NT2008-69-22

BIOTRIBOLOGY: SURFACE CHEMISTRY CHARACTERIZATION OF METAL-ON-METAL IMPLANTS IN PROTEIN RICH ENVIRONMENT

Emami N[1,2], Larsson R[1], Höglund E[1]
[1] Division of Machine Elements, Luleå University of Technology, Luleå, Sweden
[2] Ian Wark Research Institute, University of South Australia, Australia
Nazanin.emami@ltu.se

ABSTRACT

Introduction: Osteolysis induced by wear particles in metal-on-polyethylene hip implants has been the key motivation to look for alternative bearings and in fact emergence and development of new metal-on-metal (MOM) implant materials for joint replacement. However, while the volume of wear particles produced in metal-on-metal articulations is lower the number of particles produced is higher per volume of wear, due to the reduced size of wear particles. Although various surface and interface characterization methods have been applied to study the physical wear, corrosion and implant surface interactions with biological environments, presently the local and systematic effects of metal debris are poorly understood. Materials and Methods: Cobalt-chromium-molybdenium (CoCr) alloys have been used in MOM implants extensively. Metallic samples were cut and mirror polished. In the present study The samples were immersed in four different biological lubricants (Human serum, synovial fluid, MEM and Milli-Q 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 whitin the top few nanometers of materials. Significant differences in the absorbed layers and differences in the corrosive nature of Ti and CoCr implant substrates and wear particles were found. Results and discussion: Spectra from P 2p3/2, O1s, Ca2p3/2, C1s and N1s were collected. Metallic substrates behaved differently when immersed in the same lubricant. The four lubricants reacted different with metallic surfaces. Larger calcium deposits occurred in supersaturated physiological solutions. Deposition of calcium phosphate was different on CoCr alloys depending on the lubricant and the immersion period. Specimens immersed into synovial fluid gave thinner oxide layers and lower calcium phosphate deposits. For all specimens, water immersion resulted in thicker oxide layer. For many reactive metals, dissolution of ions from the metal surface takes place along with thickening of the metal oxide during passivation, or surface

corrosion. 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. The thickness of the calcium phosphate deposits was different for different metal substrate.

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 chromium-cobalt-molybdenum (Cr-Co-Mo) alloy and titanium-6aluminum-4vanadium alloy (Ti-6Al-4V) are used widely as metal-bearing materials in artificial joint systems. Both alloys have good mechanical properties, castability, corrosion resistance and wear resistance. In total hip arthroplasty (THA), osteolysis caused by the wear particles from UHMWPE has been recognized as a serious issue [2-4]. Efforts to decrease these particles have focused on bearing material improvement and the use of combinations other than metal-on-UHMWPE[5-8]. 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. Recently, different MOM artificial hip joint systems consisting surface engineered or not from Cr-Co-Mo or Ti-6Al-4V have been studied by different investigators. 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[9-12]. Various surface and interface characterizations have been applied to study the physical wear, corrosion and implant surface interactions with biological environments after placement in the body on both CrCoand Ti alloys that have been used extensively for MOM implants[8,13-16]. 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 CrCo and Ti alloy implant substrate, and of wear particles after they had been immersed in four different biological lubricants. In addition, the impact of different cleaning procedures was investigated, which showed their importance and the sensitivity of sample preparation. XPS and ToF-SIMS were employed to analyse the layer absorbed from the contacting biological media and the surface chemistry of immersed samples. 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.

HYPOTHEIS

Materials and experimental methods

Portland Orthopaedics hip joint substrate (CoCrMo alloy; supplier Carpenter Technology were studied. Metal specimens were cut and prepared to samples of 5x5 mm in diameter size. The samples were mirror polished. Four different cleaning systems (air plasma reactor, air plasma cleaner, UV ozone cleaner and conventional methanol cleaning procedure) used prior to biointerface characterization studies were compared. The successful method with high precision to expose the fresh metal surfaces and remove any contamination from surfaces were achieved by argon ion etch gun set to 5 KV at 20 mA, over a 5 mm area. 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 but generally etching of the CrCoMo alloy took less time than Ti alloy.

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.

Human serum was provided by the Australian Red Cross, 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.

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. 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.

