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Tribocorrosion of Diamond Like Carbon (DLC) coatings for biomedical applications

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ABSTRACT

Tribocorrosion has arisen as one of the most important material degradation processes in biomedical applications; thus, the improvement of the materials used in hip or knee prosthesis is very relevant.

The aim of this project is to test the outstanding properties of the diamond like carbon material as a coating; a comparison between CoCrMo with several types of DLC as ta-C, a-C:H and metal doped with Ti and Si.
Also different deposition methods will be compared like Physical Vapour Deposition (PVD) and Plasma Enhanced Chemical Vapour Deposition (PECVD).

For this purpose, electrochemical techniques in NaCl, phosphate buffer solution (PBS) and Albumin at 37ºC will be investigated.

Samples characterization will be done by means of scanning electron microscope (SEM), confocal microscope and Hardness Vickers.

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Tribocorrosion of Diamond Like Carbon (DLC) coatings for biomedical applications

Tribocorrosion is a term describing the degradation of materials, which results from the combined action of wear and corrosion. Orthopedic applications, artificial joints, e.g. hip and knee prostheses, include bearing surfaces where the material is subjected to sliding wear and immersed in the body fluid are required to possess good tribocorrosion resistance.

However, the use of metals in biomedical bearing applications is limited because of its risk in metal ions release occurred at metal-on-metal implants, in addition to their relatively poor wear resistance. These deficiencies can be overcome with a proper surface modification such as nitriding or diamond-like carbon (DLC) coatings. DLC coatings are a promising surface treatments for implants because they have the advantage of high hardness, good wear resistance, low coefficient of friction and good biocompatibility. However, there are limited studies on the tribocorrosion performance and mechanisms of DLC coatings in simulated body fluids and therefore this master thesis will focus on studying them.

Materials for this project are:

- Samples: un-coated CoCrMo, ta-C coated CoCrMo, a-C:H coated CoCrMo and a-C:H(Ti) coated CoCrMo.
- Two different electrolytes will be tested: PBS and PBS with albumin.

Specific objectives of the project are:

- Identify the tribocorrosion mechanisms of DLC coatings in simulated body fluids by using triboelectrochemical techniques (reciprocating tribometer).
- Identify the role of the coating type on the tribocorrosion mechanisms.
- Electrochemical study of the materials in different simulated body fluids.
- The tests will be performed at different electrode potentials. The potentials will be chosen after performing an electrochemical study.
- Perform a study of metal ion release to the electrolyte after tribocorrosion by ICP. This implies keeping the electrolyte after testing.
    - A protocol for collecting the electrolyte should be carefully developed and proposed.

Formal requirements:

Three weeks after start of the thesis work, an A3 sheet illustrating the work is to be handed in. A template for this presentation is available on the IPM's web site under the menu "Masteroppgave" (http://www.ntnu.no/ipm/masteroppgave). This sheet should be updated one week before the master's thesis is submitted.

Risk assessment of experimental activities shall always be performed. Experimental work defined in the problem description shall be planed and risk assessed up-front and within 3 weeks after receiving the problem text. Any specific experimental activities which are not properly covered by the general risk assessment shall be particularly assessed before performing the experimental work. Risk assessments should be signed by the supervisor and copies shall be included in the appendix of the thesis.

The thesis should include the signed problem text, and be written as a research report with summary both in English and Norwegian, conclusion, literature references, table of contents, etc. During preparation of the text, the candidate should make efforts to create a well arranged and well written report. To ease the evaluation of the thesis, it is important to cross-reference text, tables and figures. For evaluation of the work a thorough discussion of results is appreciated.

The thesis shall be submitted electronically via DAIM, NTNU's system for Digital Archiving and Submission of Master's theses.

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1. INTRODUCTION

1.1 PREAMBLE

Many studies have been carried out, during the last years, related to biomedicine. Tribocorrosion in artificial joints has arisen as a wide, prosperous and useful field of study; by enhancing prosthesis, human's lifestyle can be improved. The aim of these studies is to improve lasting, functionality and safety.

Despite the advances in the field, there are still some problems that has to be coped; along time span replacements tend to deteriorate due to the dynamic load that are subjected, thus new materials are being tested in order to enhance implants. Several problems occur along prosthesis lifespan such as wear debris, which leads to inflammation of the tissue that surrounds the joint [1] [2]. In addition to the tribology process, the corrosion has to be taken into account, since artificial joints tend to be in contact with body fluids, which are mainly composed of saline solution and proteins. Hence, oxidation wear will arise and it will be of huge importance to understand every aspect so that the effects of this can be diminished.

A material suitable to be used in joint replacements has to be both a biomaterial and biocompatible, it will be discussed later in profound, but for now it is interesting to know that a good implant will have to be sterling in these aspects.

Due to the importance of the biocompatibility of the material used in biomedical applications, metal and alloys are commonly used for this purpose because of its good properties such as wear resistance, hardness, electrical conductivity, etc. Here it is found stainless steel, CoCrMo or Ti alloys.
Not all the materials used in joint replacement have the same behaviour, the alloy CoCrMo is a good alternative against stainless steel because of its lack of Ni or Ti which are not a very suitable option in some cases, e.g. allergy to Ni or wear in Ti [3].

Diamond like carbon (DLC) emerged as a suitable material for biomedical applications with outstanding properties, due to its similarity to diamond, in terms of physical and mechanical properties, such as very low friction coefficient, low wear, high hardness, high chemical inertness, excellent thermal conductivity among others. [1] [4].

There is a lack of research of this material for this purpose, and that is going to be performed more profoundly here. In addition, it is going to be studied tribocorrosion in presence of simulated body fluids (as said above, containing proteins) which follow complex mechanisms and is highly complicated to forecast its behaviour.

1.2 PURPOSE

The aim of this master thesis is to figure out how CoCrMo behaves under different coatings such as ta-C, a-C:H, a-C:H(Ti and Si) compared to uncoated samples.
In addition, it is going to be carried out a comparison of two different methods of deposition of the coating namely Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD).

The objectives of this paper are:

- Identify the tribocorrosion mechanisms of DLC coatings in simulated body fluids by using triboelectrochemical techniques.
- Identify the role of the coating type on the tribocorrosion mechanisms.
- Electrochemical study of the materials in different simulated body fluids.

The tests will be performed at different electrode potentials. The potentials will be chosen after performing an electrochemical study.

It is going to be performed under different parameters, such as different potentials like anodic and open circuit potential (OCP) and in presence of different electrolytes.
The electrolytes used will be 0.9% NaCl, phosphate-buffered solution (PBS) and PBS+Albumin.
Phosphate buffered solution which osmolality and ion concentration is similar to the body fluid, and as the name indicates (buffer) the aim of it is to maintain the ph stable.
The electrolytes will be used in that order, respectively, in order to have an idea of how the PBS+Albumin should behave; this last solution is the one closer to the body fluid, and will differ from the other solutions because of the protein.

2. THEORY

2.1 PROSTHESIS

Tribocorrosion can be applied to a lot of fields but this work is going to be focused in orthopaedic applications, artificial joints, such as hip and knee prosthesis.

In the figures below (Figure 1 and Figure 2) it can be seen the knee with arthritis and the knee with the prosthesis, and the same with a hip replacement.

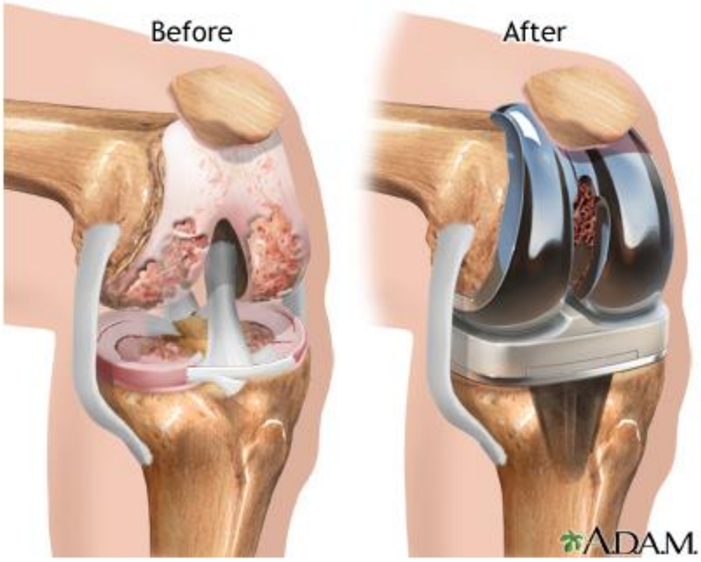


Figure 1 Damaged knee and artificial joint replacement [5]

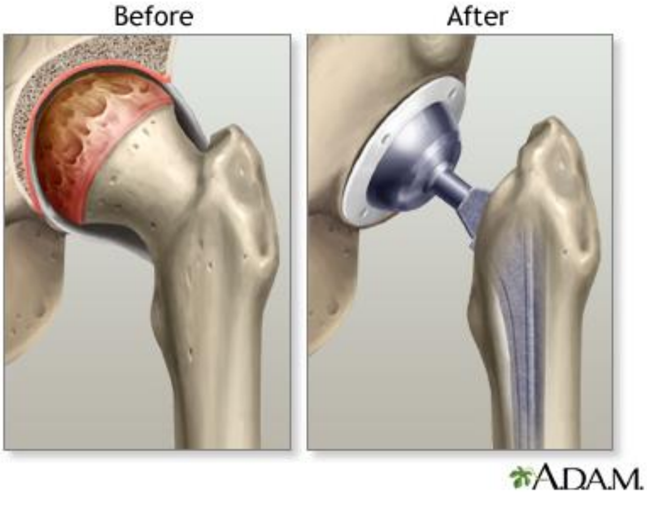


Figure 2 Damaged hip and artificial joint replacement [5]

Artificial joints are subjected to stresses, there is a sliding contact that among the parts that leads to wear and with that the debris is formed, it is proved that wear debris as well as metal ion release may cause inflammation of the tissue in the surroundings, bone loses, some patients develop also allergy to certain metals and of course decreases the lifespan of the implant [2].

2.2 CORROSION

Corrosion is the degradation of a metal by means of electrochemical reaction with the environment. Due to this process either there is a loss of the material or the environment is adsorbed by the metal. [3] [6]
As said before, corrosion can be by chemical reaction or electrochemical reaction; this paper is going to discuss the second one since it is the one present in the field of study.

In order to have this reaction it is necessary to have two electrical conductors or electrodes and an electrolyte that will allow the positive current to flow from the positive electrode to the negative one.

Electrochemical corrosion involves two processes, the reduction of the electrode (cathode) and the oxidation of the electrode (anode); examples of these reactions are:

Cathodic reaction: $H^{+} \rightarrow \frac{1}{2} H - e^{-}$ [Eq.1]

Anodic reaction: $Fe^{2+} \rightarrow Fe^{3+} + e^{+}$ [Eq.2]

During the anodic reaction there is an oxidation of the metal and during the cathodic reaction a reduction. The current goes and leaves from the cathode and anode respectively; the anode and the cathode can be different materials/metals or the same one but different areas on it.

The electrons are released to the metal and lead to a potential (measured in Volts) that can be measured with respect to the standard hydrogen ion reaction.

Different metals have different potentials, and their mutual ordering on the Electrochemical Series determines whether a particular metal will act as the anode (i.e. corrode) or act as the cathode. The more negative the potential, the more likely the metal is to corrode.

- ✓ **DAMAGES DUE TO CORROSION**

Uniform Attack: most common one, it can be seen because of rushing and tarnishing.

Localized Attack or Pitting: when not all the areas are corroded the same quantity.

In the figure above (Figure 3) different types of corrosion can be seen.

The pitting factor can be described as the ratio between the depths of the deepest pit of corrosion divided by the penetration average, all calculated from the material's lost weight.

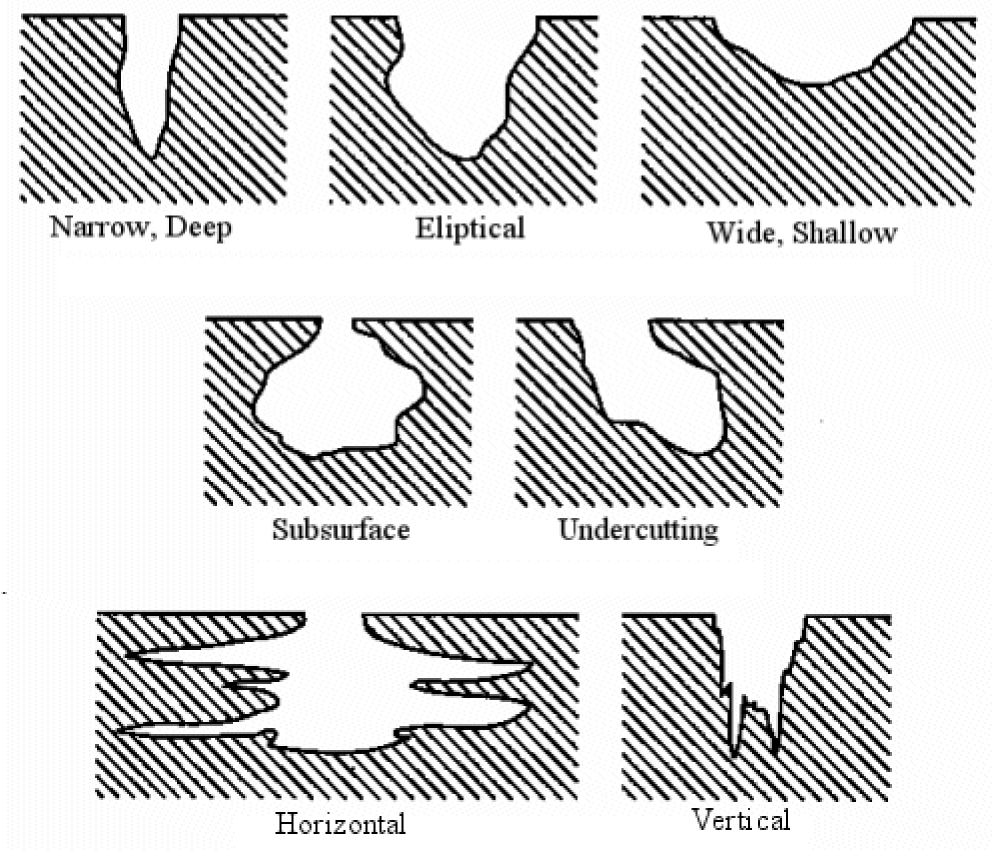


Figure 3 Types of corrosion damage [7]

- ✓ **KINETICS: POLARIZATION**

The Gibbs free energy is a high used value to measure the tendency of a reaction to go forward or backward, i.e. from product to reactive and vice versa).

$$\Delta G = \Delta H - T \cdot \Delta S \quad \text{[Eq.3]}$$

This value depends on the enthalpy, the entropy and the temperature as it can be seen. The formula is comprised of the first term (ΔH) that represents the total energy of the system and a second term (($T \cdot \Delta S$) that represents the energy that cannot be used (or take advantage of it). Therefore, this parameter is called Gibbs free energy because it is the energy that can be used.

