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Article

Wear Performance of Sequentially Cross-Linked Polyethylene Inserts against Ion-Treated CoCr, TiNbN-Coated CoCr and Al_2O_3 Ceramic Femoral Heads for Total Hip Replacement

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Abstract: The aim of the present study was to evaluate the biotribology of current surface modifications on femoral heads in terms of wettability, polyethylene wear and ion-release behavior. Three 36 mm diameter ion-treated CoCr heads and three 36 mm diameter TiNbN-coated CoCr heads were articulated against sequentially cross-linked polyethylene inserts (X3) in a hip joint simulator, according to ISO 14242. Within the scope of the study, the cobalt ion release in the lubricant, as well as contact angles at the bearing surfaces, were investigated and compared to 36 mm alumina ceramic femoral heads over a period of 5 million cycles. The mean volumetric wear rates were 2.15 ± 0.18 $mm^3 \cdot million\ cycles^{-1}$ in articulation against the ion-treated CoCr heads, 2.66 ± 0.40 $mm^3 \cdot million\ cycles^{-1}$ for the coupling with the TiNbN-coated heads and 2.17 ± 0.40 $mm^3 \cdot million\ cycles^{-1}$ for the ceramic heads. The TiNbN-coated femoral heads showed a better wettability and a lower ion level in comparison to the ion-treated CoCr heads. Consequently, the low volumes of wear debris, which is comparable to ceramics, and the low concentration of metal ions in the lubrication justifies the use of coated femoral heads.

Keywords: hip joint simulator; titanium niobium nitride; coating; contact angle; ion treatment; cross-linked polyethylene; wear

1. Introduction

Since the beginning of low-friction arthroplasty in the 1950s, there has been considerable interest in polyethylene wear and its effect on the long-term survival of total hip replacements. With further developments in the field of sterilization [1,2] and composition, such as cross-linking [3–5] or vitamin E stabilization [6–8], the wear resistance of polyethylene has been extended efficiently during the last decades. Thus, hard-on-soft bearings, in which a femoral head made of ceramic or metal articulates against a polyethylene acetabular component, represent the standard solution in total hip arthroplasty so far.

However, all improvements in polyethylene wear resistance are only of value if the tribological performance of the counterface is optimized, with regard to roughness, wettability and abrasion resistance. Actually, there are several femoral head materials available on the market. Femoral heads made of a cobalt-chromium (CoCr) alloy are commonly used in total hip arthroplasty, owing to their beneficial combination of mechanical strength and ductility. In contrast, their clinical success is limited by the loss of their smooth surface over time, resulting in a greater counterface roughness and accelerated polyethylene wear [9–11]. Popular alternatives to CoCr alloys are oxide ceramics, which are classified to be the reference in the field of hard-on-soft bearings. Significantly increased scratch resistance, improved wettability and a biologically inert behavior rank among the decisive advantages of ceramic materials [12].

In order to increase the surface hardness of standard CoCr heads, without affecting the desired ductility of the substrate, different procedures can be applied. One type of method is ion implantation in which preferably nitrogen ions are embedded into the metal surface under high energy [13]. This procedure results in a phase transformation at the surface, and may lead to hardening of up to a depth of approximately 100 nanometers [14].

Another method to increase the abrasion resistance of CoCr femoral heads is to deposit an external ceramic coating on the metal surface in the range of a few microns, without changing the chemical and mechanical properties of the substrate material. Owing to its barrier effect towards the surrounding tissue, this kind of surface modification is deemed to be one of the preferred solutions for patients with sensitivity to metal ions (e.g., cobalt, nickel and chromium) [15].

However, there are still some concerns around coating delamination and the reduced ion-release behavior with ceramic coatings which are based mainly on outdated studies [16,17]. In the past five years, there has been no *in vitro* study which has investigated the performance of current coatings, with regard to polyethylene wear, ion-release behavior and wettability. Therefore, the aim of this experimental study was to evaluate the effect of two different surface modifications of femoral heads made of cobalt-chromium on wear propagation. For this purpose, titanium niobium nitride (TiNbN) coated CoCr femoral heads, as well as ion-treated (LFIT) CoCr heads, were tested in a hip joint wear simulator. In addition, ion levels in serum and contact angles were determined. The results of the analyses were evaluated and compared with controls based on alumina ceramic (Al_2O_3) heads.

