

# Friction, wear and surface characterization of metal-on-metal implant in protein rich lubrications

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## Abstract:

Although various surface and interface characterization methods have been applied to study the physical wear, corrosion and implant surface interactions with biological environments, presently - in metal on metal (MOM) hip implant- the local and systematic effects of interaction between metal surfaces and protein rich lubrication in body are poorly understood.

*Materials and Methods:* Cobalt-chromium-molybdenum (CoCrMo) alloys have been used in MOM implants extensively. In the present study the samples were immersed in four different biological lubricants (Human serum, synovial fluid, MEM and distill water) for 10 min, 1 hr, and 5 days of immersion and then studied by X-ray Photoelectron Spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). XPS determined the chemistry of elements located within the top few nanometers of materials. Friction and wear behavior of CoCrMo substrate in different biological lubricants were also studied.

*Results and discussion:* Spectra from P2p<sub>3/2</sub>, O1s, Ca2p<sub>3/2</sub>, C1s and N1s were collected. Metallic substrates behaved differently when immersed in the same lubricant for different time intervals. The four lubricants reacted differently with metallic surfaces. Larger calcium deposits occurred in supersaturated physiological solutions. Deposition of calcium phosphate was different on CoCrMo alloys depending on the lubricant and the immersion period. Specimens immersed in synovial fluid gave thinner oxide layers and lower calcium phosphate deposits. For all specimens, water immersion resulted in thicker oxide layer. Synovial fluid gave lowest coefficient of friction when distill water gave the highest value. Generally wear was higher for disc in comparison to the pin (in the pin on plate test).

Key words: hip implant, load bearing, joint

## Introduction:

The number and occurrence of primary and revision hip and knee joint replacements are considerably increasing worldwide every year [1]. This fact induces that the quality of artificial joints is becoming increasingly important. The most widely used bearing couple in artificial hip-joint systems is the combination of an ultra-high-molecular weight polyethylene (UHMWPE) acetabular component and a metal femoral component. The cobalt chromium molybdenum (CoCrMo) alloy is used widely as metal-bearing material in artificial joint systems. CoCrMo alloy have good mechanical properties, castability,

corrosion resistance and wear resistance [2-5]. In total hip arthroplasty (THA), osteolysis caused by the wear particles from UHMWPE has been recognized as a serious concern [6-8]. Efforts to decrease these particles have focused on bearing material improvement and the use of combinations other than metal-on-UHMWPE [9-12]. Nevertheless during the past decade metal-on-metal (MOM) hip joint replacements have become used increasingly for younger patients as an effective alternative to metal-on-polyethylene (MOP) implants. The advantages of the MOM bearings are the absence of the generation of UHMWPE wear debris and decreased wear as

compared to that in the case of the MOP bearings [13-16]. The reported biocompatibility of cobalt based alloys is linked to the spontaneous formation of a thin (1-4 nm) passive oxide film on their surface consisting of a mixture of cobalt, chromium and molybdenum oxides [2]. This very thin protecting film is however susceptible to fracture due to wear and mechanical loading in the joint, resulting in exposure of the reactive base alloy to the physiological medium [17, 18].

The presence of inorganic ions such as phosphates can affect the passive film characteristics and subsequently change the electrochemical behavior of the implant [19-21]. The interplay between phosphate ions and high protein concentrations (0.5 gL<sup>-1</sup>) was discussed recently by Mischler and co-workers [21].

In the present study, X-ray Photoelectron Spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) have been used to probe for differences in the surface chemistry of the freshly produced CoCrMo alloy implant substrate after it was immersed in different protein rich media after 10 min, 1 hour or 5 days for different time intervals. Friction and wear behavior of CoCrMo alloys in different protein rich lubrications was also studied.