This definition allows three different possibilities:

- $\Delta G < 0$ Spontaneous reaction
- $\Delta G = 0$ Reaction in equilibrium
- $\Delta G < 0$ Not spontaneous reaction

In addition, this value will be of greater importance since in electrochemical corrosion, the electromotive force (emf) represents the tendency of a metal to be corroded [8] [2], this can be express also in terms of a formula:

$$\Delta G = -n \cdot F \cdot E \qquad \text{[Eq.4]}$$

Where:

- n is the number of electrons in the reaction
- F is a constant (Faraday's constant)
- E is the potential

According to that, only by measuring the potential it will be possible to figure out the spontaneity of the reaction. By the formula above:

- $E < 0$ Not spontaneous reaction
- $E = 0$ Reaction in equilibrium
- $E < 0$ Spontaneous equilibrium

✓ POLARIZATION CURVES

By means of using the Faraday's law (equation below) the weight loss can give the corrosion rate [9]

$$I = n \cdot F \cdot \frac{dn_i}{dt} \qquad \text{[Eq.5]}$$

Where:

- I is the current
- N is the charge number
- F is the Faraday's constant
- $\frac{dn_i}{dt}$ is the rate of the reaction

That's why, there is a relation between the rate of reaction and the current density flowing. [10]

Several forms can be used to plot the curves, in this paper, the potential will be plotted against the logarithm of the current density; it will be clear in the plot two branches, the anodic and the cathodic one and where they intersect, that will be the corrosion potential (E_{corr}).
The corrosion potential (E_{corr}) is the potential when the current is zero, obtained as a result of open the circuit, that is why is also called open circuit potential (OCP).

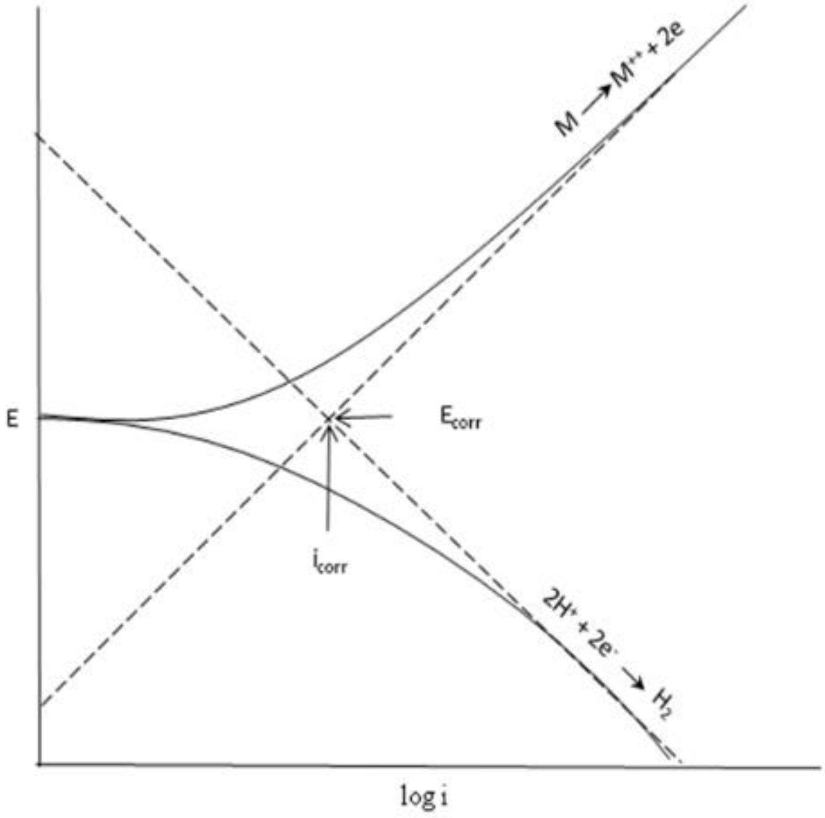


Figure 4 Polarization Curve

In the figure above (Figure 4), an example of a polarization curve is displayed.

At the point E_{corr} , the rate of cathodic reduction is equal to the rate of anodic oxidation. That value can be calculated by means of the Tafel equation:

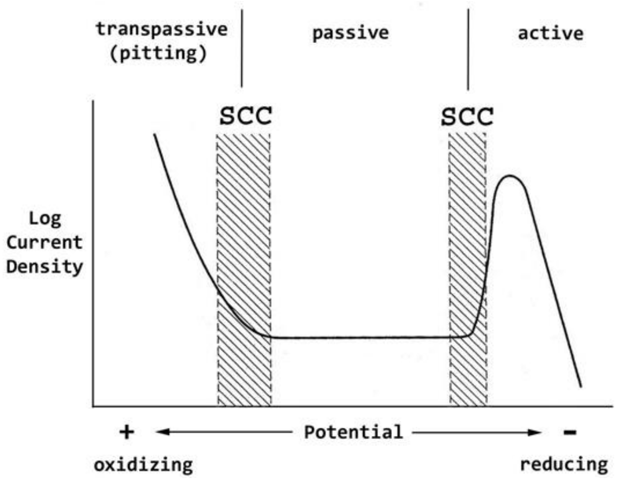
$$\mu = a + b \cdot \log(i) \text{ ; } \mu \text{ is the polarization} \quad \text{[Eq.6]}$$

This is one of the advantages of using the plot log(i) vs E, by extrapolating the linear parts of the anodic and cathodic branches the determination of the i_{corr} is possible.

- ✓ **Passivation**

Passivation is the formation of a thin layer over the surface of the material that protects it against corrosion. Typically, this film is comprised of oxides of the metal.

In Figure 5 all types of regions possible in a polarization are shown,



During the passive region the corrosion rate is lower due to this protective layer, the current density is constant.

Passivation of metals depends of different factors such as the environment, passivation current density, passivation potential and passive current density; and there are factors which also influence these factors, e.g. pH of the electrolyte.

2.3 TRIBOLOGY

Tribology is derived from the ancient Greek, comprised of two words “tribos” which means rubbing or sliding and “logy” which means knowledge of or science.

Even though this term is relatively new, the application of it can be seen from the very early of our age, e.g. when human realized that by rubbing two stones fire could be created. In the figure below, an Egyptian tomb painting from 2400 BC, a man can be seen pouring some liquid (maybe water) in front of a sledge that other men were transporting, and by doing this it is easier to transport.

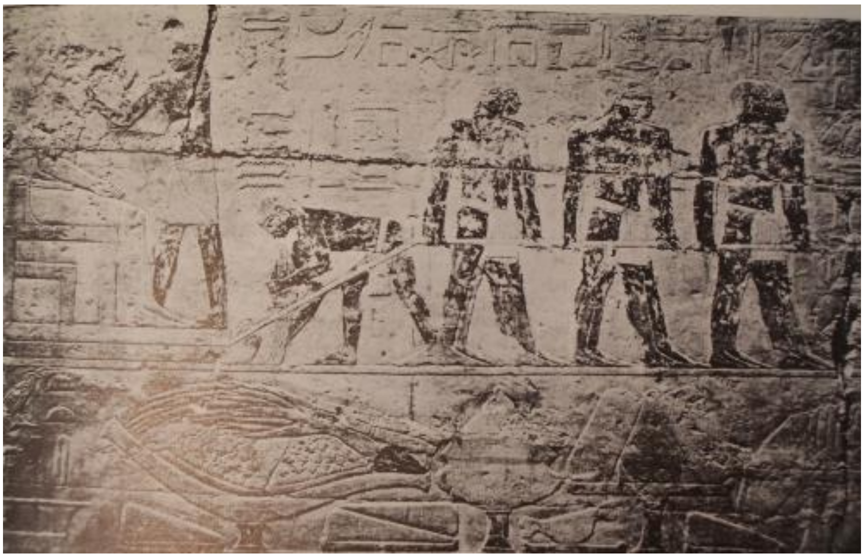


Figure 6 Egyptian tomb [26]

Figure 7 Egyptian tomb in detail. Pouring lubricant [27]

First time the word tribology was used was in 1966 by Dr. H. Peter Jost in his famous report “The Jost Report” where he explained how much money, the UK, was being squandered by not taking into account tribological principles.
First man to enunciate laws related to this field was Leonardo Da Vinci , who claimed that the areas in contact have no effect on the friction and that if the load is increased the friction coefficient will increase proportionally; that was almost 500 years ago. [11]

✓ MECHANISM

Basically, friction is the resistance that materials in contact, have to relative motion.

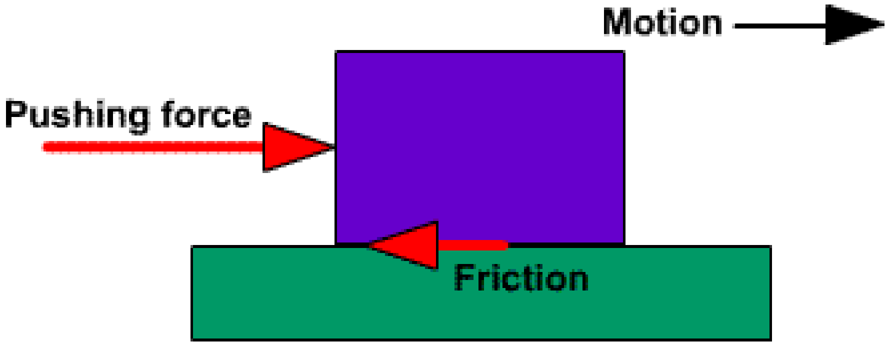


Figure 8 Friction Force [28]

Two types of friction exist:

- Static friction that appears when the sliding wants to be started to slide
- Dynamic friction is the one need to maintain the motion.

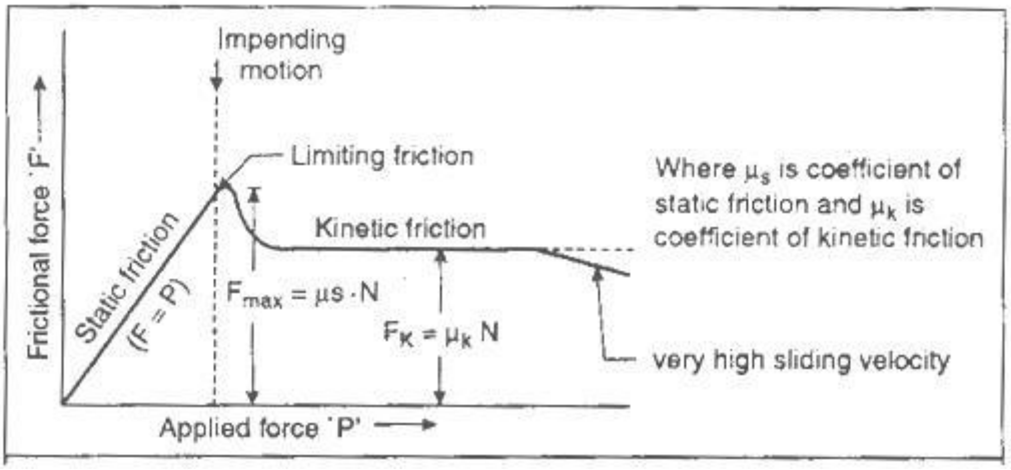


Figure 9 Variation of tangential force against time [29]

The static friction is higher than the dynamic ($\mu_s > \mu_d$). Displayed in Figure 9.

The friction force is often proportional to the normal force applied to the body, and the friction coefficient can be calculated as follows:

$$\mu = \frac{F}{W} \qquad \text{[Eq.7]}$$

Where:

- F is the tangential friction force
- W is the normal force load

Friction has to components, first one is called adhesion and the second one is plowing:

$$\mu = \mu_a + \mu_p \qquad \text{[Eq.8]}$$

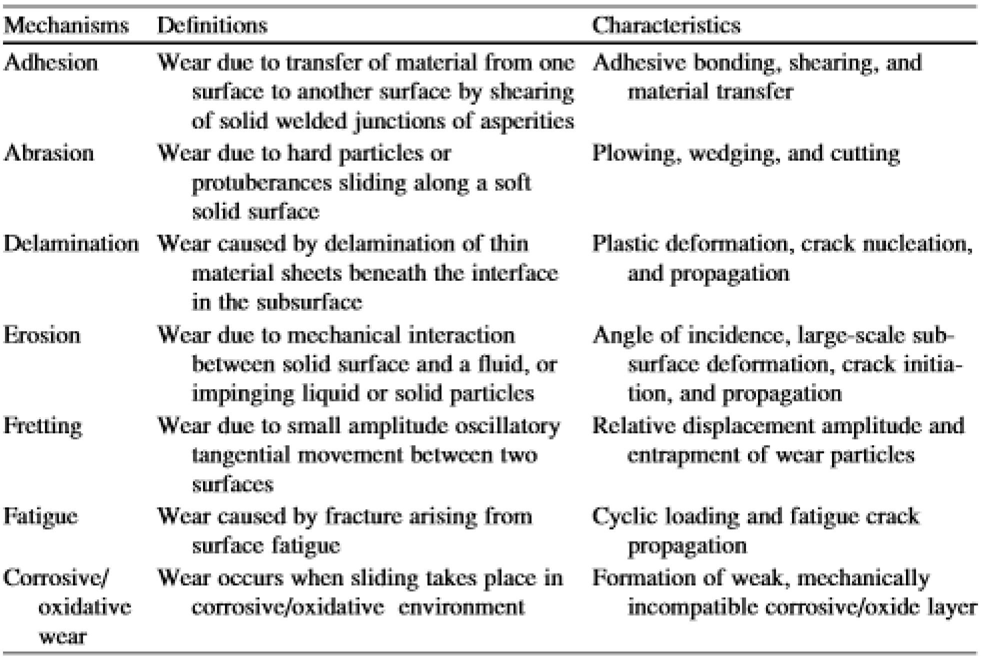
- Adhesion friction appears when the contact between two objects takes place at the asperities of these ones, so that the real contact area is very small and the pressure is high so that plastic deformation arises and the materials get adhered due to it.
- Plowing friction emerges if objects in contact are not same hard or soft, in this case, the hard one will penetrate the softer one by deforming plastically itself. [12]

There are several factors that can influence the friction, they are not going to be explained here since it is out of the matter of this paper but the complexity of these mechanisms has to be shown.

- Surface roughness
- Surface topography
- Crystal structure (this will be a relevant component since the DLC coatings that were used in this research have different structures)
- Strain hardening and hardness
- Elastic and shear modulus
- Grain size
- Surface energy
- Normal Load
- Sliding Velocity
- Environment
- Temperature

2.4 WEAR

Wear is defined as the loss of material by a mechanical action. During this process, the material on the surface is displaced and the properties of the material can be varied.