2. Material and Methods

2.1. Test Specimens

Sequentially cross-linked polyethylene inserts (Trident X3, Stryker GmbH & Co. KG, Duisburg, Germany) were combined with 36 mm femoral heads. As acetabular components, suitable Trident PSL

56 mm acetabular cups (Stryker GmbH & Co. KG, Duisburg, Germany) were used. The cross-linking process of the sequentially cross-linked polyethylene insert was performed using compression-molded resin sheets out of GUR 1020 by irradiation with 3 MRads and annealing below the melting temperature, repeated three times alternately [18]. The sequentially cross-linked polyethylene material had a density of 0.9392 g/cm^3, which is used for the calculation of the volumetric wear. Before wear testing, the inserts were pre-soaked in the test liquid used for wear test for 55 days at room temperature. For each combination of sequentially cross-linked polyethylene and femoral head material three running samples and a loaded soak control were used to control the liquid absorption of the inserts.

The polyethylene inserts were combined with 36 mm femoral heads made of Co28Cr6Mo (Stryker GmbH & Co. KG, Duisburg, Germany). Three of the running heads were treated with nitrogen ions (LFIT TM, Stryker GmbH & Co. KG, Duisburg, Germany). In addition, three femoral heads were modified using a titanium niobium nitride coating (TiNbN, DOT GmbH, Rostock, Germany) by strongly poisoned cathode surface technology (SPCS), a special type of physical vapor deposition (PVD) arc deposition technology. In this procedure, the number of inhomogeneities (droplets) in the coating structure is drastically reduced during evaporation. The thickness of the TiNbN coating was 4.5 ± 1.5 µm, which is commonly used in clinically practice.

Furthermore, three 36 mm femoral heads made of alumina ceramic (BIOLOX®*forte*, CeramTec AG, Plochingen, Germany) were used for reference. These ceramic heads were tested as part of a previous wear study [19] which used the same loading scenario. Within the present study, contact angle measurements have been made at these ceramic heads. Furthermore, the lubricant generated within the previous wear test [19] was used to analyze the ion level.

2.2. Hip Simulator Wear Test

The wear tests were performed according to ISO 14242 using a six-station hip wear simulator (Endolab GmbH, Rosenheim, Germany). The applied axial load and movements, containing flexion/extension, adduction/abduction and rotation, during one gait cycle, are shown in Figure 1. The tests were performed for 5×10^6 cycles at 1 Hz, in temperature-controlled (37 ± 2 °C) chambers. A lubricant bovine serum (Biochrom AG, Berlin, Germany) with a protein concentration of 30 g/L was used. Ethylenediaminetetraacetic acid (5.85 g/L) and sodium azide (1.85 g/L) were added to the lubricant to prevent the precipitation of metallic ions, and calcium phosphate and bacterial contamination. After every 500,000 cycles the lubricant was changed and wear was detected gravimetrically with a high precision balance (Sartorius ME235S, Sartorius AG, Goettingen, Germany). All samples were changed periodically, every 500,000 cycles, throughout the six stations of the hip simulator. The volumetric wear was calculated by dividing the gravimetrical wear (mg) by the density of the sequentially cross-linked polyethylene (0.9392 g/cm^3). In order to calculate the absorption of the lubricant at the inserts, two further polyethylene inserts were just axially loaded and used as a soak control.