RESULTS

Cleaning procedures: None of the traditional cleaning methods were effective in order to reduce the C1s and O1s from the surface of the specimens. UV cleaning method had no affect of the samples surface, where the plasma cleaner methods not only did not reduced the oxide and carbonated layer but also added other type of contaminations on the surfaces such as florin, which was very difficult to remove later on. The methanol and acetone cleaning method which has been used by most of investigators prior to immersion and surface characterization did add some more C1s to the surfaces. In the present study, the most successful method for elimination of different contaminations from substrate surfaces, were achieved by using the ion gun etching with the help of XPS

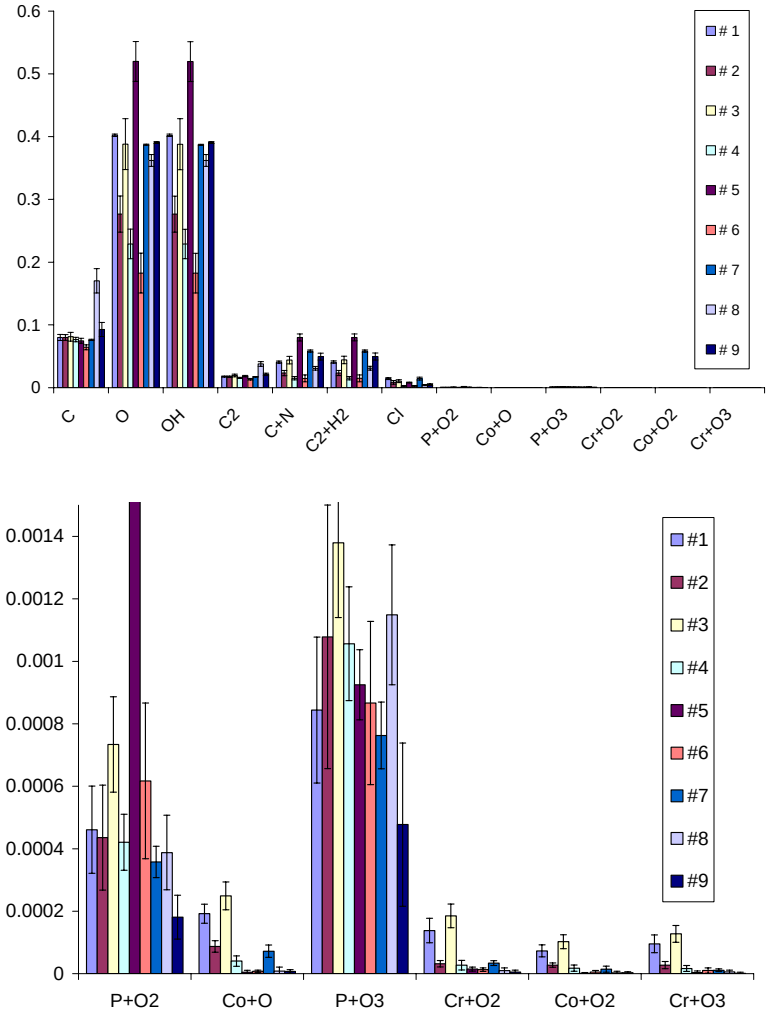
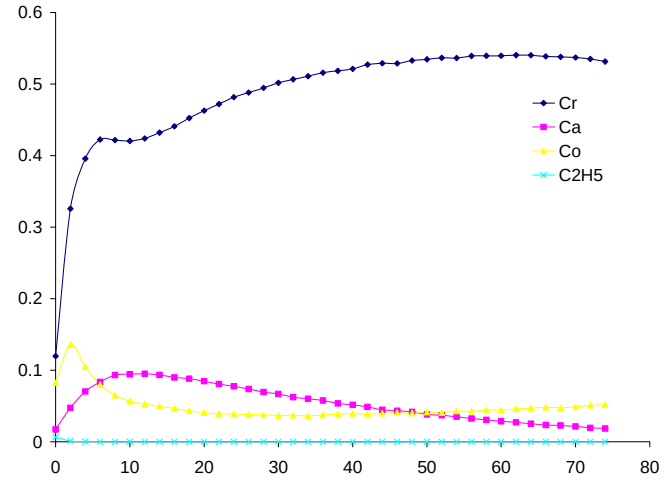
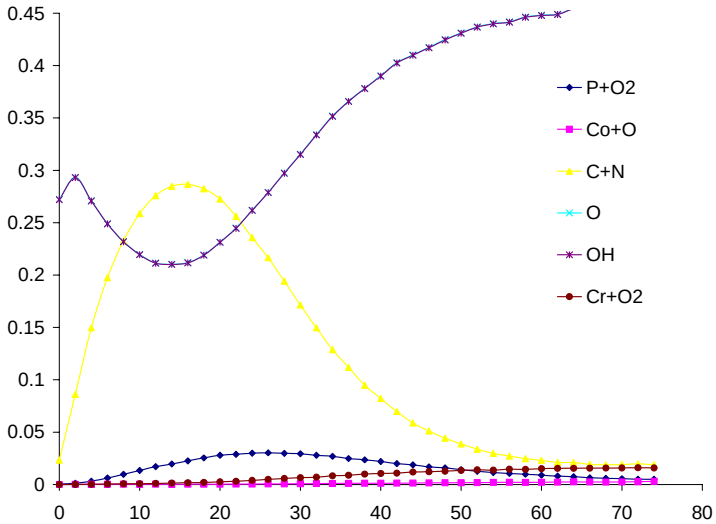