In this study the following hypothesis were investigated:

- Is ion etching with XPS successful method to eliminate totally oxide layers or other contaminations from metal surfaces prior to immersion into biological lubrications?
- The fresh active metal surfaces behave differently in different protein rich environments.
- Relationship between metal surface, metal oxide and the dissolved component in the solutions at different time intervals is related strongly to the surface chemistry of the substrate before immersion
- Is the friction and wear behavior of substrate affected by nature of the lubricant

#### **Materials and experimental methods:**

Portland Orthopaedics hip joint substrate (CoCrMo alloy; supplier Carpenter Technology were studied. Human serum was provided by the national Blood Service, after defrosting the pH

was measured to be 7.4. Synovial fluid was recovered from primary total joint replacement surgery; the pH was measured 7.9 to 8.1. Filtered fetal bovine serum (FBS) was supplied by Invitrogen and was added as 10 wt% to alpha-MEM (Minimum Essential Medium) with pH of 7.6.

#### Surface characterization:

*Surface sputtering with XPS:* Metal specimens were cut and prepared to samples of 5x5 mm in diameter size. The samples were mirror polished. Three different immersion periods were studied (10 min, 1 hour and 5 days). The specimens were removed and rinsed with Milli-Q water and dried at the end of the immersion period before they were placed in XPS or ToF-SIMS.

To eliminate any contamination or oxidation from surface of the metal substrates argon ion etch gun set to 5 KV at 20 mA, over a 5 mm area were used. The etch cycles consisting of 60 sec etch 30 sec settle time followed by small spot survey spectra and the survey shows that surface were clean from any contamination or oxide layer after different time intervals.

Specimens were analysed by XPS and ToF-SIMS separately after they were polished, cleaned, ion etched, and immersed for different time intervals in the four different biological fluids. XPS determines the amounts of elements located within the top few nanometers of materials. Peaks were fitted using CasaXPS, and several XPS databases were referenced for the interpretation of different BEs.

A PHI TRIFT 2100 time-of-flight secondary ion mass spectrometer (ToF-SIMS) equipped with a gallium liquid metal ion gun was used for ToF-SIMS measurements. The sputter depth was of 30nm. Comparison of similar samples is feasible with ToF-SIMS, as the relative intensities of small signals due, for instance, to small amounts of adsorbed proteins can be assessed semi-quantitatively as long as matrix effects are similar.

#### Tribology testing:

Cetr UMT micro macro test machine. Reciprocating pin on plate configuration. Output variables are wear rate and friction. Micro macro is a multi-purpose machine, utilising a number of drive “modules” to permit the performance of a

wide variety of tests, both on the micro- and macro scales. These can be used with both dry and fully lubricated contacts. Sensors allow, amongst other factors, friction, wear rate, temperature and loading to be monitored continuously. Horizontal reciprocating drive was used with custom made holders for plates. The machine contained a stainless steel bath and lubrication level was maintained by the continual addition of fluid. Wear rate are measured and calculated by use of a Mettler Toledo AT201 scale.

Specimens (CoCrMo) were manufactured with spark eroding and turning and mirror polished. Hardness of specimens was measured in a micro hardness indenter (vicker hardness). The surface roughness (Ra) of the components prior to testing was less than 0.01  $\mu\text{m}$ . Three freshly prepared substrates were tested lubricants. SyF, HS, MEM and DW were compared as lubrication system.

Cleaning of specimens and holders: Samples were cleaned through 5 min ultrasonic cleaner in acetone, then 48 h in ethanol, finished with 5 min ultrasonic cleaner in ethanol prior testing

Specimen dimension: Pin dimension (Diameter: 6.35 mm, Length: 20 mm, Nose radius: 50 mm).

Plate (Length: 25 mm, Width: 11 mm, Depth: 5 mm)

The test pin was held in contact with the plate by a pin holder held centrally over the moving components. The pin holder was allowed to move vertically so that the pin was always in contact with the plate, regardless of the amount of wear occurring. The pin was loaded with 50 N. The reciprocating frequency was 1 Hertz with stroke length of 20 mm. Initial hertzian mean contact pressure of 250 MPa, dropped during the wear process. Tests were carried out for duration of 24 hours, then the rig was stopped and load was removed. Tested lubrication were distilled water (DW), filtered human serum (HS), MEM+ 10wt%FBS (MEM) or synovial fluid (SyF).