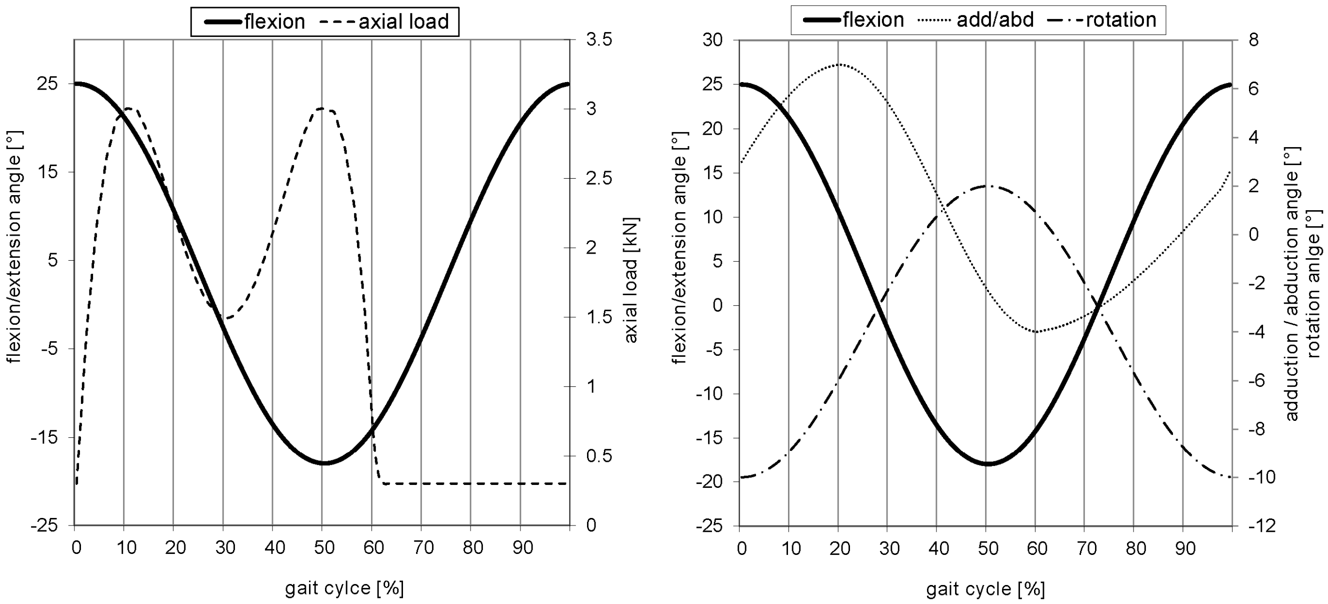

Figure 1. Applied movements throughout the wear simulation as prescribed by the current ISO 14242-1 standard [20].

2.3. Contact Angle Measurements

The wetting behavior of the lubricating fluid at the surface of the femoral heads was determined using a drop-shape analyzer (DSA25 Expert, KRÜSS GmbH, Hamburg, Germany). After hip simulator wear testing contact angles were measured at each femoral head in two different areas: first, at the pole of the femoral head representing the main contact area of the bearing; and second, at the inferior area of the femoral head near to the equator, representing a much less stressed articulation area (Figure 2).

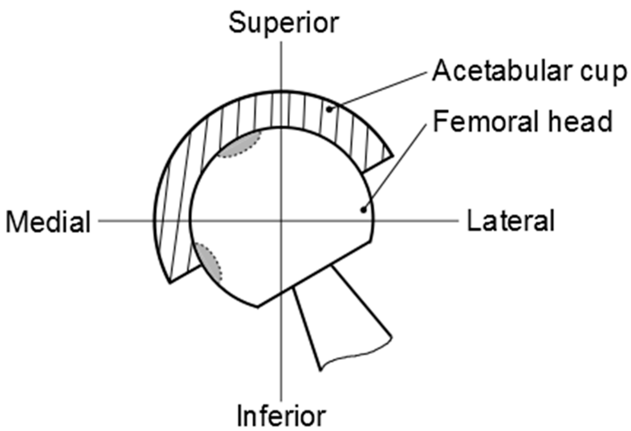

Figure 2. Antero-posterior view of the schematic mounting position according to ISO 14242, with locations of the contact angle measurement area (grey, delimited with dashed lines) at the femoral head.