Mechanisms	Definitions	Characteristics
Adhesion	Wear due to transfer of material from one surface to another surface by shearing of solid welded junctions of asperities	Adhesive bonding, shearing, and material transfer
Abrasion	Wear due to hard particles or protuberances sliding along a soft solid surface	Plowing, wedging, and cutting
Delamination	Wear caused by delamination of thin material sheets beneath the interface in the subsurface	Plastic deformation, crack nucleation, and propagation
Erosion	Wear due to mechanical interaction between solid surface and a fluid, or impinging liquid or solid particles	Angle of incidence, large-scale subsurface deformation, crack initiation, and propagation
Fretting	Wear due to small amplitude oscillatory tangential movement between two surfaces	Relative displacement amplitude and entrapment of wear particles
Fatigue	Wear caused by fracture arising from surface fatigue	Cyclic loading and fatigue crack propagation
Corrosive/ oxidative wear	Wear occurs when sliding takes place in corrosive/oxidative environment	Formation of weak, mechanically incompatible corrosive/oxide layer

Figure 10 Different types of wear mechanisms [12]

Above (Figure 10) there is a table with different types of wear mechanisms, but only the most usual mechanisms are going to be discussed here, since the combination of adhesion and abrasion are two-thirds of all wear processes that can be seen in the industry.
Adhesion and abrasive mechanisms have been discussed before in the two components of friction.

Oxidation wear also called since the 90s tribocorrosion is going to be present in all experiments and sample; therefore it is going to be explained in more detail in next section.

2.5 TRIBOCORROSION

This mechanism appears when at the same time to the wear, corrosion is taking place. As the aim of this paper is biomedical applications, in join and hip replacements, the environment is the body with its fluids and there will be also wear due to the relative motion, so it is going to be present always.

In the case that these two processes appear at the same time, four stages could be seen:

The most desired stage; it will appear a layer strong enough to protect the material from either the corrosion or the rubbing.

A thin layer will be created but it will not be strong enough to remain permanently so the rubbing will remove it and it will be created afterwards; this will lead to a high corrosion rate and will be repeated in a cyclic process.

The layer might be worn out, not totally like the case above, and a galvanic coupling will lead to an intense corrosion by anodic in this gaps.

Corrosion and wear acting separately.

The most common stage is the second one since the layer is thin so it cannot protect the material permanently.

There are several approaches to measure the tribocorrosion, in this paper will be considered: synergistic, mechanistic and third body. [14]

✓ SYNERGISTIC APPROACH

This method was proposed by a group in the US Bureau of Mines (mid80s) based on the reports by Pitt and Chang (1986) and Kotlyar et al. (1988).

This approach calculates the total material loss due to tribocorrosion by means of calculating each mechanism separately and adding a synergistic factor.
The synergistic factor is comprised of two values, one measure how the wear varies the corrosion rate (ΔC_W) and the other one measures how the corrosion varies the wear rate (ΔW_C).

$$S = \Delta \mathrm{CW}_C + \Delta \mathrm{WC}_W \qquad \text{[Eq.9]}$$

Then, the total material loss can be calculate by adding the action of the corrosion (C_0),measured alone, without other mechanisms, pure corrosion, the contribution of the wear (W_0) measured at cathodic potential (to be sure that there is no contribution of the corrosion) and the synergistic factor already explained.

$$T = C_0 + W_0 + S \qquad \text{[Eq.10]}$$

✓ MECHANISTIC APPROACH

This approach is comprised by two separate mechanisms, first one is the anodic dissolution and the second one is the mechanical wear.

At Ecole Polytechnique Fédérale de Lausanne (EPFL, Switzerland), it was discovered a way to quantify both mechanisms.

The total wear volume (W_t) is calculated as the sum of the metal loss due to mechanical wear (V_w) and to chemical or electrochemical oxidation (V_o).

$$W_t = V_w + V_o \qquad \text{[Eq. 11]}$$

The chemical value can be calculated by means of equation 12. Where Q is the electric charge flowing, M is the atomic mass, n is apparent valence, F is Faraday’s constant and ρ is the density of the metal.

$$V_0 = \frac{Q \cdot M}{n \cdot F \cdot \rho} \qquad \text{[Eq. 12]}$$

The total wear volume can be measured experimentally and thus the mechanical value can be calculated by using equation 11.

✓ THIRD BODY APPROACH

This approach concentrates on the study of the different third bodies that can arise during tribocorrosion mechanisms. First and second bodies are the two different materials in contact, and the third body is the debris that stays in the contact area before being eliminated, watch schematic figure 11.

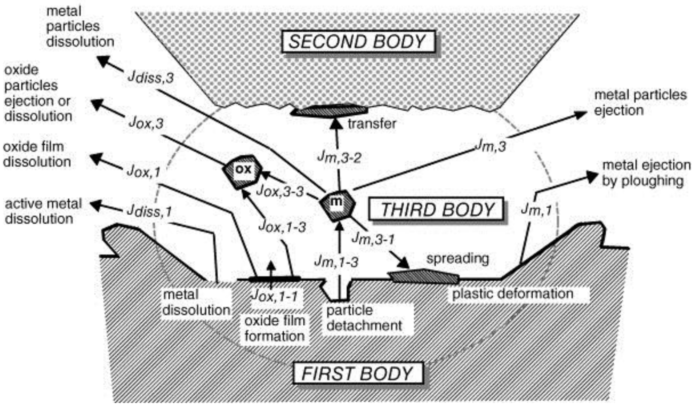


Figure 11 Material flow [15]

As the other approach, one thing can be calculated taking into account different contributors. In this case, the volume loss of metal (V_{met}) is the sum of solid metal particles ($V_{met}^{particle}$), metal ions dissolved in the electrolyte (V_{met}^{ions}) and metal oxidized (V_{met}^{oxide}) as shown in equation 13.

$$V_{met} = V_{met}^{particle} + V_{met}^{ions} + V_{met}^{oxide} \qquad \text{[Eq.13]}$$

In addition, the solid metal particles are a sum of different contributions, as shown in equation 14.

$$V_{met}^{particle} = V_{met,particle}^{ejected} + V_{met,particle}^{ions} + V_{met,particle}^{oxide} + V_{met,particle}^{smeared} \qquad \text{[Eq.14]}$$

Therefore, the volume of the wear track that can be measured experimentally can be calculated by using equation number 15.

$$V_t = V_{met} - V_{met,particle}^{smeared} \qquad \text{[Eq.15]}$$

2.6 COATINGS

Usually, low values of friction and wear are desired, in order to enhance the material or the functionality of a process several options are available.

- The most obvious one would be to change the material used for another with better properties.
- Another option is to lubricate the process so that the friction coefficient and the wear decrease apart from the decrease of the temperature.
- Adding a coating with better properties than the substrate.

The first option can be a good solution but by adding a thin layer of this material, with enhanced properties than the initial one, the cost can be decreased.
Lubrication is also a good option, but sometimes it is not suitable, e.g. in food industry where the lubrication has high chances to contaminate the food or in some biomedical applications where the replacement is already in contact with the body fluids.
Therefore, coatings are sometimes the greater option to take into account to enhance the efficiency. For example, in biomedical applications like joint or hip replacement, DLC coatings have outstanding properties like high hardness, low friction biocompatibility. Coatings are sometimes named as solid lubrication when the aim of them is to decrease the friction.

✓ CLASSIFICATION OF COATINGS FOR BIOMEDICAL APPLICATIONS

Before the classification, some definitions have to be explained.

Biomaterial is whatever material that can be used to replace, support or enhance a tissue, organ, joint or part of the body.

Biocompatibility is the desired effect that the biomaterial does without damaging the bioenvironment where it is integrated.

- Bioactive coatings: those coatings that have a positive effect upon the tissue, organisms, etc. where they are located. For example, those that can help the regeneration of a bone, e.g. calcium phosphate
- Biotolerant coatings: those coatings that release materials that are not harmful for the environment (body) and that may cause beneficial situations due to a good compatibility.
- Bioinert coatings: those coatings that have a minimum or negligible effect with the tissue.

DLC coating are included in the second option, the biotolerant coatings, due to its ability to form a layer that protects the coating from the wear; even though this still have to be studied more profoundly since this layer might not be capable to resist under tribocorrosion processes [1].

2.7 DLC

✓ HISTORY

First time the term diamond-like-carbon (DLC) was used was in 1971 by Aisenberg and Chabot; during research outstanding properties were found and the structure was described as partially crystalline with lattice similar to the one present in diamond [16].

Before this, several researches were made in order to know if layers could be generated via glow discharge, like the one Schmellenmeier did in 1953. [17]

After Aisenberg and Chabot other researches were made by using techniques similar to the one they did. After that, the study of this coating increased profusely due to its promising properties. Widely history of the evolution of the DLC knowledge along the years can be found in [18].

✓ STRUCTURE

In order to understand the structure of the diamond like carbon, it has to be discussed profoundly, the carbon and its ways of configuration.
Carbon can be found in the nature in three forms: amorphous carbon, graphite and diamond (fullerene has been discovered recently but this is out of the extent of the study here). Carbon can share electrons with up to four other atoms, which can be done with other elements or with more carbon.

Diamond is a crystalline form of carbon that has 100% sp^3 carbon bond hybridization; atoms are structured symmetrically in diamond lattice. Due to this perfect symmetrical structure the properties of this material are overwhelming, such as highest hardness, chemical inertness, high electrical resistivity, etc.

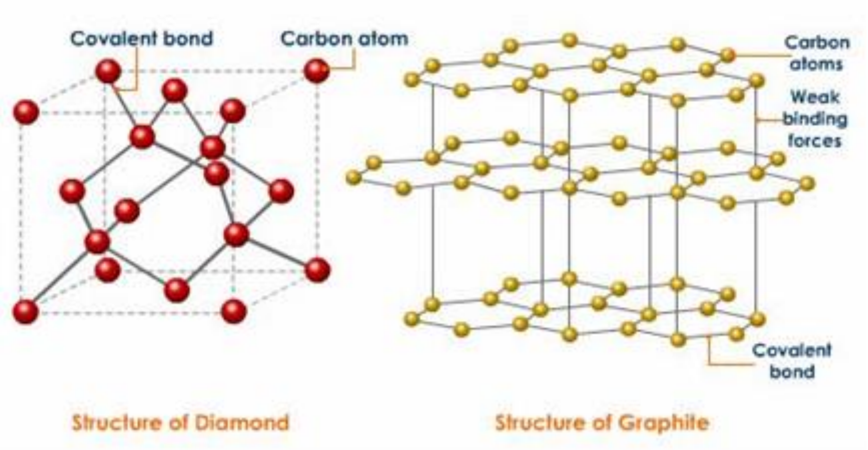


Figure 12 Diamond and Graphite Structure [30]

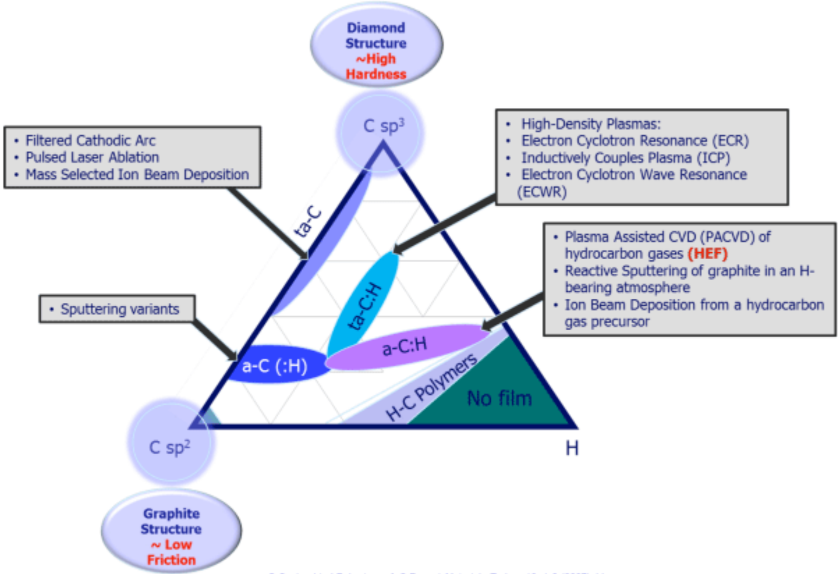
While carbon has such amazing properties, graphite, in contrast, is soft; this is because it is formed by sp^2 bonds, so that it forms hexagonal patterns in one plane, and weak joints in the third axis; in contrast with the diamond which has a very strong an dense structure in three dimensions.
This different structure explains all the different (huge) properties between graphite and diamond, for instance, the density of the diamond is 3.53 g/cm^3 while graphite's density is 2.66 g/cm^3 (at 20ºC).

Another interesting property difference which might affect the tests is the electrical conductivity. As said, while diamond has all four valence electrons linked through covalent bonds, they are not free to conduct electricity; on the other hand, graphite has three out of four valence electrons in use, which means that there will be one "free" to conduct electricity. Therefore, graphite is good electrical conductor while diamond is an insulator.

Diamond like carbon is an amorphous form of carbon, containing high fractions of sp^3 but also sp^2 type C bonds and several concentrations of hydrogen; e.g. 50% the a-C:H or 1% the a-C. Here it is going to be discussed the following ones a-C:H (hydrogenated amorphous carbon) , ta-C (tetrahedral amorphous carbon) and Ti doped.

There are several forms of DLC (see figure 13) the ones used in this work are:

- a-C:H, which contains both sp^2 and sp^3 bonds.
- ta-C, that contains a very high percentage of sp^3 bonds.
- Metal doped-C:H, dominated by sp^2 bonds, the metal improves adhesion and electrical conductivity.



C.Casiraghi, J.Robertson, A.C.Ferrari, Materials Today, 10, 1-2 (2007) 44.

Figure 13 Types of DLC [20]

- ✓ **DEPOSITION**

There are several processes to add the coatings, here only PVD and CVD will be discussed, since that is going to be the approach of this paper.
Both of them are based on the same mechanism, but have some differences, shared steps are:

- Creation of the vapour phase (this process can be made by numerous techniques such as puttering, evaporation, etc.
- Guidance of the vapour to the substrate
- Adherence of the material to the substrate.

The main difference between CVD and PVD is that in the first case the material to deposit does not exist previously, it is synthetized. In this method, a precursor gas flows into the chamber where the material that wants to be coated is heated, then a chemical reaction occurs and the gas is deposited on the surface of the substrate.

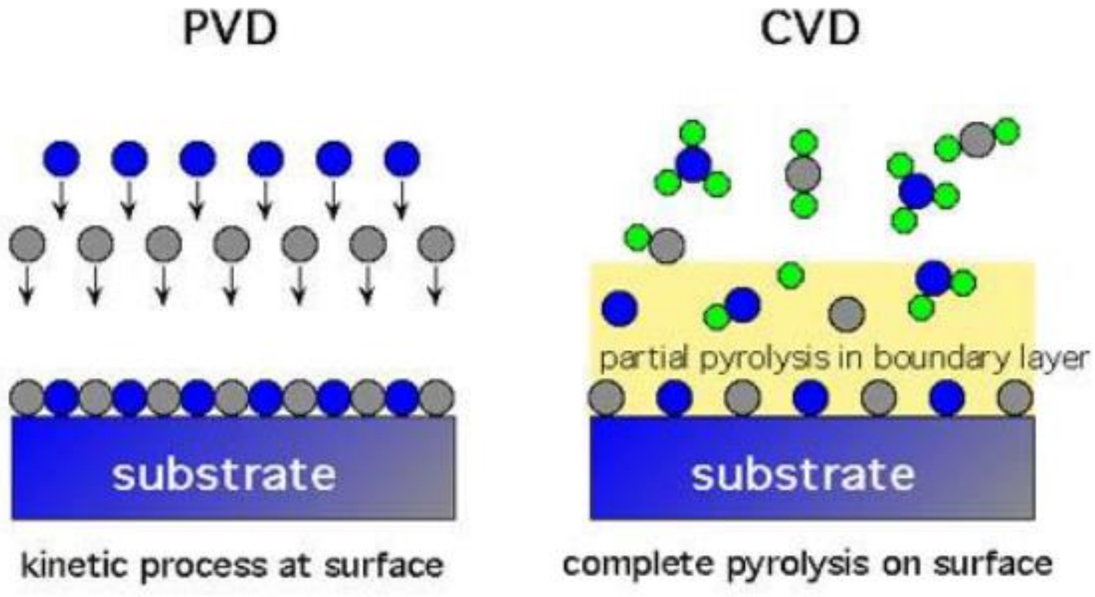


Figure 14 Schematic Representation of PVD and CVD [20]

Physical vapour deposition (PVD) starts with the vaporization, thermically, of a solid or liquid source, transported along the chamber (different ways possible) until the substrate and then condensed over it.