Wear factor calculation:

**Volume loss of the material can be calculated**

by

$$v = \frac{m_1 - m_2}{\rho} \text{ mm}^3$$

**Results**

Surface characterization:

XPS and ToF-SIMS were employed to analyse the surface chemistry of the CoCrMo substrate after immersion in different biological lubrications. The differences in the corrosive nature of these four media after 10 min, 1 hour and 5 days of immersion was emphasized by differences in the oxide layer, which varied in thickness for different media.

In the present study, the ion gun etching with the help of XPS were employed to eliminate different contaminations/oxidation from substrate surfaces. After ion etching of the CoCrMo substrate, a final spectrum were collected to assure that there are no contaminations such as adventitious C1s or metal oxides on the surface before they immersed in different protein rich median.

The oxide/passive layer on the metal surface is essential to preserve the surface of the alloy from corrosion and chromium oxide barrier protects the underlying metal from further corrosion. A complex oxide layer is formed when the fresh surface of alloy is electrochemically biased and immersed in biological media. Through XPS surface analyses, the absolute peak area of chromium oxide were measured and purity of the oxide and the thickness and the density of the overlying deposits of protein, calcium phosphate or any other absorbed molecules or contaminations.

The comparison between metal signal before and after ion etching, and after immersion shows that the amount of metal oxide and metal elements which revealed in XPS measurements depends upon the thickness and concentration of adsorbed layer from the biological lubrication on the substrate. As the metal oxide overlies the base metal, the ratio of Cr<sub>2</sub>O<sub>3</sub> to Cr was also related to the thickness and concentration of the elements adsorbed on the alloy surface.

The XPS spectra were collected from all samples of the following photoelectronic regions: C1s, N1s, P2p<sub>3/2</sub>, Ca2p<sub>3/2</sub>, O1s, Cr2p<sub>3/2</sub>, and Co2p<sub>3/2</sub> and Mo3d.

In contrast to most of the investigations which has been carried out previously, CoCrMo alloy samples did not have adventitious carbon and oxygen due to the ion etching procedure prior to immersion, therefore the analysis of C1s is meaningful in order to

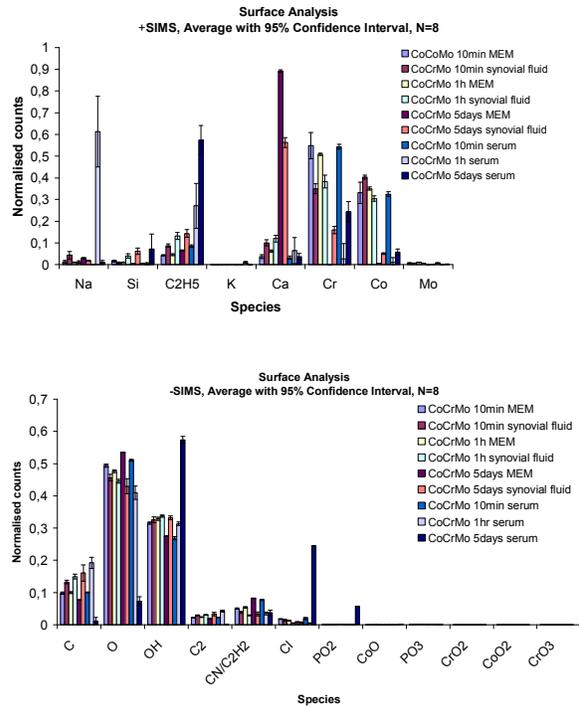
analyses the type of carbon which was added to the surfaces from different treatments and different time intervals.