In the beginning of each measurement the femoral heads were wetted with one droplet of the same lubricant which has been used in the wear simulator test before. Subsequently, an image of the droplet was captured which served as the basis for contact angle analyses. Each measurement at the pole area, as well as at the inferior area of the equator, was applied three times, always using a new droplet.

Between the individual droplet analyses, the femoral heads were cleaned in an ultrasonic bath, followed by rinsing in ultrapure-water, and drying at 80 °C for 20 min.

2.4. Analysis of the Cobalt Ion Level

The concentration of cobalt (Co) released from the femoral heads was measured by atomic absorption spectrometry (AAS) (ZEEnit 650, Analytik Jena AG, Jena, Germany) with electrothermal atomization. For detection a cobalt hollow cathode lamp (lamp current: 7.0 mA) emitting light with the wavelength of 240.7 nm was used. Before measurement the AAS was calibrated with well-defined Co concentrations, and the lubricants of the different bearings were diluted to a suitable concentration. The Co-ion level in the lubrication was measured in the lubricant of each bearing, every 500,000 cycles. Subsequently, 20 µL of the diluted lubricant was placed through the sample hole, and onto the platform of the graphite tube from an automated micropipette and sample changer. The tube was heated in a pre-programmed series of steps optimized for Co. The lubricant was evaporated in three steps: 1. 90 °C for 20 s; 2. 105 °C for 20 s; and 3. 110 °C for 10 s. The pyrolize step followed for 10 s at 1000 °C to eliminate residual organic material and to combust the sample into ash. Using a fast heating rate (1300 °C/s) the tube was heated to 2250 °C for about 4 s to vaporize and atomize elements into free atoms. This step included the element analysis. Some of the light emitted by the Co hollow cathode was absorbed in the test chamber by atomized Co atoms. The amount of passed light with the special wavelength was recorded by a detector, and compared with known passed light of adapted concentrations of Co, and thus the ion concentration could be calculated. The tube was cleaned by a final heating step at 2400 °C about 4 s.

2.5. Statistical Analysis

The statistical significance of the volumetric wear of the sequentially cross-linked polyethylene combined with the different femoral heads, the contact angles and Co-ion level of the different bearings, was assessed using the ONEWAY ANOVA test (IBM® SPSS® Statistics version 20 (IBM Corporation, New York, NY, USA)). For comparison of the contact angles at the pole area and at the equator area of the different femoral heads, the independent Student *t*-test was used. The presented data are shown as mean value ± standard deviation. *p*-values of <0.05 were considered significant.

3. Results

3.1. Wear Rates

The wear results for the CoCr and ceramic femoral heads against sequentially cross-linked polyethylene inserts are presented in Figure 3a. All types of femoral heads caused a linear wear behavior of the polyethylene over 5 million cycles without indications of initial bedding-in wear. The polyethylene inserts, combined with nitrogen-treated femoral heads, produced the lowest overall wear with 10 ± 0.88 mm^3, compared to the TiNbN bearings with 13.32 ± 2.00 mm^3.

Based on the overall wear results of this study, the mean wear rates (mm^3 million $cycles^{-1}$) are demonstrated in Figure 3b. The LFIT CoCr heads produced a polyethylene wear rate of 2.15 ± 0.18 mm^3·million $cycles^{-1}$ in comparison to the TiNbN-coated femoral heads with 2.66 ±

0.40 mm^3 million cycles^{-1}, as well as the alumina ceramic heads with 2.17 ± 0.40 mm^3·million cycles^{-1}. However, the wear rates were not significantly different ($p > 0.05$).