Methods to evaporate the material are several (this two are the most common):

- Evaporative deposition: where the material is heated by regular electrical resistance
- Sputter deposition: where as we’ve seen in the history of DLC Schemellenmeier glowed plasma discharge bombards the material sputtering some away as a vapour for subsequent deposition.

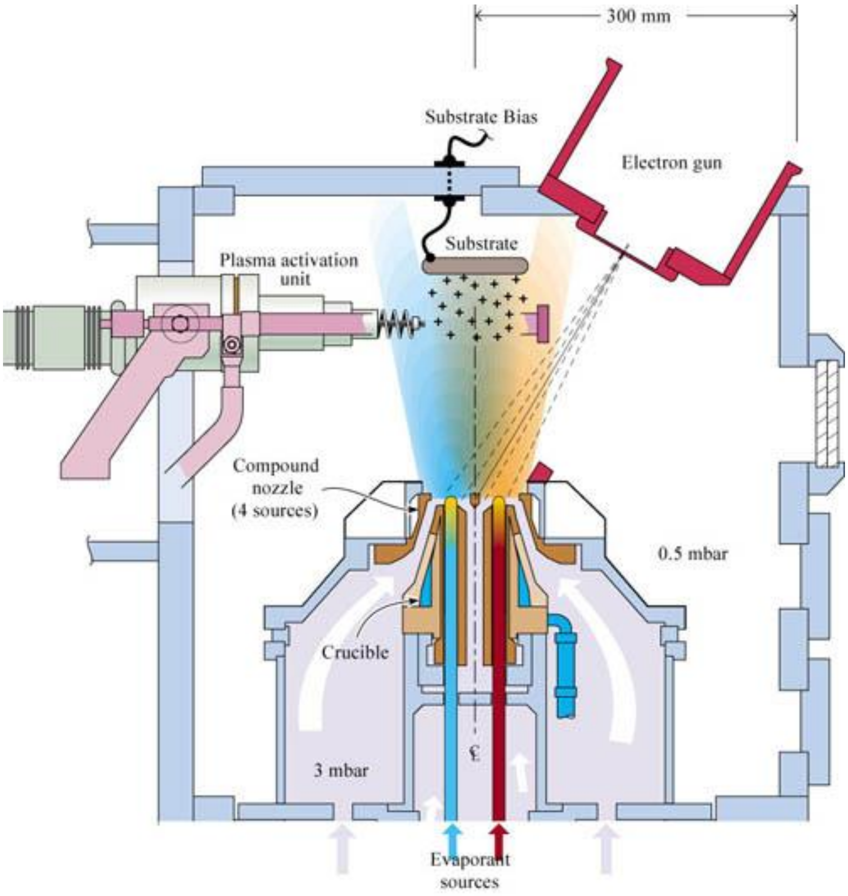


Figure 15 PVD Machine [21]

Chemical vapour deposition (CVD) is comprised of the following steps, first the precursor gas is introduced in the chamber where it is guided to the substrate that is already heated, due to the chemical reactions occurred the material to be deposit is already formed and will be deposited over the substrate.
As well as in the case of CVD, there are several methods, for example Atmospheric Pressure CVD (APCVD) or Low pressure (LPCVD) or Plasma Enhanced (PECVD), etc.
One of the coatings used in this paper has been deposited by Plasma-Assisted CVD so it is going to be explained more in detail.

The main advantage of this method is that it is done at lower temperatures than regular CVD. The material precursors are gases which are activated in the plasma phase through dissociation, excitation and ionization processes. By using this method temperatures around 200ºC can be achieved by using high frequency or pulsed-glow discharges.

Below (Figure 16) is displayed a schematic figure about the PACVD.

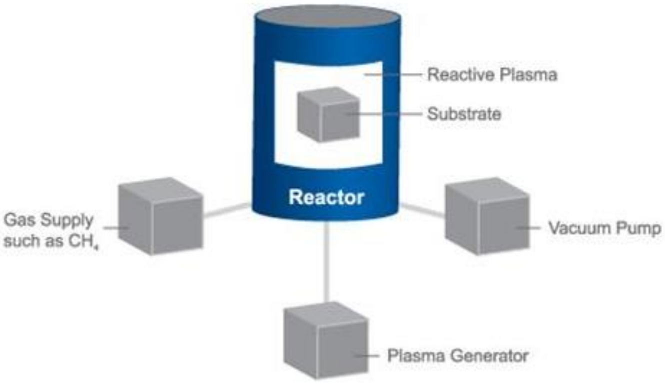


Figure 16 PACVD Methodology [22]

In the diagram below, it is displayed how the thickness can be influenced by the substrate temperature and how different deposition methods can lead to different final results.
DLC-coatings don’t need a temperature above 200ºC and the thickness is from small micron to almost 10µm.

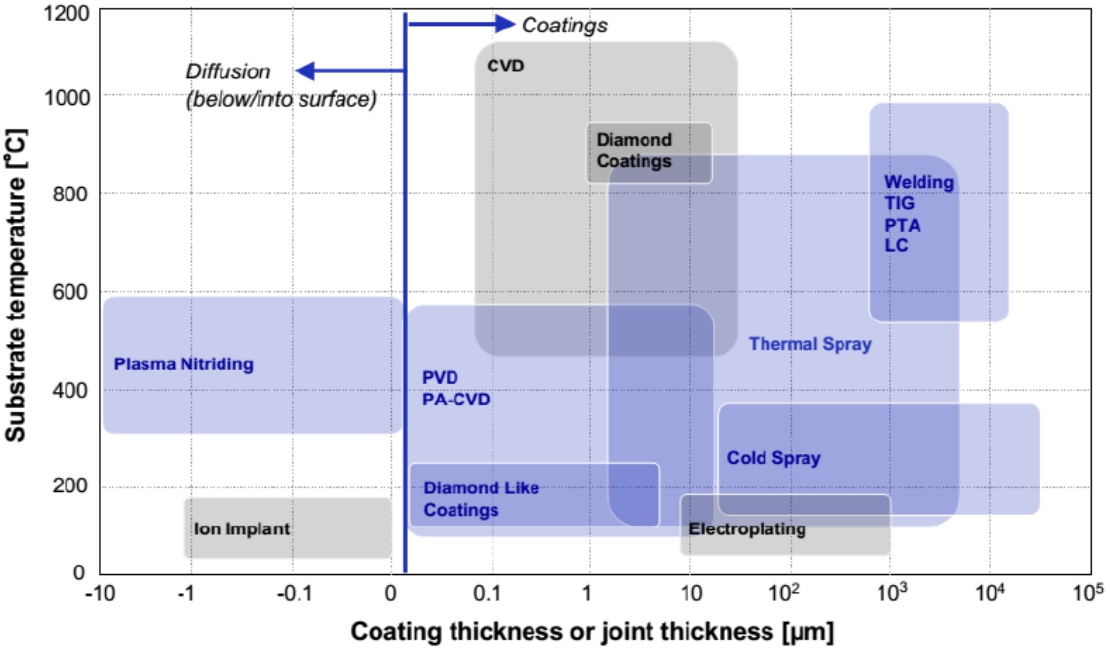


Figure 17 Temperature against thickness [22]

3. EXPERIMENTAL SECTION

3.1 SAMPLES PREPARATION

Un-coated samples were ground and polished to mirror surface and cleaned in an ultrasonic bath with ethanol before every test.

Coated DLC samples were cleaned with an ultrasonic bath with ethanol before every test.

3.1.1 ULTRASONIC BATH

Before each test, samples were cleaned in an ultrasonic bath for 5 minutes to eliminate any dirt.
The sample is introduced in a beaker submerged in ethanol and then this beaker is introduced in the ultrasonic machine that is full, at three-fourths, of tap water.
The operating principle is the high frequency waves produced by the machine create cavitation bubbles. This bubbles will increase during the first phase to be compressed later, this will increase the temperature of the gas contained in the bubbles until they will implode releasing lot of impact energy that will hit the surface of the sample.

Figure 18 Ultrasonic Bath Machine [31]

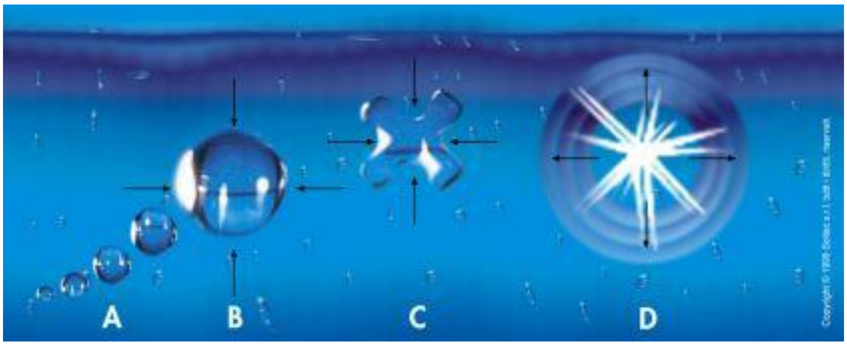
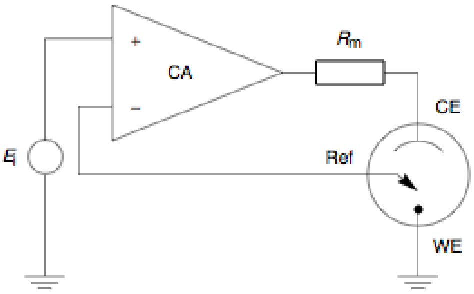


Figure 19 Bubbles imploding [32]

3.1.2 ELECTROCHEMICAL TEST

The aim of the experiment was to obtain the polarization curve of each material either to know the corrosion behaviour and to figure out the different stages such as anodic, cathodic and OCP parts of the curve (in addition to the passive and transpassive regions). This second objective was necessary to choose the potential to set the tribocorrosion tests.

The assembly of the test is pretty simple, it is a potentiostat comprised of:



1. Working electrode (WE)
2. Reference electrode (RE)
3. Counter electrode (CE)

Figure 20 Potentiostat Diagram [33]

The operating principle is the following; the reference electrode allows measuring the potential of the working electrode without allowing passing current through it, while the counter electrode allows passing current. If oxidation occurs at the working electrode, reduction using the same magnitude of current is sustained at the counter electrode and hence there is no current flow between working and reference electrode (high input impedance) enabling to follow changes in working electrode potential accurately

In our case, the working electrode was the sample, the reference electrode was Silver/Silver Chloride (Ag/AgCl/KCl 3M) and the counter electrode made of platinum.

All of this was submerged in an electrolyte solution, three different electrolytes were used, 0.9 WT %NaCl, PBS and PBS + Albumin.

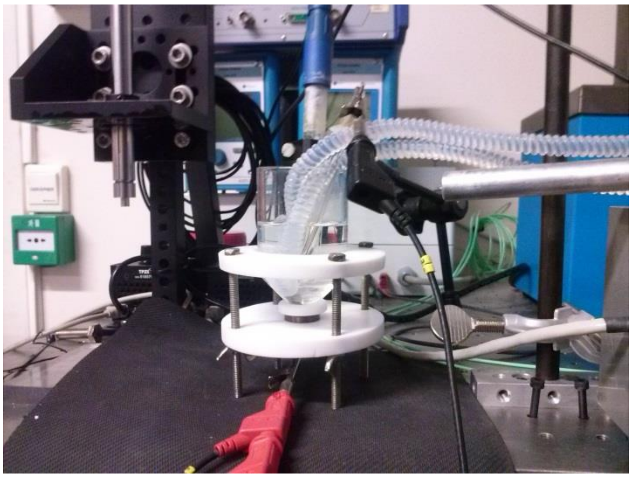


Figure 21 Polarization Curve Test

The parameters used for the test where 5mV/min, with a variation of the potential from –1V to +1V, initially it was from -0.7V to +0.7V because of the previous experience with the CoCrMo polarization curves but since the DLC stabilization took longer the variation was increased.

3.1.3 TRIBOCORROSION TESTS

By means of performing this test it can be tested the real environment where the materials wanted to be used. Replacements, as said before, will be under tribology and corrosion efforts at the same time due to the corrosion of the body fluids and the wear of the normal use of an artificial joint.
The set up consists on an electrochemical cell which contains the electrolyte and connects the sample to the pin. A pin which holds the ball (alumina with a diameter of 6mm) that will rub the sample; this holder is attached to the arm of a motor that will provide an oscillatory displacement of 5mm with a constant motion and also receives the load that is applied (in our case 2N). That is for the tribology part, the corrosion parameters and set up are the same as in the electrochemical test, with counter, working and reference electrodes connected. Obviously, every test will be accomplished at 37ºC, to simulate body temperature.

After the electrochemical tests, potentials will be chosen from different areas of the polarization curves and will be applied to the tribocorrosion test in order to observe the behaviour of the different samples. Usually, potentials are chosen so that all areas in the polarization curves are contemplated, i.e. active, passive, transpassive and ocp

- In the OCP test, the results will be plotted as potential against time to; there will be ten minutes before and after the rubbing measuring also to see how the rub affects.

At this test, the counter reference will not be connected since it is completely unnecessary.

- In the passive test, as the potential is settled, the plot will be current against time.