Figure1a and 1b: A typical spectrum (negative SIMS) for CrCo specimens immersed in serum, synovial fluid and MEM for different time intervals.

Figure 1 shows a representative ToF-SIMS spectrum of CrCo alloy samples immersed in different protein rich biological lubricants for 10 min, 1h and 5 days. The sputter depth was of 30nm. Major peaks at 16 and 17 Daltons indicated O^- and OH^- ions, respectively. Carbon related peaks are present at 12 (C^-), 24 (C_2^-) and 26 (CN^-). Smaller peaks are also observed from Cl^- (35 and 37 Da) and ions from phosphate species PO_2^- (63 Da) and PO_3^- (79 Da).

Metal oxide peaks from the alloy are occurred (fig 1b) at 75, 84, 91 and 100 Da, corresponding to the species CoO^-, CrO_2^-, CoO_2^- and CrO_3^-, respectively. CrO_3^- and $CaOH^-$ (57 Da) were used to infer the nature of the surface layers of the samples.





Figures 2 and 3 show the depth profiles (+SIMS and –SIMS) of the Cr, Ca, Co C2H5 and PO_2^-, CrO_2^-, CoO^-, O^-, $CaOH^-$ and OH^- ions at the surface of the CoCr specimens after immersion in MEM for 10 min and 1h.

The depth profiles characterisation revealed that samples immersed in different biological lubricants had very different corrosion depth profile and only samples immersed in serum showed more calcium phosphate deposit, represented by the large PO_2^- ion signal and $CaOH^-$. The PO_2^- signals from the synovial fluid immersed samples were significantly lower than for the serum samples. This suggested that the deposit from synovial fluid was not coherent but located in islands, a commen observation where deposition of HAP occurs at low concentration [17, 18].

On the other hand, the CrO_2^- signals from these samples were much stronger. The water immersed samples did not show any PO_2^- signal, but the FWHM values for the O^- and CO_2^- signals gave a thicker oxide ~ 3.5 nm. At the surface of the human serum immersed sample, the Cr and Co oxy-ion signals were reduced due to the presence of a calcium phosphate layer. After sputtering through this layer, the Cr and Co oxy-ion signals increased and then decreased as the bulk metal was encountered, as shown in figure 2. 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[19] 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 [20]

XPS results: X-ray photoelectron spectra were collected from all samples of the following photoelectronic regions: P 2p3/2, Ca 2p3/2, O 1s, Cr 2P3/2, and Co 2P3/2. An example of wide spectrum of CrCo immersed in peak fitting for the Cr2p doublet for the samples immersed in human serum for I h is shown in figure 4.