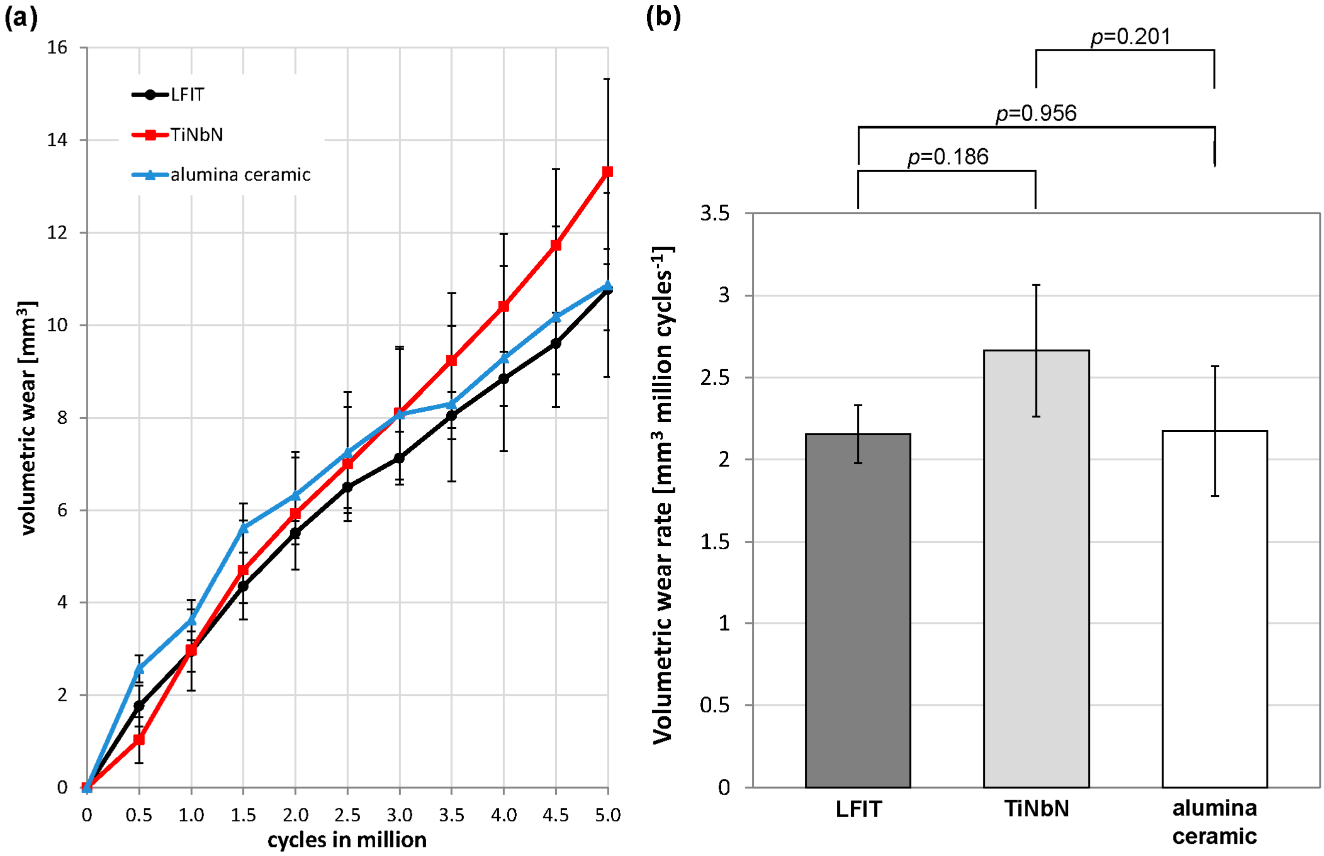

Figure 3. (**a**) Mean volumetric wear and (**b**) wear rates of the sequentially cross-linked polyethylene inserts combined with 36 mm diameter femoral heads modified with nitrogen treatment, TiNbN coating, as well as alumina ceramic [19].

At the end of the hip simulator test, both the CoCr femoral heads as well as the polyethylene inserts showed very small individual scratches on the main contact areas. The TiNbN coatings were undamaged without indications of breakthrough, voids or surface asperities.