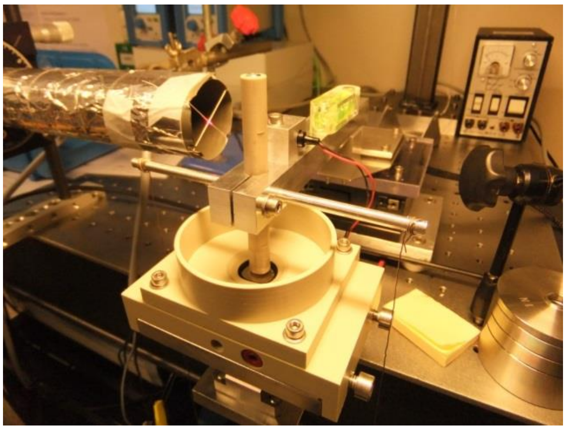


Figure 22 Tribology Test [34]

The parameters introduced will be:

- For the autolab: 4800seg, covering the first 10 minutes without rubbing, 60 minutes rubbing and after that another 10 minutes without rubbing, this will lead to a 80 minutes of test.
  In addition, there will be two different test, one at OCP and another one with a potential applied of +0.3V (belonging to the active part of the polarization curve).
- For the tribology parameters:
  - Length of the pin motion: 5mm
  - Speed: 10m/s
  - Dwell time: 0.001 seg
  - Number of cycles: 3600
  - Frequency: 1 HZ
  - Applied load: 2 N

3.2 SAMPLES CHARACTERIZATION

3.2.1 MICROHARDNESS TEST

The hardness test consists on the indentation of the sample with a pyramid square base indenter made of diamond that applies a certain load during certain time. After that the diagonals of the mark are measured with the microscope and with this values and the force it can be calculated the Vickers hardness (VH) by using the equation 16:

$$VH = \frac{2 \cdot P \cdot sen\,(\frac{\theta}{2})}{d_{average}^{2}} \quad \text{[Eq. 16]}$$

Where:

- P is the load applied, 0.3N for CoCrMo and 0.1N for DLC, the different values are due to the size of the wear track after the tribocorrosion test.

- Θ is the angle between opposite faces.

- d is the average between d1 and d2.

A representation of the test is displayed in Figure 19.

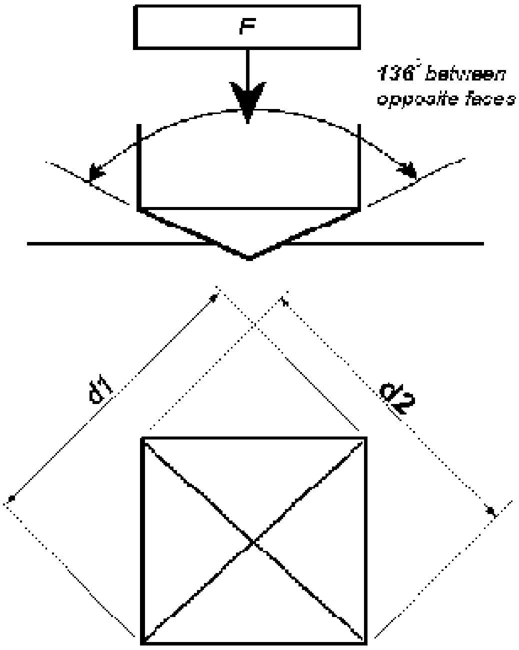


Figure 23 Hardness Vickers Test [35]

3.2.2 SCANNING ELECTRON MICROSCOPE (SEM)

The microscope works with a focused beam of electrons instead of light, this is due to the restrictions that the shorter wavelength of the light has, electrons have longer wavelength and that allows getting better resolution.

An electro gun produces the electrons at the highest part of the column and those electrons are guided along the column and pass through lenses to produce a focused beam of electrons, the chamber is at vacuum so that the electrons can travel.
The beam hits the sample and the electrons interact with the atoms producing signals that are detected and send to a computer to form the image.

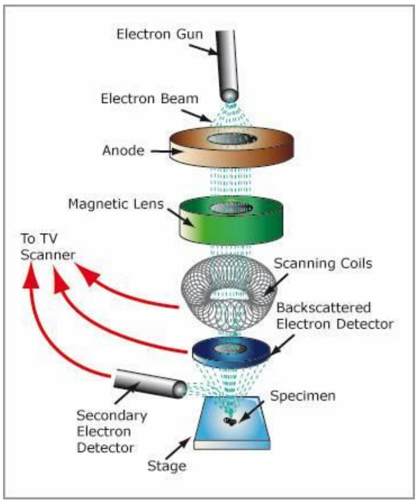


Figure 24 Scanning Electron Microscope components [36]

One issue of this microscope is that the samples need to conductive.

In figure 18 can be seen all components of a scanning electron microscope.

In our case, to capture the images, the test was run with a voltage of 15Kv and with a working distance of approximately 10mm.

Figure 25 Scanning Electron Microscope

4. RESULTS

4.1 ELECTROCHEMICAL TESTS

Here several experiments were carried out, for each curve, two tests with same material and electrolyte were made in order to obtain reliable results, therefore there are repetitions for each curve that proves the results, only one of the curves will be display to not overcharge the paper with images.

To summarize the tests made, below a table can be found. The second batch of samples arrived (due to delivery problems) one week before the deadline of the master thesis that is why only specific tests were done due to lack of time.

Sample\Electrolyte	0.9% NaCl	PBS	PBS + Albumin
CoCrMo	2	2	2
a-C:H	2	2	2
ta-C	2	2	2
Ti doped	2	2	0

All this tests are gathered together by means of the electrolyte.

For each polarization curve it will be displayed the logarithm of the current density against the potential, different areas will be distinguished, from left to right it can be seen:

1. Cathodic branch where reduction occurs, this is harmless situation without oxidation.
2. OCP or the point where both branches, the anodic and the cathodic converge.
3. Anodic branch where oxidation occurs, in this branch different parts can be seen
    a. The active, where the gradient is higher and that means that the rate of oxidizing is high also.
    b. Transpassive, where the gradient is lower than the active but still there is oxidation.
    c. Passive, where the gradient is flat which means even the potential increases the rate of corrosion will remain constant.

For the tests with coated samples, the time to calculate the OCP before starting to build the polarization curve was increased from the ten minutes, used for the

CoCrMo, to fifteen minutes, this was because the time to stabilize the potential was longer, in the first polarization curves, the OCP measured and the one in the polarization curve did not coincide.

✓ 0.9 WT % NaCl

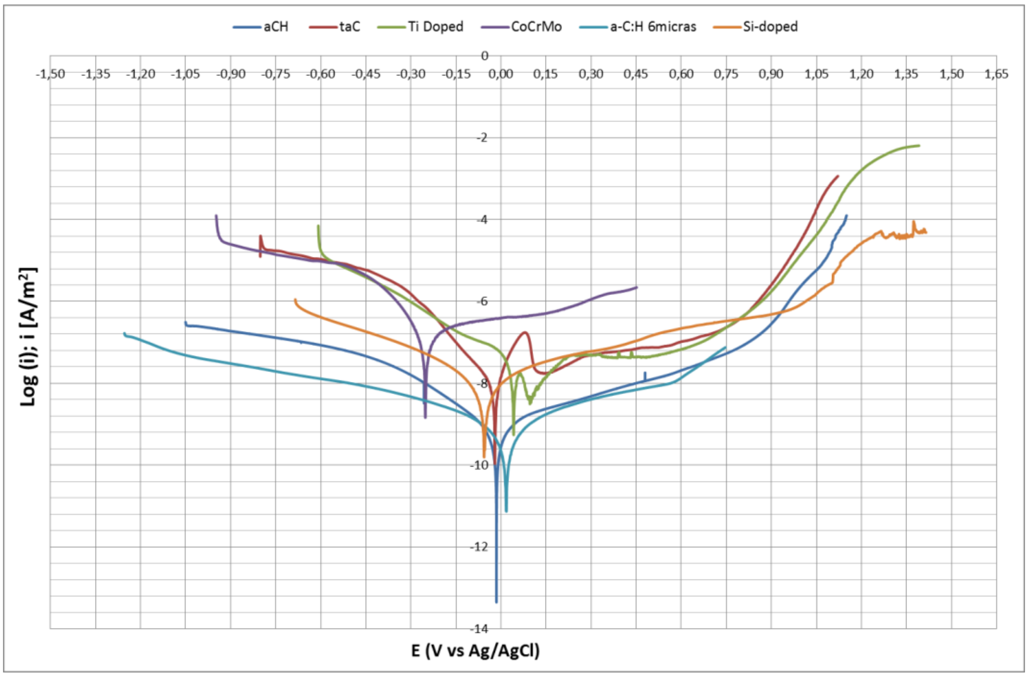


Figure 26 Polarization Curves of the samples in 0.9% NaCl

First of all, the cathodic branch of all DLC coatings is longer than the CoCrMo, so the OCP is higher than the un-coated sample, this are good news since that means that the sample will start to corrode with higher values or said in another way it will resist more. The location of the OCP in a-C:H and ta-C is practically the same, negligible difference, but the doped with Titanium is better, not a big difference though, approximately 0.075V.

By focusing on the OCP, the Ti doped coating seems to the one that better resists corrosion, but there is another parameter that has to be taken into account, it is the current density, the current density for both the ta-C and the Ti-doped are similar (even though as said before, the OCP point is not the same) but it is better in the case of the a-C:H, by a difference of $|\Delta \log(i)|=1.8$.

Both the tetragonal and the doped have an active phase after the OCP followed by a deflection and another increase, like a valley, this could mean that the material creates a passive film, that is why the there is a deflection, but the corrosion is too strong and goes through this film and continues oxidizing. After this region, there is an almost flat part where a close to passive area arises. Therefore, the behaviour of the tetragonal and the doped ones is very similar, but for the OCP which, in fact, is also pretty similar.

For the hydrogenated coating, the behaviour is pretty similar to the one observed in the un-coated sample, talking about the shape of the curve, not the location of it in the plot. After the OCP the anodic branch is an active region where the corrosion increases, after the transpassive region in the ta-C and in Ti-doped, both of this two and the a-C:H continuous increasing concurrently.

Other remarkable facts are, first the similarity between both a-C:H and second the worsening of the Si-doped coating, even though it is still and improvement compared to the un-coated sample.

✓ PBS

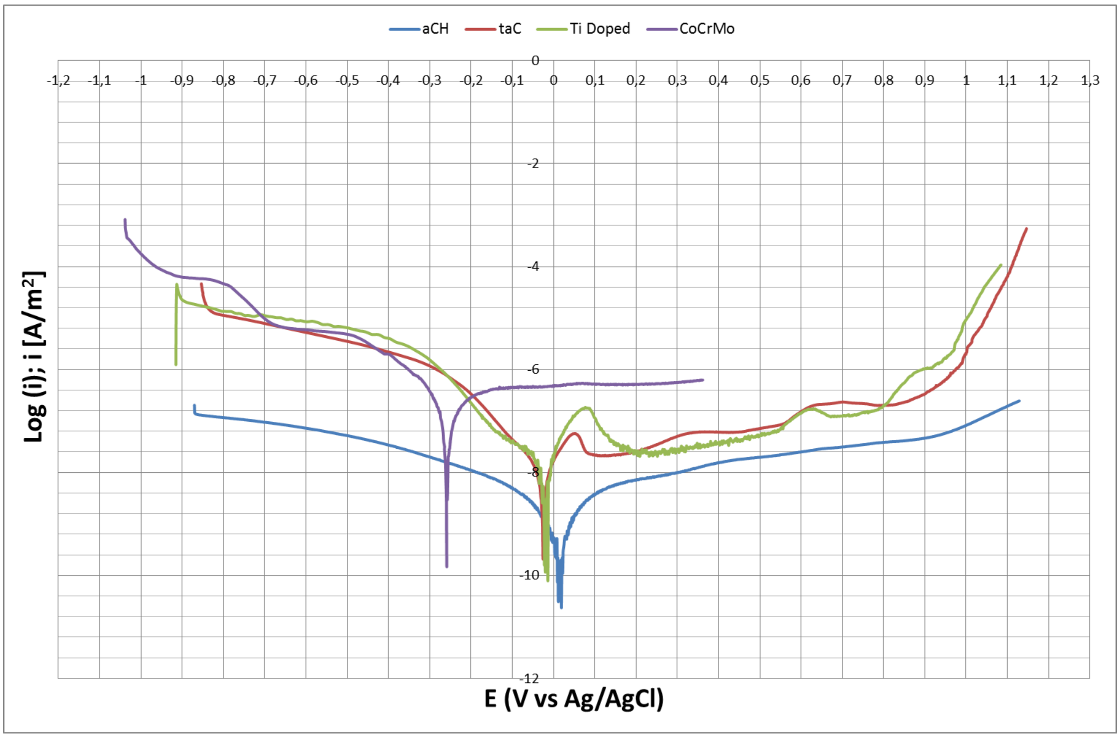


Figure 27 Polarization Curves of the samples in PBS

With this electrolyte, the behaviour is pretty similar, the OCP is improved for all of the coated samples compared to the CoCrMo one, the a-C:H has a better behaviour due to its current density, and either a-C:H and Ti-doped have this valley after the OCP.

The most significant difference can be seen in the anodic brand where the almost passive region lasts more than in the NaCl electrolyte, from +0.6V to +0.8V approximately, even more for the hydrogenated coating where the active region is almost inexistent, at least until the +1.1V.

In the Ti-doped sample, at +0.55V and at +0.8V there is an increase of the corrosion followed by another decrease which could mean that the passive films is broken and self-healed again. If this new layer would have not been formed, the active branch would have arisen before.

The similarity between the a-C:H and the ta-C and Ti-doped at the end of the anodic branch disappear with this electrolyte.

✓ **PBS & Albumin**

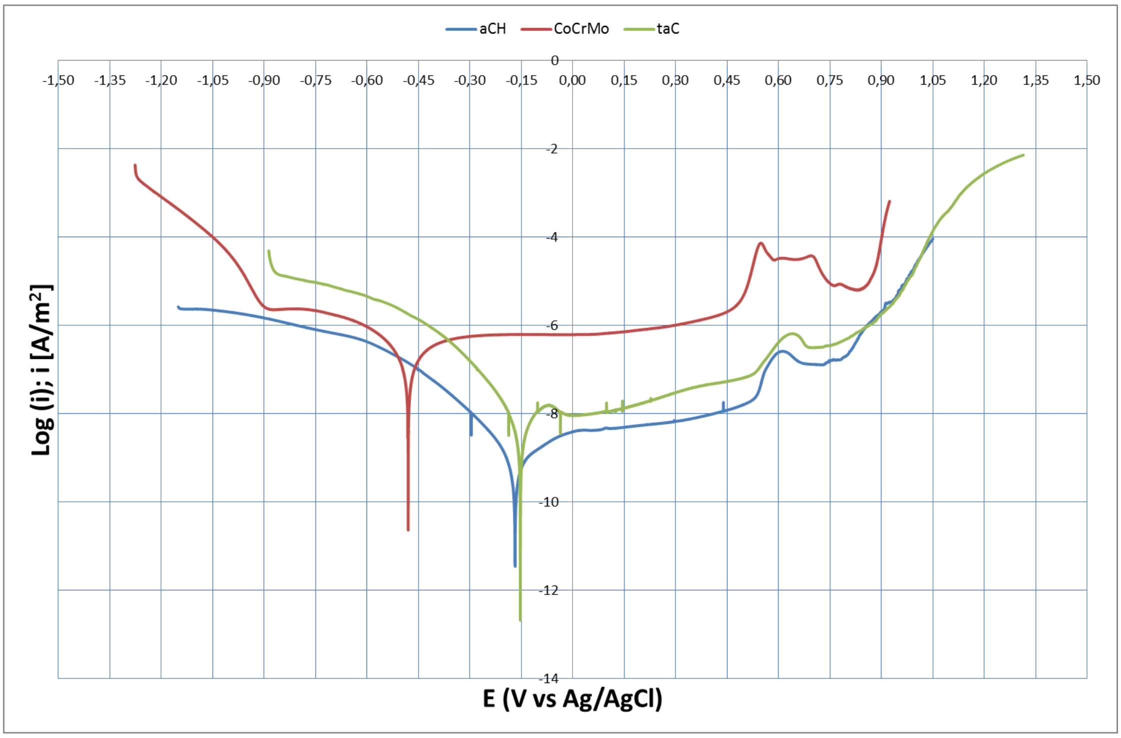


Figure 28 Polarization Curves of the samples in Albumin

This is the most accurate simulation of the reality. As the previous electrolytes, the position is pretty much the same, no big differences.

