius 2 μm). A progressive load up to 300 mN over 600 μm (loading rate 150 mN/min) was applied. Additional pre- and post-scans were carried out with a load of 3 mN in the same direction. Critical loads LC1 and LC2, indicating the onset of cohesive and adhesive failure of the coatings, respectively, were determined using load vs. depth profiles in combination with optical and SEM (LEO 440, Zeiss, Germany). Wear tests in a ball-on-disc equipment were conducted based on ASTM F 732-00 (2006). The samples were tested against a Si3N4-ball (6 mm in diameter, Spekuma, Sweden), to simulate the coating sliding against itself. The disc specimen was rotated at a speed of 0.04 m/s applying a normal load of 1 N, forming a wear track of 5 mm in diameter. Due to differences in wear performance, tests were run for 1 000 and 10 000 revolutions, for SixCyNz and SixNy coatings, respectively. In order to simulate physiological conditions, the wear tests were run in a serum solution of 25% fetal bovine serum

3. Results

The relative C concentration was estimated using EDS, and was found to increase with increasing Ctarget power and decreasing power on the Si target.

3.1. Hardness and elastic modulus

All coatings were found to be harder than CoCr but softer than bulk Si3N4. Generally, the SixNy coatings were harder than the SixCyNz coatings. Very similar hardness values of the coatings were recorded on both substrates (Si or CoCr), confirming that there was no influence from the substrate in the hardness and elastic modulus measurements.

3.2. Micro scratching

The micro scratching revealed adhesive failure for the SixNy coatings at loads above 214 mN, and coatings SiN (3/-/l), (4/-/l), and (3/-/h) resisted loads up to the maximum 300 mN without any rupture. The adhesive failure of SixNy coatings occurred by extensive flaking in front of and behind the scratching tip. The deformation and redistribution of the material before failure for all SixNy coatings, except SiN (1/-/l), was accompanied by the formation of micro cracks on the ridges. The SiN (1/-/l) coating deformed without visible micro cracking up to final failure. Cohesive failure of the SixCyNz coatings occurred at loads around 50 mN and adhesive failure below 105 mN. Coatings deposited with higher Si target power (4 kW) showed cohesive failure by flaking. While coatings deposited at the lower target power (1 kW) showed cohesive failure by transverse cracks, both followed by adhesive failure of the coating. SixCyNz 7 coatings deposited on CoCr showed half the cohesive and adhesive failure loads of those deposited on Si-wafers.

3.3. Friction and wear

The SixNy coatings showed a stable friction coefficient between 0.2 and 0.3 over 10 000 revolutions. An exception was SiN (4/-/l), which had a drastic friction increase in the beginning and later reached a stable friction coefficient of 0.33. Both reference materials showed a lower friction coefficient than the SixNy coatings. Cross-section profiles of the wear tracks on the SixNy coating, sintered Si3N4 and CoCr. The SiN (4/-/l) coating wore down to a depth of 2 μm and is not shown in the figure. With respect to CoCr, the SixNy coatings, except SiN (4/-/l), showed a much higher wear resistance, similar to that of Si3N4.

The SixCyNz coatings were tested for 1 000 revolutions in the ball-on-disc tests, as previously mentioned. The majority of these coatings were worn through and failed during the test. The lowest wear rate of the SixCyNz coatings was 100 x 10-7 mm3 /N m, obtained for SiCN.