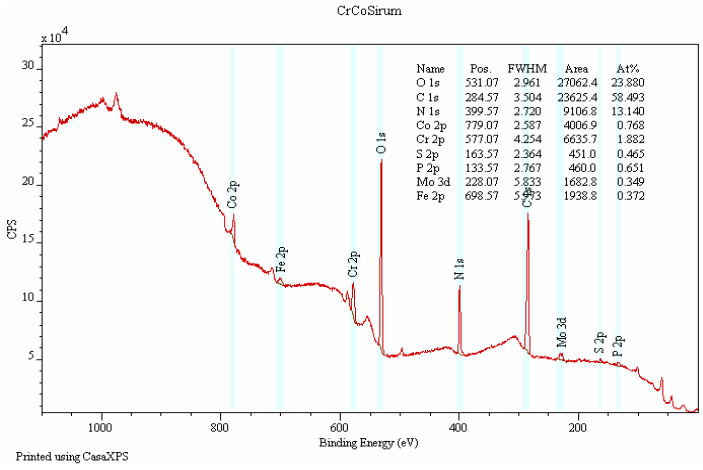


Figure 4: CrCo immersed in Human serum for 1h.

The contribution of the oxide and metal to the Cr2P core level is clearly demonstrated. As a result of the detection limit of XPS (~ 0.1%), 5 days human serum and synovial fluid immersed samples did not show all these spectral peaks clearly, even where samples were immersed in solutions containing the compounds. Thus, significant calcium phosphate deposit was detected by XPS. Synovial fluid immersed samples showed a small peak where no Cr and Co were detected on human serum samples due to the poor XPS sensitivity and thick calcium phosphate coverage on the samples after 5 days. 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 serum immersed sample which has thick calcium phosphate coverage.

Corrosion in water resulted in oxides and hydroxides of chromium and cobalt, as shown by the prominent peaks for Cr, Co and O. The same peaks were observed for samples immersed in MEM, synovial fluid and serum but CrCo are reduced and Ca and N are observed. The human serum immersed samples had no Cr and Co peaks after 5 days and instead strong signal of Ca, P and N were observed.

DISCUSSION

The affect of different media on the corrosion for CrCo was varied depending which solution it was immersed into. Human serum produced a thick deposit of calcium phosphate, recognisable on the XPS wide scan (figure 4) and ToF-SIMS depth profile. Litreture indicates calcium phosphate deposit occur in supersaturated physiological solution[17,21,22]. Synovial fluid sample had a thin deposit of calcium phosphate.

The migration of ions from the metal surface has been demonstrated to be the source of dissolved ions and the cause of thickening of the metal oxide during passivation or surface corrosion in many reactive metals[23,24].

ToF-SIMS and XPS analyses showed calcium phosphate deposits from MEM, human serum, and synovial fluid on the surfaces of the specimens. The noticeable amount of phosphate anion deposit is perhaps due to the composition of the CrCo alloy used as hip implant substrate, which is known to consist predominantly hydroxyl-phosphate compounds. 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 synovial fluid (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. It is very important to notice the depth of the standard analysis by XPS which is few nanometers[25,26] and therefore the compositional information is not possible below approximately 5 nm. 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 (specially relevant for the serum immersed specimens).

Metallic specimens corroded and resulted in oxides and hydroxides of Cr, Co in all four lubricants, thought 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. Ca, P and N were dominating on the specimens immersed in human serum.

CONCLUSION

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. Therefore, the relationship between different cleaning procedures, metallic oxides and metal surface and the dissolved component in the solutions at different time intervals were studied. 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 ration of Cr_2O_3 to Cr was calculated for CrCo alloy and was related to the thickness and/or concentration of the oxide in different lubricants. 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.

REFERENCES

[1]. Kurtz S, Mowat F, Ong K, Chan N, Lau E, Halpern M. Prevalence of primary and revision total hip and knee arthroplasty in the United State from 1990 through 2002. J Bone Joint Surg Am 2005;87(7):1487-97.

[2]. Harris WH. The problem is osteolysis. Clin Orthop 1995;311:46-53.

[3]. Kobayashi A, Freeman MA, Bonfield W, Kadoya Y, Yamac T, Al-Saffar N, et al. Number of polyethylene particles and osteolysis in total joint replacements. A quantitative study using a tissue-digestion method. J Bone Joint Surg Br 1997;79(5):844-8

[4]. Sochart DH. Relationship of acetabular wear to osteolysis and loosening in total hip arthroplasty. Clin Orthop 1999;363:135-50.

[5]. McKellop H, Shen FW, Lu B, Campbell P, Salovery R. Development of an extremely wear-resistant ultra high molecular weight polyethylene for hip replacements. J Orthop Res 1999;17(2):157-67.

[6]. Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH. A novel method of crosslinking ultra-high-molecular-weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties: recipient of the 1999 HAP Paul Award. J Arthroplasty 2001;16(2):149-60.