More visible differences can be seen along the branches of each curve, the behaviour of all materials gets closer than with the other electrolytes within the anodic branch; there is a peak around the +0.45V that might be caused because of the adsorption of the albumin.

The CoCrMo polarization curve in presence of albumin differs also from other electrolytes at the anodic branch, where there is a change of tendency at -0.5V.

✓ DECISION

The polarization curve of the Ti doped in presence of albumin is missing since there was a lack of samples; it was not indispensable to have this one since with the others it is possible to figure out the tendency of the curves.
In addition, the second batch of samples weren't tested because delivery problems, they arrive too late, hence and with the idea of which potential should be adequate to perform the tribocorrosion tests

Therefore, as a result of this plots, it was decided that the tribocorrosion tests will be carried out under two configurations:

- OCP potential, measuring the current against the time
- +0.3V, to see the how the corrosion affects the wear.

4.2 TRIBOLOGY TESTS

In order to see the expected outstanding properties of the DLC coatings, dry tests were performed, with all the coatings and also the un-coated samples, so it can be compared afterwards.

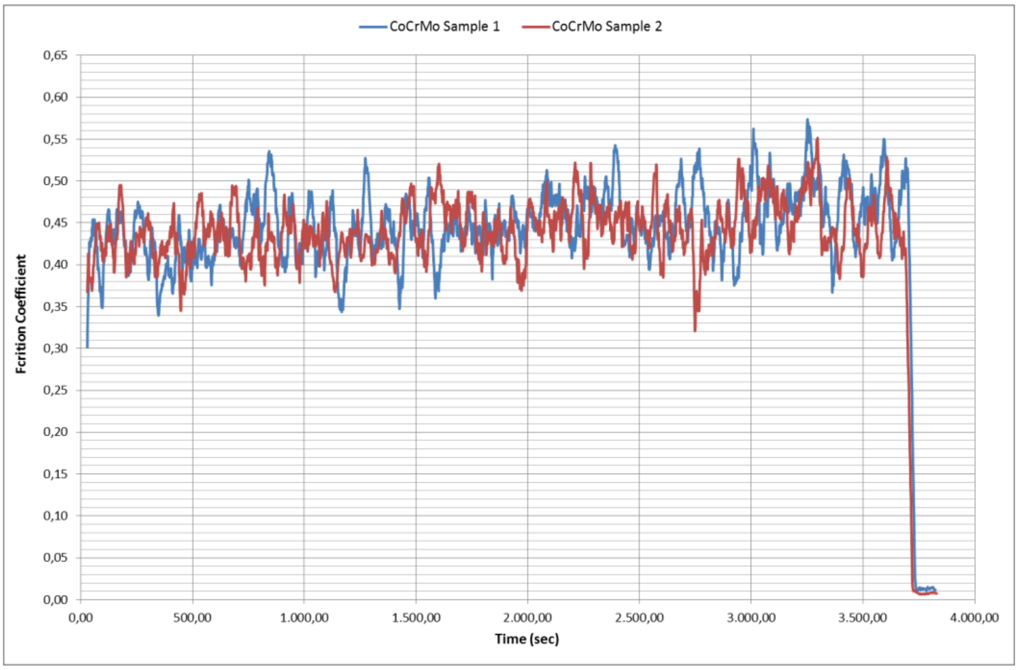


Figure 29 COF vs Time of CoCrMo

In the figure above (Figure 29), CoCrMo sample without coating was tested; values of friction coefficient (COF) of approximately 0.45 were obtained.

Friction coefficient for the DLC coatings can vary, significantly, from different kinds of DLC, the microstructure can vary remarkably since main discrepancy is due to the amount of sp^3 or sp^2 bonds present.

In addition, the deposition method can also vary properties considerably.

For the a-C:H coated sample (Figure 30), the mean value of the COF is approx. 0.06, which proves the exceptional properties of this material. At the beginning of the rubbing there are values of up to 0.35 which can be caused either due to the higher resistance to the ball to start to rub or to the fact that the debris that the rubbing causes has to yet appear so that the material did not have time to create a layer to protect itself, or also, as the thickness of the coatings were quite small, (in this case, it was a layer of about 1.9µm) it could be also that the first rubbing break through the coating and after that the debris fell into this wear track and was able to create a protective layer.

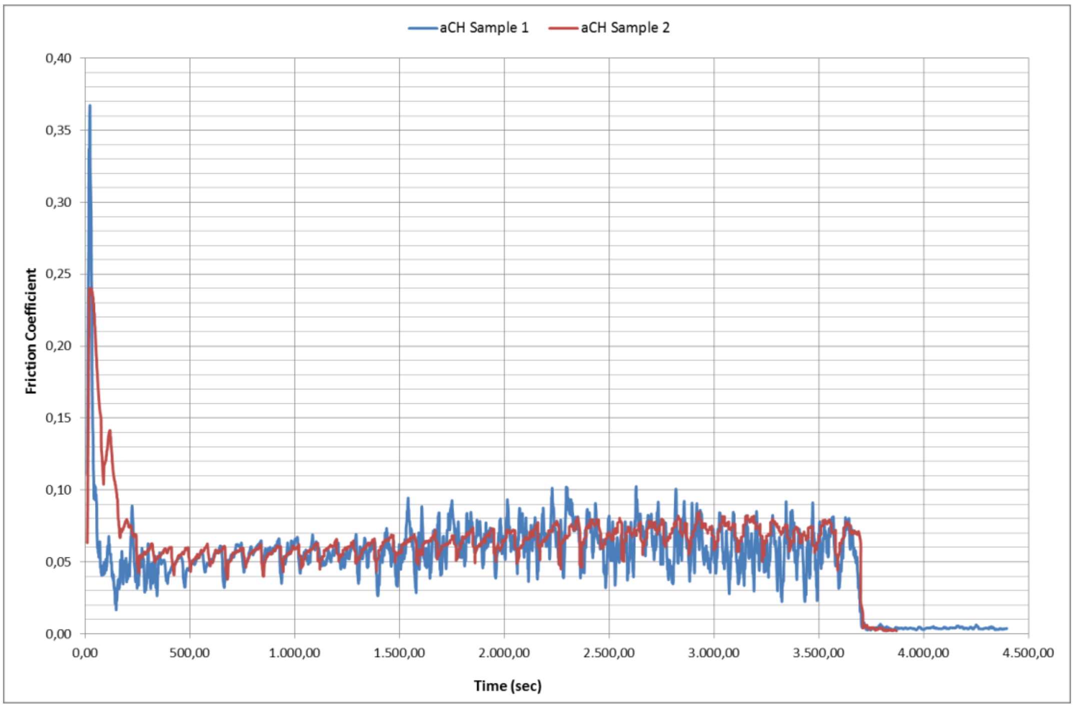


Figure 30 COF vs Time of a-C:H

In the test with the tetragonal coating (Figure 31), the tendency is similar, with high COF values at the very beginning of the experiment, there is a peak, in one of the tests, which could have emerge because the rubbing was strong enough to break through the protective layer, but after 100 seconds approximately, the COF decreases again, which must be cause because of the self-healing, another layer should have be deposited over the surface to protect it.

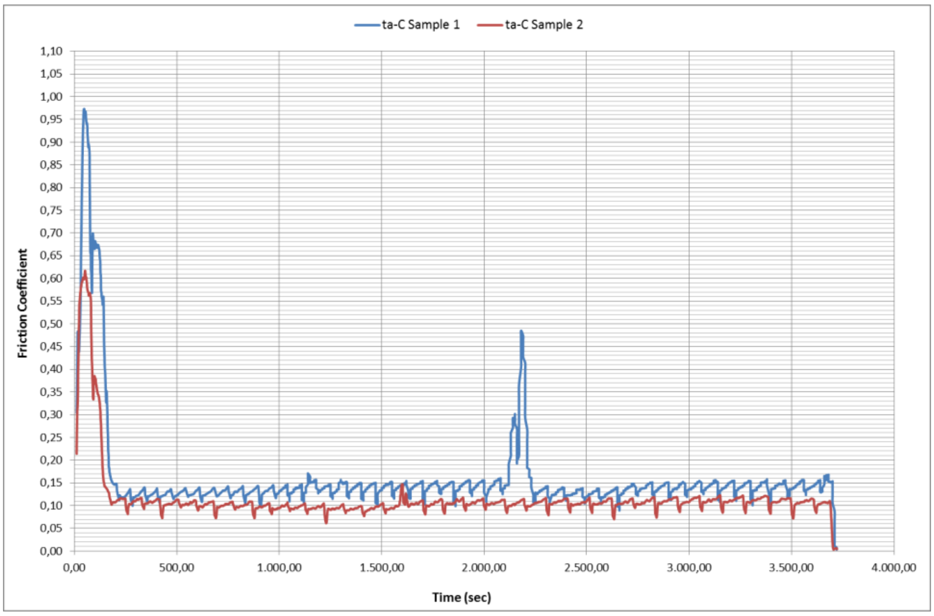


Figure 31 COF vs Time of ta-C

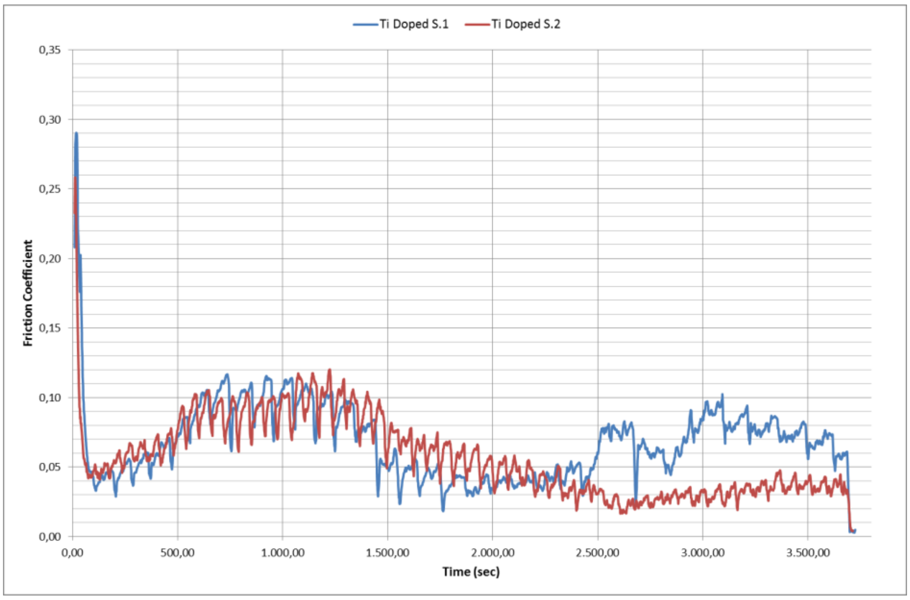


Figure 32 COF vs Time of Ti-doped

For the Ti doped coating (Figure 32), the friction coefficient is less stable, there are bigger variations, this is most likely due to the fact of the titanium which does not have such good properties as the DLC. Even though, compared to the un-coated sample there is a still a good range of improvement.

Figure 33 COF vs Time of all samples

The improvement is out of doubt (Figure 33), in the case of the hydrogenated coating it is nine time less friction coefficient. It is true that the CoCrMo does not have problems at the beginning of the rubbing, opposite to the coated samples that need time to create that protective layer.

Now there are going to be displayed the results for the other batch of samples.

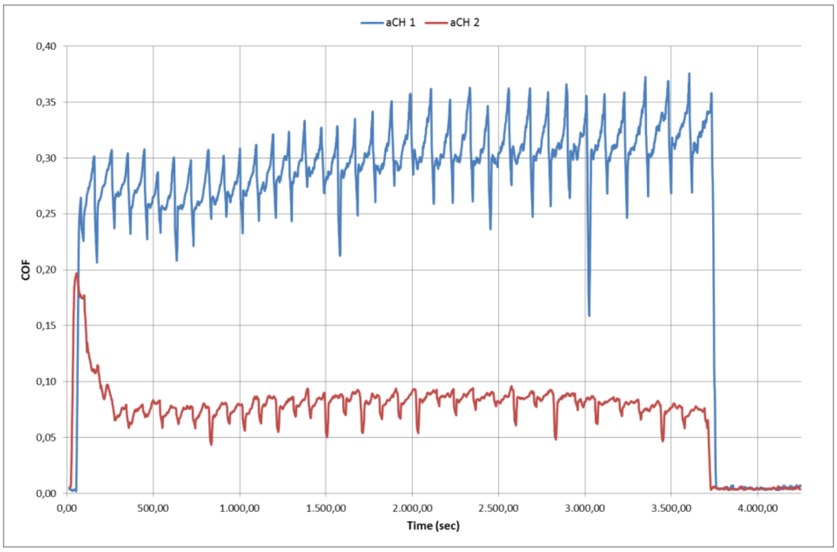


Figure 34 COF vs Time of a-C:H 6µm

For the a-C:H (Figure 34), two tests were carried out and different results were obtained, due to the fact that the thickness of this samples was 6µm, higher than the other a-C:H that had 1.9µm the most, makes sense to think that the coating has not been destroyed and that the different values obtained must differ because of the protective thin layer than in one was able to be created and on the other one not.

In the case of a-C:H but with a coating thickness of 17.4 µm (Figure 35), the values are better but there is still a range of about 10 minutes since the beginning of the rubbing until the stabilization with values below 0.1.

Last dry test done was Si-doped coating (Figure 36), same situation as in Figure 30 arose, two different values. Most likely, same reason also to explain why that happened.