3.2. Contact Angle Measurement

The contact angles of the investigated bearing surfaces are shown in Figure 4. The lowest contact angles were determined for the TiNbN coating, followed by angles of the alumina ceramic femoral heads. The differences of the contact angles in the pole area between the different materials were all significant ($p < 0.001$ for LFIT *vs.* TiNbN; LFIT *vs.* alumina ceramic; and TiNbN *vs.* alumina ceramic). At the less stressed equator area, the difference of the angles was not significant for LFIT compared to alumina ceramics ($p = 0.075$). Between LFIT *vs.* TiNbN and TiNbN *vs.* alumina ceramic the angles in the equator area were significantly different: both $p < 0.001$. For the surface-modified femoral heads, the contact angles were significantly higher in the pole area in contrast to the less stressed equator area (LFIT: $p < 0.001$, TiNbN: $p = 0.013$). At the alumina ceramic heads the contact angle was lower in the pole compared with the equator area. This difference was significant ($p = 0.011$).

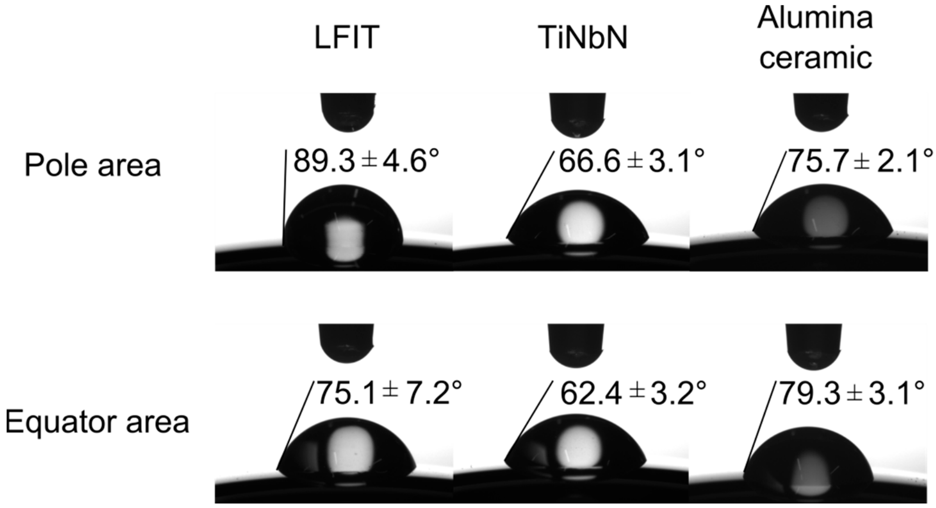

Figure 4. Contact angle measurement at different femoral counterfaces.

3.3. Cobalt Ion Concentration

Cobalt ions released into serum during wear testing were detected using atomic absorption spectrometry. The cumulative cobalt concentration after five million cycles was 1511.6 ± 128.2 µg/L for the LFIT femoral heads, 214.5 ± 150.0 µg/L for the TiNbN coupling, and 46.4 ± 4.7 µg/L for alumina ceramic heads. The lubricant of the alumina ceramic bearing demonstrated a small level of cobalt ions, indicating contamination originating from the metallic mountings of the test stations. The overall cumulative Co-ion concentration of the LFIT group was significantly higher than the alumina ceramic ($p < 0.001$) and TiNbN ($p = 0.001$). The difference between alumina ceramic and TiNbN was not significant ($p = 0.191$). Generally, the cobalt ion concentration showed a much larger steady increase for the nitrogen-treated femoral heads compared with the TiNbN specimens (Figure 5). Furthermore, the amount of cobalt ions decreased with the increasing number of cycles for the TiNbN-coated heads.