In all cases, a decreasing metal signal is observed with increasing protein or calcium phosphate layer on the substrate. After 10 min and 1h immersion in MEM+10%FBS, synovial fluid and human serum still metal elements e.g.  $\text{Co}_{2p}$ ,  $\text{Cr}_{2p}$  and low amount of  $\text{Mo}_{3d}$  still was detectable from CoCrMo alloy surface. After 5 days immersion in human serum and MEM+10%FBS, as a result of the detection limit of XPS ( $\sim 0.1\%$ ) and calcium phosphate shielding, the underlying metal elements and oxides were not detected. Thus, significant calcium phosphate deposit was detected by XPS on these two samples. Synovial fluid immersed samples showed a small peak of metal elements after 5 days. CoCrMo immersed in human serum for 5 days had thinner/less calcium phosphate shielding compare to the two other lubrications. It is essential to remark that the depth of analysis of standard XPS is a few nanometers, and compositional information is not possible below approximately 5 nm. This is especially relevant for samples immersed for 5 days in biological media, where a thick calcium phosphate coverage and strong signal of Ca, P and N were observed.

Corrosion in water resulted in oxides and hydroxides of chromium and cobalt, as shown by the prominent wt% for Cr, Co and O. The metal oxidation and corrosion in different medium was also observed on the surfaces together with calcium and nitrogen.

**ToF-SIMS surface analysis:** Figure 1a and 1b shows a representative -SIMS and +SIMS spectrum of CoCrMo alloy samples immersed in different protein rich biological lubricants for 10 min, 1h and days. Major peaks at 16 and 17 Daltons indicated  $\text{O}^-$  and

$\text{OH}^-$  ions, respectively. Carbon related peaks are present at 12 ( $\text{C}^-$ ), 24 ( $\text{C}_2^-$ ) and 26 ( $\text{CN}^-$ ). Smaller peaks are also observed from  $\text{Cl}^-$  (35 and 37 Da) and ions from phosphate species  $\text{PO}_2^-$  (63 Da) and  $\text{PO}_3^-$  (79 Da). Metal oxide peaks from the alloy are occurred at 75, 84, 91 and 100 Da, corresponding to the species  $\text{CoO}^-$ ,  $\text{CrO}_2^-$ ,  $\text{CoO}_2^-$  and  $\text{CrO}_3^-$ , respectively.  $\text{CrO}_3^-$  and  $\text{CaOH}^-$  (57 Da) were used to infer the nature of the surface layers of the samples.

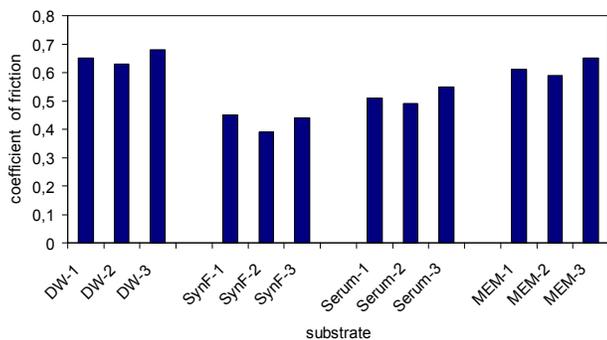


**Figure 1a and 1b:** show the depth profiles (+SIMS and -SIMS) of the Cr, Ca, Co  $\text{C}_2\text{H}_5$  and  $\text{PO}_2^-$ ,  $\text{CrO}_2^-$ ,  $\text{CoO}^-$ ,  $\text{O}^-$ ,  $\text{CaOH}^-$  and  $\text{OH}^-$  ions at the surface of the CoCr specimens after immersion in synovial fluid, MEM+10%FBS and serum for 10 min, 1h and 5 days.