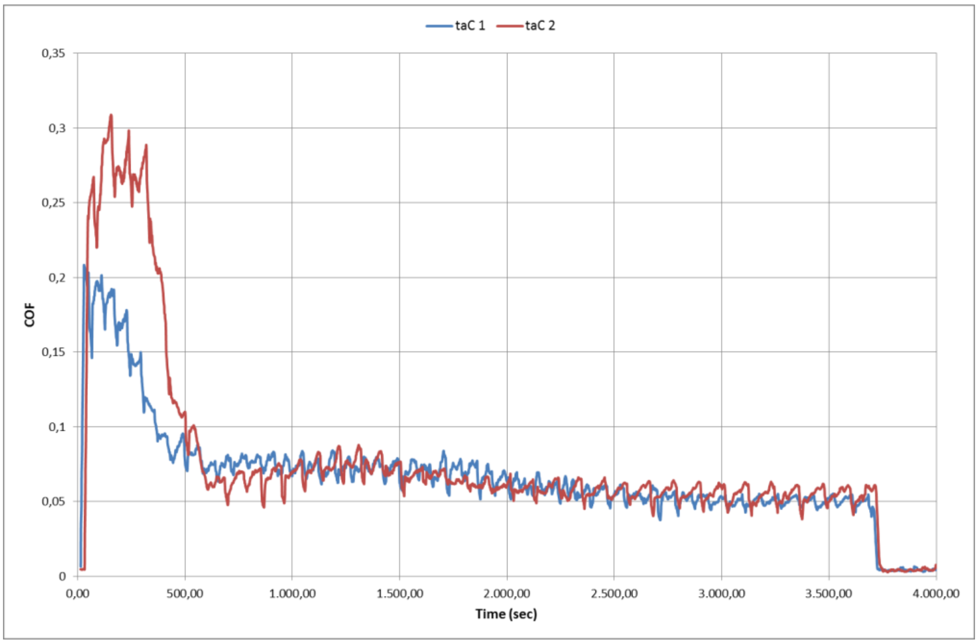


Figure 35 COF vs Time of a-C:H 17.4μm

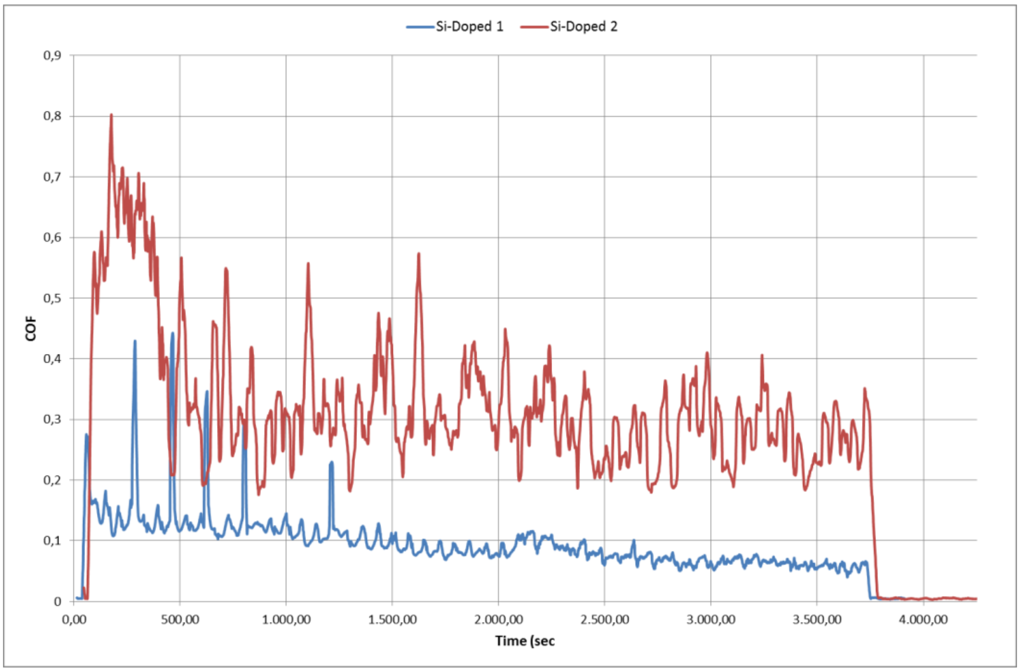


Figure 36 COF vs Time of Si-doped

4.3 ELECTRICAL CONDUCTIVITY

In other to prove the electrical conductivity results expected, due to the structure of the different coatings, simple resistance test was carried out.

Figure 37 Multimeter used to measure the conductivity

With a multimeter, it was tried to measure the potential, it was measured open loop (OL) which means that the resistance is too high to measure the potential, it happens the same when the proves are not touching the display, that means the air does not conduct, and that result coincides with the theory that says it is not a good conductor.

Both the ta-C and the a-C:H was measured the same, in the case of the metal doped (Ti and Si) it was measured potential but with very high variations, that must be due to the fact that the electricity founds path to cross the sample along the metal.

In the case of the second batch of samples, the conductivity seems to be even lower; this conclusion is done after watching the tribocorrosion tests where the plot of the potential coincides with insulated materials.

4.4.TRIBOCORROSION

In this section, the tribocorrosion tests carried out are shown for each sample and electrolyte.

There are two regions in these plots, the beginning of the tests where the rubbing has not started yet, it lasts approximately 4800seg, then the rubbing starts and lasts for one hour, after it stops there is a period without rubbing, about ten minutes.

At the table below it is summarized the tests.

		0.9% NaCl		PBS		PBS + Albumin	
		OCP	+0.3V	OCP	+0.3V	OCP	+0.3V
Un-coated	CoCrMo	2	2	2	2	2	2
Coated (DLC)	a-C:H	2	2	2	2	2	2
	ta-C	2	2	2	2	2	2
	Ti						
Coated (2nd Batch)	a-C:H (6µm)	1					
	a-C:H (17.4µm)	1					
	Si-doped	1					

During these tests, when the ball starts to rub, a galvanic cell will be created, the anodic electrode will be the wear track area and the cathodic electrode will be the rest of the sample (where there is no rub).

The experiments will be organized by electrolytes, starting with 0.9% NaCl and ending with Albumin.

✓ **0.9% NaCl Electrolyte**

It can be seen in the figure below (Figure 38) the behaviour of the CoCrMo sample immersed in 0.9% NaCl electrolyte under OCP potential.

For the OCP potential, it is not expected to see corrosion since, in the polarization curve, this point is placed between the cathodic and the anodic branches.

There are two well differenced parts in the plots, a place where to reach the steady state, this lasts fifteen minutes, then the rubbing starts for one hour and after that the rubbing stops but the data is still collected for fifteen minutes more and the sample stabilizes again.

As the rub starts, the potential decreases, this means the protection against corrosion decreases also, to understand this better, this would be as if in the polarization curve, the curve is displaced to the left, so the anodic part stats before and that is why it starts to oxide at lower potentials.

If the friction coefficient is compared with the one obtained in dry conditions, it is improved with the electrolyte, and it goes from an average of approximately 0.425 (in dry) to an average of approx. 0.36.

For the +0.3V potential test (Figure 39), first of all, the test is run at a fixed potential, that's why the vertical axis instead of being the potential is the current.

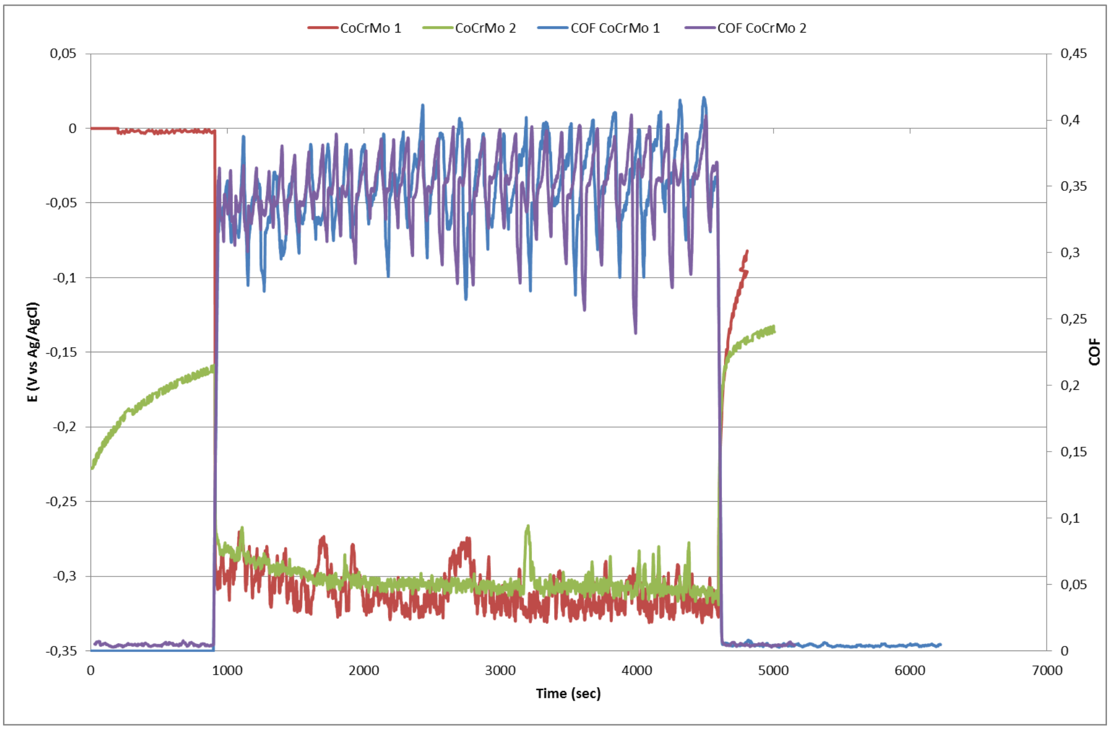


Figure 38 Potential and COF vs Time of CoCrMo OCP 0.9% NaCl

The COF in one of the samples decrease that might be due to the creation of a passivation layer that protects from corrosion.
In this case, the current increases when the rub starts, that means as in the case of the OCP test, that the behaviour under corrosion worsens.

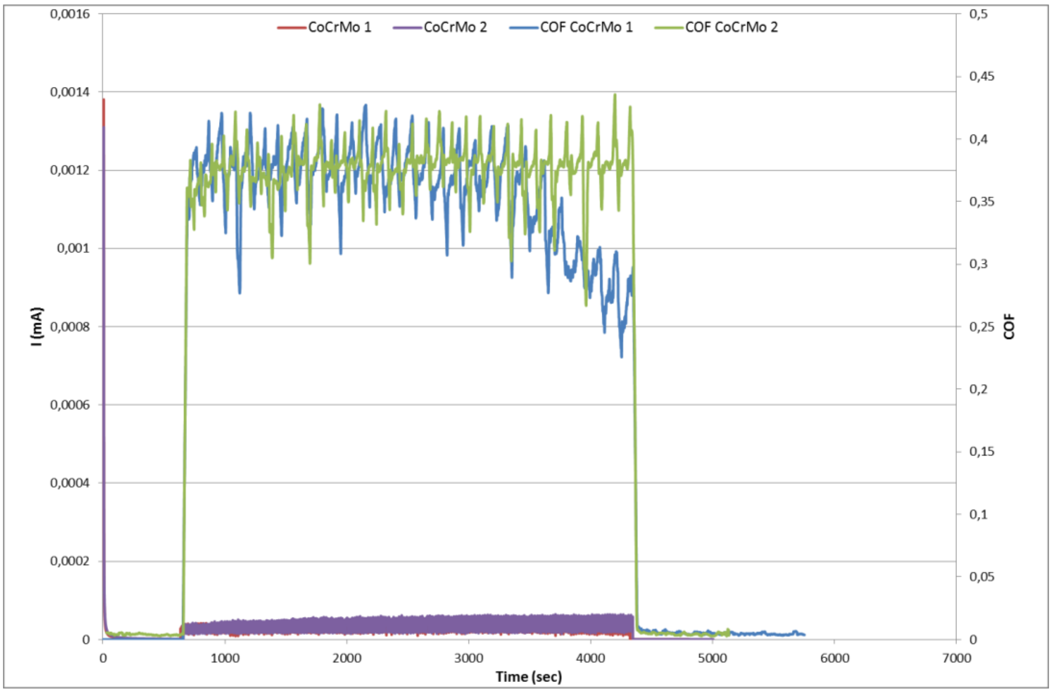


Figure 39 Current and COF vs Time of CoCrMo +0.3V NaCl

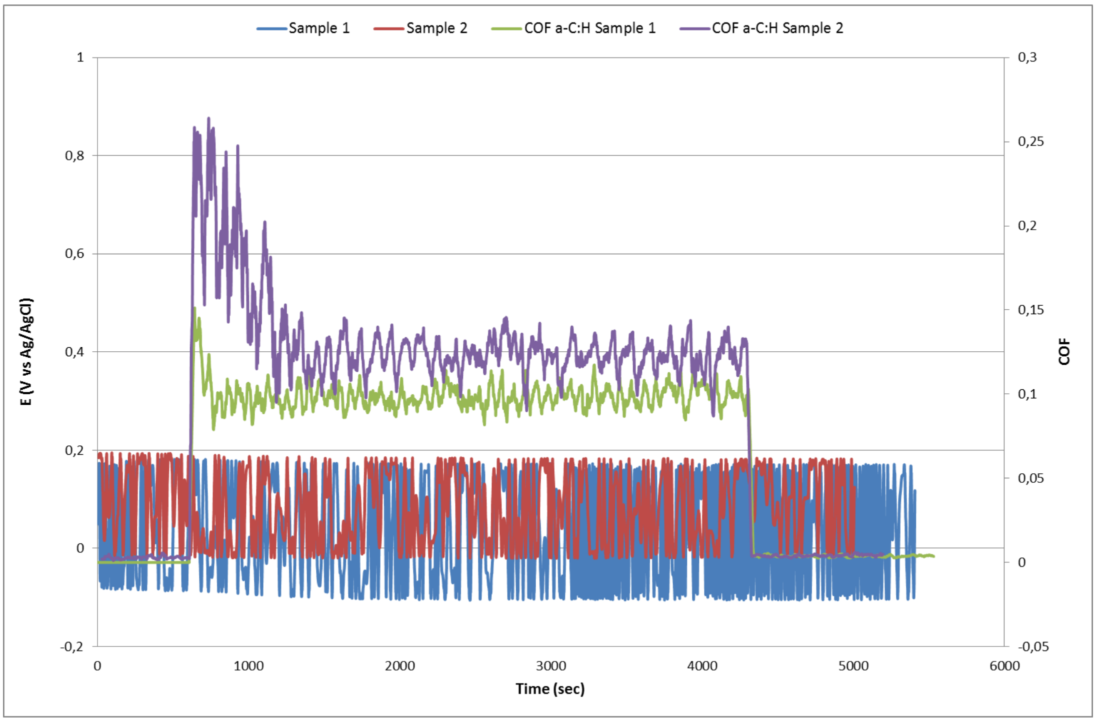


Figure 40 Potential and COF vs Time of a-C:H OCP NaCl

For the hydrogenated DLC (Figure 40) the potential does not follow a pattern as in the case of the CoCrMo, this could be due to the poor conductivity of the a-C:H, it is not even possible to distinguish when the rubbing starts or ends.

In the friction coefficient, compared to the dry test, it worsens, in the dry the COF is around 0.05 while in the electrolyte case it is above 0.1. In both cases when the rubbing starts there are high values until the creation of the protective layer.