[7]. Urban JA, Garvin KL, Boese CK, Bryson L, Pedersen DR, Callaghan JJ, et al. Ceramic-on-polyethylene bearing surfaces in total hip arthroplasty. Seventeen to twenty-one-year results. J Bone Joint Surg Am. 2001;83(11):1688-94.

[8]. Emami N, Griesser H. Biointerface characterization of metal-on-metal implant materials using XPS and ToF-SIMS: A comparison of Human serum, synovial fluid, MEM and water. ICONN 2008- Melbourne

[9]. St John KR, Zardiackas LD, Poggie RA. Wear evaluation of cobalt-chromium alloy for use in a metal-on-metal hip prosthesis. J Biomed Mater Res B Appl Biomater 2004;68(1):1-14.

[10]. McMinn DJ, Daniel J, Pynsent PB, Pradhan C. Mini-incision resurfacing arthroplasty of hip through the posterior approach. Clin Orthop Relat Res 2005;441:91-8

[11] Clarke IC, Good V, William P, Schroeder D, Anissian L, Stark A, et al. Ultra-low wear rates of Rigid-on-rigid bearings in total hip replacements. Proc Inst Mech Eng [H] 2000;214(4):331-47

[12] Fisher J, Hu XQ, Stewart TD, William S, Tipper JL, Ingham E, et al. Wear of surface enginnering metal-on-metal hip prostheses. J Mater Sci Mater Med 2004;15(3):225-35.

[13] Kyomoto M, Iwasaki Y, Moro T, et al. High lubricious surface of cobalt-chromium-molybdenium alloy prepared by grafting poly(2-methacryloyloxyethyl phosphrylcholine). Biomater 2007;28:3121-30

[14] Lin HY, Bumgardner JD. Changes in the surface oxide composition of Cr-Co-Mo implants alloy by macrophage cells and their released reactive chemical species. Biomater 2004;25:1233-38.

[15]. Decking R, Reuter P, Huttner M, Puhl W, Claes LE, Scharf HP. Surface composition analysis of failed cementless CoCr- and Ti-based alloy total hip implants. J Biomed Mater Res;2003:64B(2):99-107

[16] Lin HY, Bumgardner JD. Changes in surface composition of the Ti-6Al-4V implant alloy cultured macrophage cells 2004;225:21-8.

[17]. Kokubo T. Design of bioactive bone substitutes based on biomineralization process. Mater Sci Eng C Biosci 2005;25:97-104

[18]. Matiz MF, Pham MT, Matz W, et al., Promoted calcium-phosphate precipitation from solution on titanium for improved biocompatibility by ion implantation. Surf Coat Technol.2002;158:151-56

[19]. Sundgren JE, Bodo P, Lundstrom I, et al. Auger electron spectroscopic studies of stainless-steel implants. J Biomed Mater Res.1985;19:663-71

[20]. Lewis AC, Kilburn MR, Papageorgiou I, et al. The effect of synovial fluid, phosphate buffered saline solution and water on the dissolution and corrosion properties of CoCrMo alloys as used in orthopaedic implants. J Biomed Mater Res. 2005;73A:456-67.

[21]. Chusuei CC, Goodman DW, Van Stipdonk MJ etal., -soild-liquid adsorption of calcium phosphate on TiO2. Langmuir. 1999:15;7355-60.

[22].Lu X, Leng Y. Theoretical analysis of calcium phosphate precipitation in simulated body fluid. Biomaterials. 2005;26:1097-1108.

[23]. Tomashov ND, Chernova GP, Ruscol YS. The passivation of alloys of titanium bases. Electrochem Acta. 1974;19:159-72.

[24]. Shih CC, Shih CM, Su YY. Effect of surface oxide properties on corrosion resistance of 316L stainless steel for biomedical applications. Corros Sci. 2004;46:427-41.

[25]. Watts JF, Wolstenholme J. 2003. Chichester, UK: John Wiley & Sons Ltd.

[26]. H.J. Griesser; McArthur, S.L.; Wagner, M.S.; Castner, D.G.; Kingshott, P.; McLean, K.M, Biopolymers at Interfaces, 2nd Edition, Ed. Malmsten, M. (Marcel Dekker Inc) p. 641-669 (2003)