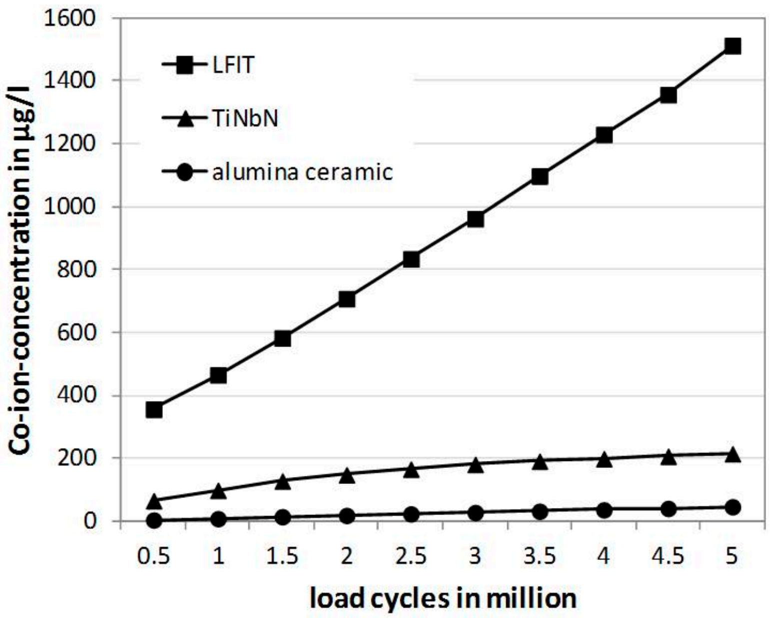

Figure 5. Cumulative cobalt ion concentration over a period of five million cycles analyzed from the used lubricant.

4. Discussion

The aim of this experimental study was to evaluate the influence of two different surface modifications on the wear behavior of sequentially cross-linked polyethylene inserts as well as their effect on the metal ion release.

In total hip arthroplasty, polyethylene wear is one of the major factors limiting the lifetime of the implant inside the human body [21]. Polyethylene wear debris may lead to adverse tissue reactions, followed by extensive bone loss and loosening of the fixation [22,23]. One approach to decrease polyethylene wear is to use CoCr femoral heads with a modified surface.

In our hip simulator wear study, with 36-mm diameter modified CoCr femoral heads against sequentially cross-linked polyethylene inserts, the mean wear rate was 2.15 ± 0.18 $mm^3 \cdot million\ cycles^{-1}$ in combination with the LFIT, and 2.66 ± 0.40 $mm^3 \cdot million\ cycles^{-1}$ for the TiNbN-coated femoral heads. In comparison to previous *in vitro* studies, the results showed that wear rates of both surface modifications were at least three-fold lower than these of traditional 36 mm CoCr-on-cross-linked polyethylene bearings [24–27]. Furthermore, the polyethylene wear could be reduced to the level of alumina ceramic heads [19,26].

In the present contribution, the TiNbN-coated femoral heads demonstrated smooth and intact articulation surfaces without localized damage, such as breakthrough, delamination or cohesive failure over the entire testing period of five million cycles. This excellent wear resistance was consistent with the findings of Galvin *et al.* [28] and Gutmanas *et al.* [29] after hip simulator wear testing with titanium nitride and chromium nitride coated femoral heads against ultra-high-molecular-weight polyethylene. In contrast to the promising *in vitro* results for coatings, some clinical reports showed failures of ceramic coatings in combination with hard-on-soft bearings some years ago. In a case report, Harman *et al.* [16] examined the articular surface of a titanium nitride (TiN) coated CoCr femoral head retrieved after one year of *in-situ* function. Circular voids without TiN coating and surface asperities were evident on the coated femoral heads. In another retrieval study of Raimondi *et al.* [17] fretting and coating breakthrough were observed at 2 out of 4 TiN-coated femoral heads from four patients, 18 to 96 months post-operatively. Both studies concluded an unsafe use of ceramic coatings in the field of hip arthroplasty. The occurred signs of fatigue can be attributed to limitations in the former coating technology, which may have resulted in inhomogeneous layer structures and poor adhesion of the coating. In the past, sputtering was a widely spread process in order to provide a coating at the bearing surfaces, using physical vapor deposition. The purpose was to generate denser coatings with a reduced roughness [13]. However, during sputtering the degree of ionization of the evaporated material is pretty low in comparison to arc deposition (close to 100% right next to the target surface) [30]. The higher the number of ions in the vacuum chamber, the more particles can be accelerated by the bias voltage. Therefore, with arc deposition the particles have a much higher kinetic energy and create coatings with a clearly higher adhesive strength and hardness compared to other deposition methods. In the present study, the TiNbN coating at the femoral heads was applied by a strongly poisoned cathode surface technology (SPCS). In this special type of arc deposition technology, the escape of the reactive gas during physical vapor deposition was guided specifically in order to reduce the number of inhomogeneities (droplets) in the coating structure. Moreover, the surface quality and density achieved with this procedure is comparable to those of the so-called "filtered arc technology", but without its drawbacks such as time- and cost-intensive filter cleaning or low deposition rates.