**Table 1:** XPS data of C1s, N1s, O1s, P2p and Ca2p for CoCrMo immersed in serum, synovial fluid and MEM

XPS analyses of CoCrMo alloy specimens											
Sample condition		C 1s		N 1s		O 1s		P 2p		Ca 2p	
		Area% & FWHM	Area% (BE)	Area% & FWHM	Area% (BE)	Area% & FWHM	Area% (BE)	Area% & FWHM	Area% (BE)	Area% & FWHM	Area% (BE)
10min	Syn f	45.58% (3.481)	285 (75.5%) 288.2 (15.8%) 286.5 (8.7%)	12.64% (2.764)	400.1 (86.5%) 400.9 (13.5%)	28.82% (3.292)	531.4 (91.3%) 529.2 (8.7%)	-----	-----	-----	-----
	serum	25.7% (3.183)	20.7% (285.2) 62.7% (287.5) 16.6% (290.3)	16.9% (2.52)	11.1% (397.2) 62.6% (400.1) 26.4% (402)	25.7% (3.183)	71.6% (531.5) 28.4% (533.8)	-----	-----	-----	-----
	MEM	57.44% (3.023)	285 (64.3%) 286.5 (28.8%) 288.2 (5.5%) 290.3 (1.4%)	12.2% (2.809)	400 (100%)	24.04% (3.055)	531.7 (95.2%) 533.57 (4.8%)	-----	-----	-----	-----
1 h	Syn f	49.75% (3.047)	55.6% (285.5) 15.5% (288.2) 28.89% (286.8)	11.8% (2.593)	88.7% (399.9) 11.3% (401)	26.65% (3.607)	87.37% (531.16) 12.63% (532.9)	-----	-----	-----	-----
	serum	56.03% (3.452)	79.04% (285.04) 20.96% (287.94)	13.7% (2.733)	100% (398.9)	56.03% (3.425)	94.2% (530.83) 5.8% (529.69)	0.49% (3.543)	100% (132.99)	-----	-----
	MEM	58.14% (3.725)	285 (71%) 288.2 (19.9%) 286.5 (9.1%)	12.51% (2.837)	399.90 (90.3%) 400.78 (9.7%)	23.53% (3.156)	531.83 (95.3%) 531.1 (4.7%)	-----	-----	-----	-----
5days	Syn f	64.35% (3.371)	52.35% (285) 16.92% (288.23) 30.74% (286.19)	13% (2.454)	92.35% (400.1) 7.65% (401.54)	20.4% (3.03)	86.81% (531.5) 13.19% (532.93)	-----	-----	-----	-----
	Serum	56.09% (3.22)	70.17% (285) 17.03% (287) 12.8% (288.6)	0.31% (2.907)	100% (400)	26.2% (2.95)	88.83% (531.66) 11.17% (2.207)	1.99% (2.96)	100% (133.7)	2.31% (2.73)	66.99% (348.4) 33.01% (351.9)
	MEM	40.24% (4.09)	71.21% (285) 15.12% (286.7) 13.67% (288.5)	9.42% (2.478)	93.29% (400) 6.71% (401.8)	37.93% (2.89)	100% (531.8)	5.18% (2.589)	100% (133.5)	7.23% (2.562)	66.78% (348.4) 33.22% (351.9)

*Tribological testing*:: Coefficient of friction for tested substrates is shown in Figure 2. Different lubricants were compared.



**Figure 2:** CoCrMo friction coefficient in different lubricants

Friction was lowest when synovial fluid was used as the lubricant and highest when distill water was used as lubricant.

In general weight loss was higher in pin in comparison to the plate. Higher weight loss, when serum was used as lubricant weight loss for pin was  $0.02$  to  $0.038 \pm 10\%$  and for plate it was  $0.008$  to  $0.01 \pm 15\%$ .

Vickers hardness test: Hardness test has been carried out by using Vickers micro hardness. The hardness of CoCrMo specimen was  $428 \pm 4.73$ .

### Discussion:

The present investigation advances the knowledge base of the field of orthopaedic materials and implants. The project innovation lies in the idea of generating fresh and reactive surfaces of CoCrMo alloy by ion beam etching under ultra-high vacuum (UHV) conditions and then studying their surfaces before allowing them to interact with the relevant body fluids. The proposed interaction of freshly generated substrates with synovial fluid, a key fluid of practical relevance, is an added innovation, because almost all of the research effort in the area has been focussed on alloy substrates which are treated somehow and then made to interact with fluids like serum and MEM which are not as relevant as synovial fluid for orthopaedic implants applications.

The affect of different media on the corrosion and friction coefficient for CoCrMo was varied depending which solution it was immersed into. Human serum produced thinner deposit of calcium phosphate, recognisable from the XPS and ToF-SIMS depth profile. Literature indicates calcium phosphate deposit occur in supersaturated physiological solution [22-24]. Synovial fluid

sample had a thin deposit of calcium phosphate and MEM showed the highest.