4. Discussion

In this study, SixNy and SixCyNz coatings were produced using HiPIMS and evaluated in terms of mechanical properties using nanoindentation (for hardness and elastic modulus), micro scratching (for cohesive and adhesive properties), and in a ball-on-disc setup (for friction and wear properties). The amount of C in the coatings was analyzed by EDS. However, these C concentrations should be interpreted as relative concentrations within this study, rather than absolute quantitative values. This caution is necessary since no standard was used for calibration of the measurements, and EDS has limitations in detecting light elements. Despite this, the values presented can be used for relative comparisons within the study and the C concentrations correlate well with what was expected from the deposition rates from the targets. 8 An electron flight simulation based on a Monte Carlo model was performed assuming an acceleration voltage of 5 kV in Si3N4 and estimated the maximum information depth to 0.3 μm. Also, the absence of Co, Cr and Mo signals in the EDS analysis of coatings deposited on Co Cr, confirms that the chemical information was obtained from the coating only. For hip joints there is a risk that wear particles or bone cement particles become trapped in the contact and cause abrasion (Bragdon et al., 2003; Dowling et al., 1978 ; Wang and Essner, 2001). A higher hardness of the joint bearing surfaces could therefore be an advantage by increasing the resistance to two and three body abrasive wear. The SixNy coatings were found to possess a high hardness, up to 21 GPa, while the hardness of some of the SixCyNz coatings were half of that. These variation are likely caused by the chemical and microstructural differences between the two types of coatings, caused by the C content and the layered structure (from the sample rotation, see section 2.1) of the SixCyNz coatings. The hardness and elastic modulus of the SixNy and SixCyNz coatings (especially for coatings with a low C content) was similar to literature data for coatings deposited using different sputtering methods (DC, r.f. and HiPIMS) (Olofsson et al., 2012; Pusch et al., 2011; Shi et al., 2012). For the SixNy coatings, a lower Si target power resulted in harder coatings, while no dependence of the deposition temperature was evident. The relation is probably linked to chemical differences between the SixNy coatings. These trends did not apply to the SixCyNz coatings. The reason for a lower hardness and elastic modulus for SiCN (1/0.7-1.4/l) is not yet fully understood. The difference in deposition temperature possibly affects the morphology, microstructure and/or chemistry in the coating and will be further investigated in a follow up study. The elastic moduli of the majority of the coatings were similar to that of CoCr, except SiCN (1/0.7-1.4/l), as discussed above. The coatings differed in thickness, consequently the failure loads (Lc1 and Lc2) were not compared. However, the modes of failure in micro scratching were found to correlate with the wear properties. For the SixNy coatings, the wear resistance appeared to relate to the ability to avoid micro cracks before adhesive failure. The SEM analysis showed that no micro cracks were formed before failure for SiN. This coating also showed the highest hardness, i.e. the 9 best ability to resist plastic deformation. A more brittle fracture can be seen for the harder SiN coatings in Fig. 2a and b, compared to the more ductile behavior seen for SiCN coatings. SiN (1/-/l) also showed the lowest wear rates and the highest H/E ratio. Leyland described the H/E ratio as a better way of predicting wear performance than hardness or elastic modulus individually (Leyland and Matthews, 2000). This approach predicts the poor wear performance for CoCr, but shows no trend for the remaining samples. The cohesive failure types for SixCyNz coatings, cracks and flakes, are believed to be related to different microstructures of the coatings, caused by deposition at different Si target powers. A higher Si target power is hypothesized to give a laminar structure and a lower power a columnar structure, since failure of a laminar structure appears between the lamellas, whereas for a columnar structure the failure arises between the columns. This may be a drawback for the SixCyNz coating, since weaker parts in the coatings risk a non-homogenously distributed failure through the coating, which can be hard to predict. When coatings were deposited on CoCr, the failure loads were only half of those on Si-wafers, which indicates that further optimization of the coating adhesion to CoCr is possible. It is not yet completely understood why coating SiN (4/-/l) differs from the remaining SixNy coatings in the wear test. The high wear rate is most likely related to the initially higher friction and possibly also the lower hardness, causing a larger contact area in the wear test. Neither could the low wear resistance of SixCyNz coatings be fully explained. Coatings SiN (1 to 3/-/l) and (2 to 3/-/h) displayed notably lower wear rates than the other coatings. The rates were close to Si3N4-on-Si3N4. In comparison with similar studies, the SixNy coatings matched the wear rates of Si3N4-TiN-compositeon-Al2O3 (Mazzocchi et al., 2008), CrN-on-CrN and CrCN-on-CrCN, and performed better than TiNon-TiN and CoCr-on-CoCr (Williams et al., 2003), and were also superior to most CoCr-onUHMWPE ((Saikko et al., 2001). In relation to w.r.f. sputtered SixNy coatings in a study by (Olofsson et al., 2012), the wear rates with the HiPIMS deposited SixNy coatings had similar to slightly lower wear rates, although the friction were somewhat higher in this study. Coatings deposited at lower Si target power had a slightly lower wear rate, these coatings also show the highest hardness, as discussed. Therefor caution needs to be taken when making direct comparisons with other studies. Future work should focus on understanding not only the wear but also the wear particles, since dissolution of wear particles may reduce a possible negative body response. The amount, size, shape, composition, bonding structure of the particles as well as pH etc. could affect the dissolution rate. The dissolution rate needs to be tuned so that the wear particles can dissolve but not the coating to a high extent. The test configuration with a ceramic ball sliding against the various coatings was used in order to simulate SixNy or SixCyNz coatings wearing against themselves. The most common in vivo configuration for CoCr is towards UHMWPE, where the majority of material loss occurs on the polymer. This is in contrast to the tested configuration Si3N4-on-CoCr, where mainly the CoCr was worn. However, the model test can relate the coatings wear resistance in to Si3N4-on-Si3N4 and Si3N4-on-CoCr. An initial study of using SixNy and SixCyNz for joint replacements was performed, motivated by previous DFT calculations. However, further development and investigations are needed. Wear studies were made in model tests comparing the coatings among each other and in relation to present materials for the specific application, future wear tests should include hip or knee simulator studies. In order to approach the application, an understanding of the structure and chemistry of the coatings has to be acquired along with the biological response both to the coating, wear particles, and the lubrication around the implant. As for the bearing surface of joint replacements a thickness of tenths of micrometers is needed, for this, excellent coating adhesion is required and needs, thus further investigations. Nevertheless, this initial promising result motivates further work on SixNy and SixCyNz for joint replacements.

5. Conclusions

SixNy and SixCyNz coatings have been deposited using HiPIMS in order to explore a wear resistant alternative for bearing surfaces in total joint replacements. The coatings showed hardness ranging 11 from that of sintered Si3N4 to CoCr. The elastic modulus of the majority of SixNy and SixCyNz coatings were similar to that of CoCr. The wear resistance of all of the SixNy coatings except one was in a range similar to that of sintered Si3N4 and significantly higher than that of CoCr. This promising mechanical property may be explained by the coating’s ability to avoid cohesive cracks. None of the SixCyNz coatings showed wear resistance matching that of Si3N4 or the SixNy coatings under the tested conditions. Also, there is room for process optimization to increase the adhesion to CoCr substrates. In conclusion, SixNy coatings are of great interest for further studies because of their combination of hardness, elastic modulus, and wear resistance. In particular the SiN (1/-/l) coating, which exhibited the highest hardness (21 GPa), one of the higher elastic moduli (212 GPa), the lowest wear rate and also fractured in a homogenous way in the scratch test.

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