In addition to the TiNbN-coating, nitrogen treated CoCr femoral heads were used for testing. Similar to the coated femoral heads, a very small number of individual scratches were seen on the main bearing area with the naked eye, indicating that adverse third-bodies influenced the wear testing procedure. Ion treatment with nitrogen and therefore the phase transformation in the microstructure, had a positive impact on the wear behavior of sequentially annealed polyethylene. The surface modification resulted in the lowest average wear rate compared with the TiNbN-coated femoral heads. Nevertheless, differences in wear for the ion-treatment, as well as for the TiNbN-coating, were not statistically significant. In a clinical study, McGrory *et al.* [14] examined roughness and hardness characteristics of retrieved CoCr femoral heads from the same manufacturer, both with and without nitrogen ion treatment. The roughness parameters with ion treatment were lower compared with the non-treated surfaces, indicating that ion treatment increased the scratch resistance of the femoral heads. However, the achieved increased hardness with ion treatment appeared to degrade over time *in vivo* [14].

The secondary purpose of our study was to analyze the wetting behavior of both surface modifications and to compare them with values from alumina ceramics. Therefore we measured the contact angle in the loaded pole area, as well as in the less stressed inferior area of the femoral head near to the equator. The analysis demonstrated significant higher contact angles in the pole area in comparison to the equator area for both surface modifications, whereas the difference was clearly higher for the LFIT femoral heads. In contrast, alumina femoral heads showed increased contact angles in the equator area. Basically, lower contact angles at the bearing surface should indicate a more hydrophilic surface behavior, resulting in a better wettability [31]. However, within the present simulator study no correlation with contact angles and polyethylene wear could be demonstrated. This was consistent with the findings of Galvin *et al.* [28].

The evaluation of ion levels in the used bovine serum showed that cobalt ion release was higher for the LFIT compared with the TiNbN-coated CoCr heads. Both surface modifications were not able to avoid the ion release. However, with the TiNbN coating the release could be reduced by orders of magnitude.

Nevertheless, the ion level found with alumina ceramics ranged around the analytical detection limit of the measuring device, and therefore can be considered for reference.

The investigated surface-modified CoCr femoral heads provide an alternative to ceramic heads for total hip replacement. Within this experimental study, idealized load conditions according to the ISO standard [20] were considered which did not represent all aspects of everyday life activities [32]. Further experimental studies should analyze the effect of adverse conditions and an increased number of load cycles on the wear resistance of coated and ion-treated femoral heads.

5. Conclusions

The wear performance of sequentially cross-linked polyethylene inserts may be improved by ion-treated CoCr and TiNbN-coated CoCr femoral heads. Differences in polyethylene wear were not statistically significant compared with alumina heads. This comparable behavior could be attributed to the increased hardness of the modified CoCr surfaces, leading to more scratch resistance and long-term smoothness. Both surface modifications showed specific wettability, although a correlation with contact angles and polyethylene wear was not detectable within the study.

Cobalt ion release from the substrate could be reduced efficiently by the use of a TiNbN coating in contrast to CoCr heads treated with nitrogen ions.

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Author Contributions

Christian Fabry designed the study, performed the experiments and wrote the initial manuscript. Carmen Zietz performed the experiments, analyzed the data and did the statistical analysis. Axel Baumann prepared the TiNbN coating and supported the data analysis. Rainer Bader was the principal investigator for this research, and designed the study.

Conflicts of Interest

Christian Fabry and Axel Baumann are employees of DOT GmbH, Rostock, Germany. The other authors declare no conflict of interest.

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