The migration of ions from metal surface has been demonstrated to be the source of dissolved ions and the cause of thickening of the metal oxide during surface corrosion in many reactive metals [25,26].

ToF-SIMS and XPS analyses showed calcium phosphate deposits from MEM, human serum, and synovial fluid on the surfaces of the specimens. Proteoglycons, pyrophosphates, phospholipids, lubricin, and superficial zone protein are some well known components of synovial fluid and have been identified as possible causes of the lack of significant calcium phosphate deposition in this environment. Circulation of these compounds around the whole implant may inhibit calcium phosphate deposition. The significant calcium phosphate deposit was only detected for specimens immersed for 5-days in serum and MEM+10%FBS (smaller peak of calcium phosphate observed for synovial fluid). After 5 days immersion due to the calcium phosphate shielding on the surface of the CoCr alloys and the limitation of the depth of measurement of XPS the metal elements of the bulk substrate e.g. Cr and Co were not detected. This fact is noticeable for specimens immersed for 5 days in lubricants where there is more than 10 nm thick coverage by elements on the surface of the substrates. Metallic specimens corroded and resulted in oxides and hydroxides of Cr, Co in all four lubricants, though lower oxides and hydroxides were observed when specimens were immersed in synovial fluid, serum and MEM, and Ca, N, P and S were observed as well.

**ToF-SIMS analyses:** The depth profiles characterisation revealed that samples immersed in different biological lubricants had very different corrosion depth profile. Samples immersed in MEM+10%FEB and serum showed more calcium and phosphate deposit, represented by the large  $PO_2^-$  ion signal and  $Ca^+$ . The  $PO_2^-$  signals from the synovial fluid immersed samples were significantly lower than for the serum samples. After sputtering through this layer, the Cr and Co oxy-ion signals increased and then decreased as the bulk metal was encountered.

Within the calcium phosphate layer, however, Cr and Co oxy-ions were observed, and it is clear that these ions were incorporated into the calcium phosphate deposit and originate from the surface of the alloy. Sundgren et al [29] using Auger electron spectroscopy, also found phosphate and calcium ions in the oxide layer of titanium and stainless steel after many years implantation in vivo. It has been shown that synovial fluid produced a surprising thin oxide layer on CoCrMo alloys, and it was hypothesised that an organic compound acted as a protective layer [30].

***Wear and friction testing (comparison of different lubrications):*** Due to the lubrication various hydrodynamic and elastrohydrodynamic mechanisms, friction is minimum or almost close to zero in a healthy human joint. Under normal conditions the lubricant separates the two bearing surfaces from each other. When these natural materials are replaced with artificial materials, due to the materials' inability to produce a permanent lubrication, the tribological conditions are greatly jeopardised. Thereafter these artificial materials are subject to increased friction and wear [31]. For comparative screening purposes pin on plate tests were carried out. These were severe tests to determine the wear resistance of tested materials. Tipper et al, 1999 and Firkins 2001b [32,33], showed that this might tend to produce higher wear factors than in a dynamically loaded hip simulator. Wear was not significantly different when different lubrication was used, though in synovial fluid less wear was observed. This also could relate to the characteristics of the proteins in synovial fluid.

**Conclusion:** Conclusion: Glycoaminoglycans (GAG) and related proteins may hinder calcium phosphate deposition on samples immersed in synovial fluid. ToF-SIMS measurements showed that the resulting corrosion products depend upon the nature of the environment.

Passivation of the metal surface is fundamental to corrosion resistance where a metallic oxide (like chromium oxide) barrier protects the underlying metal from further corrosion. The amount and purity of the oxide layer on immersed specimens depends on the density and thickness of the overlying deposits of calcium phosphate, proteins

and other adsorbed molecules, as well the contaminations. The lower calcium phosphate deposit in synovial fluid might be due to the present of components such as GAG and associated proteins, which stop the calcium deposition due to the circulation of the fluid in the effective joint space.

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