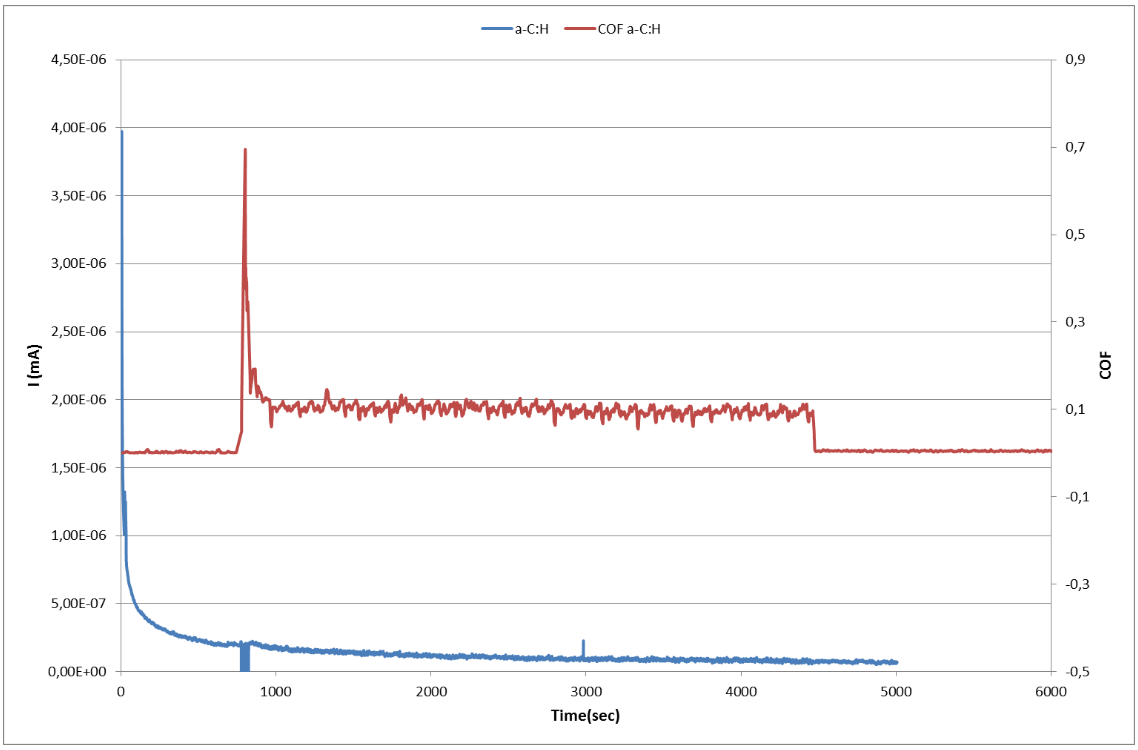


Figure 41 Potential and COF vs Time of a-C:H +0.3V NaCl

In the test at +0.3V (Figure 41), it happened the same with the current, there is no way to distinguish the rubbing, but as it is displayed, the current is almost zero, it has very low values.

Referring to the friction coefficient, the value worsens also compared to the dry test; but it is better than the one obtained in the test at OCP potential.

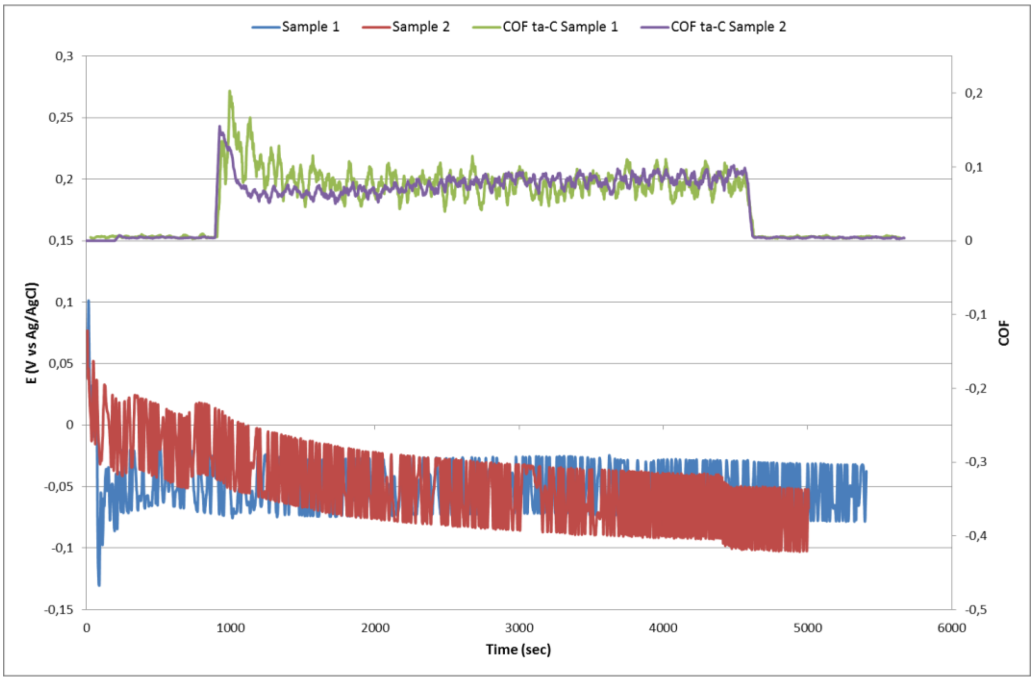


Figure 42 Potential and COF vs Time of ta-C OCP NaCl

In the figure above (Figure 42), it is displayed the ta-C sample in 0.9% NaCl electrolyte, at OCP potential.

As with the a-C:H, the potential is not very helpful. The friction coefficient improves from 0.1 to an average value below 0.1.

For anodic potential, (Figure 43), first of all, there are some peaks after 2000 seconds these peaks are due to noise, that’s why they won’t be taken into account; apart from that the current display does not tell us more than its low conductivity, apart from that, the behaviour of the tribology part has an improvement of the friction coefficient, compared to the dry test, and a value very close to the one obtained at OCP. Also, the values at the beginning are higher due to the starting of the rubbing which has higher resistance there, after some time the layer is created and the COF decreases to the expected values. Therefore, the combination of the corrosion and the tribology, is not worse than both mechanisms acting separately.

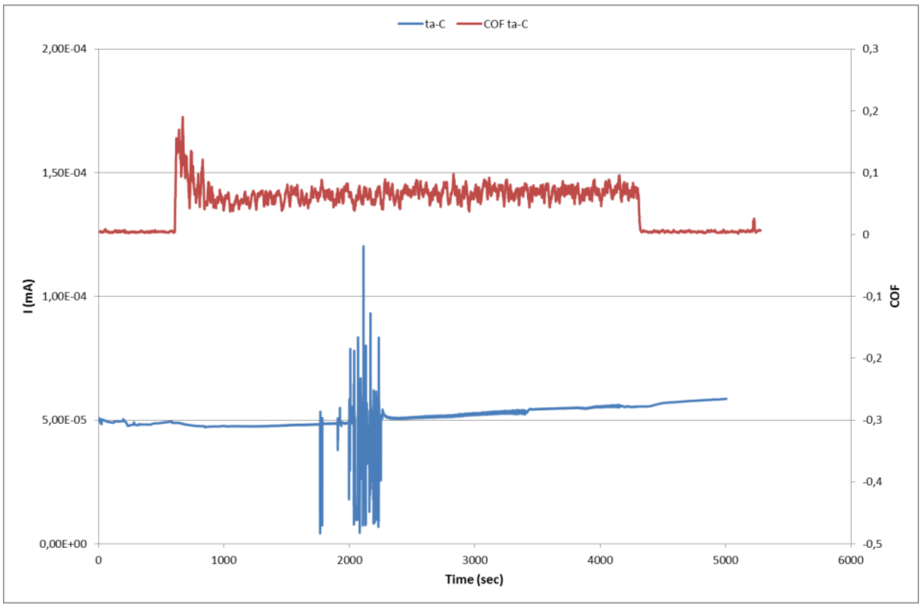


Figure 43 Potential and COF vs Time of ta-C +0.3V NaCl

Next results belong to the second batch received. The figure below (Figure 44) shows the results of the tribocorrosion test to a-C:H samples with a thickness of 6µm immersed in 0.9% NaCl electrolyte at OCP potential. The potential measured varies within 20V difference, this is because it is an insulated material, the potentiostat could not measure higher values due to overloads, that are why the voltage stays at 10V, positive and negative, but it could have been higher.

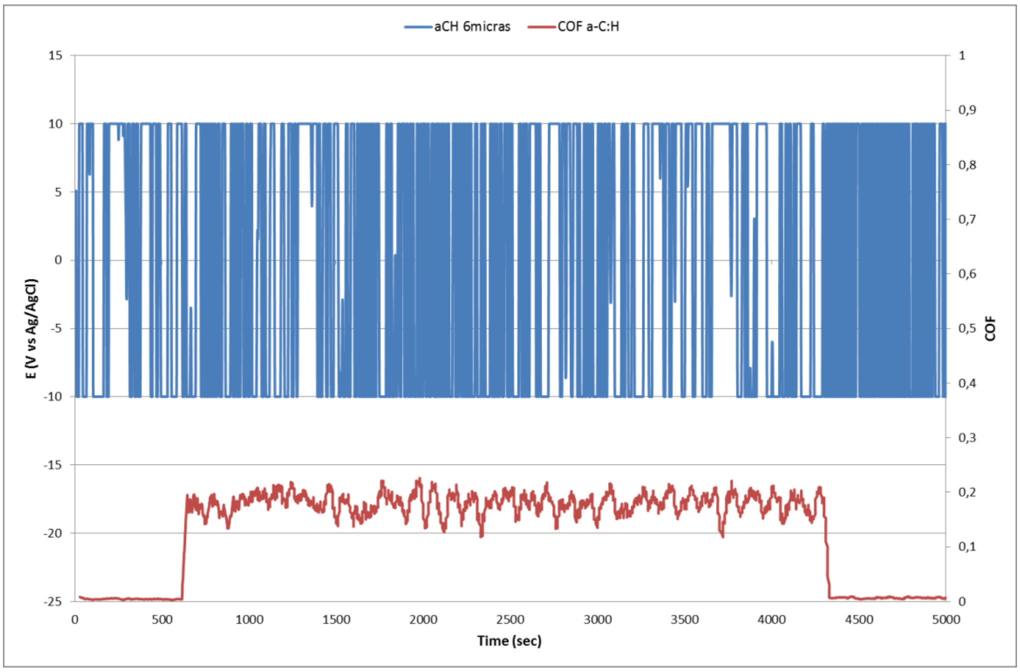


Figure 44 Potential and COF vs Time of a-C:H 6micras 0.9% NaCl OCP

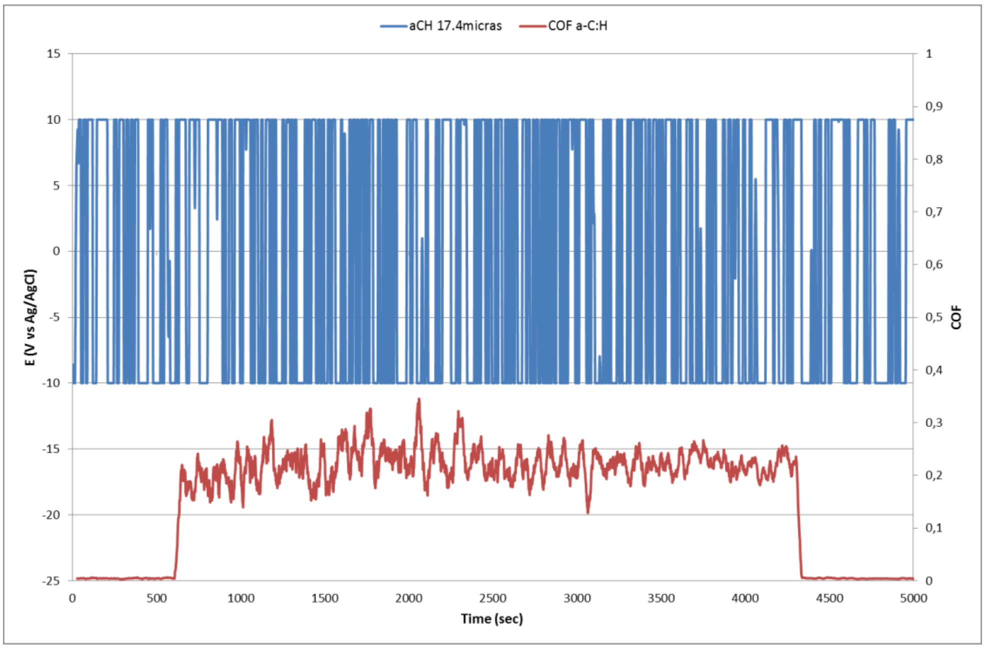


Figure 45 Potential and COF vs Time of a-C:H 17.4micras 0.9% NaCl OCP

For the thicker a-C:H sample (Figure 45) the values are similar, with higher friction coefficient but a slight difference, about 0.05. The potential again is not very helpful, not even possible to see where the rubbing starts.

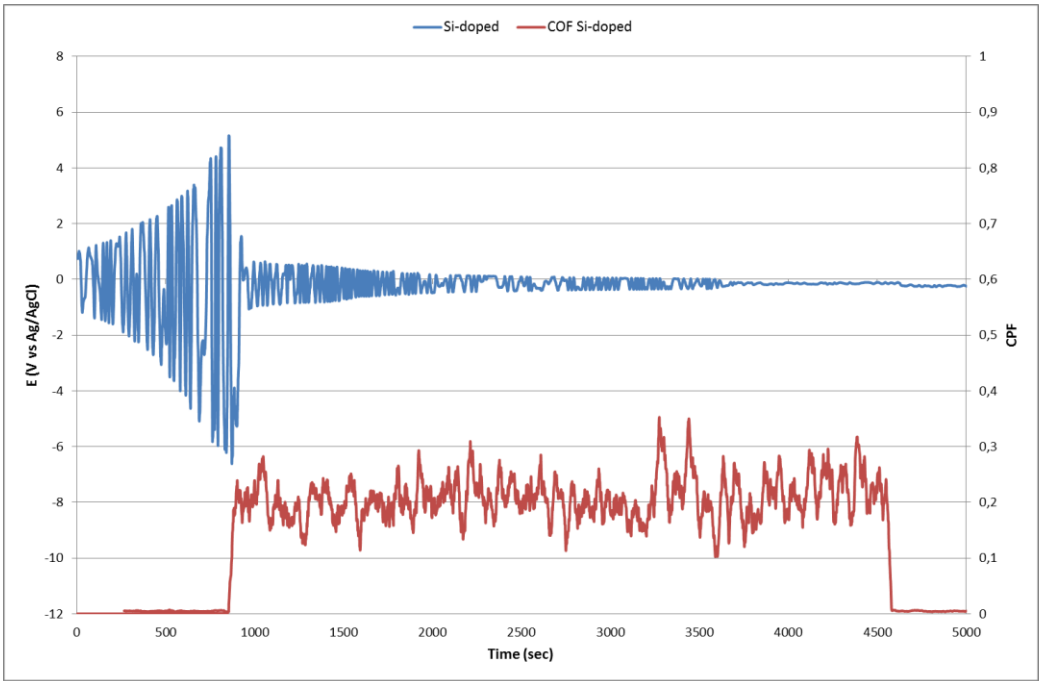


Figure 46 Potential and COF vs Time of Si-doped OCP 0.9% NaCl

In Figure 46 the behaviour of the Si-doped coating is shown, this one does not present the same insulation as the other due to the Si, as it happened also with the Ti-doped samples. When the rubbing starts there is a change in the potential and when it stops so it does also, despite the fact that is very small change there is still a variation.

✓ PBS Electrolyte

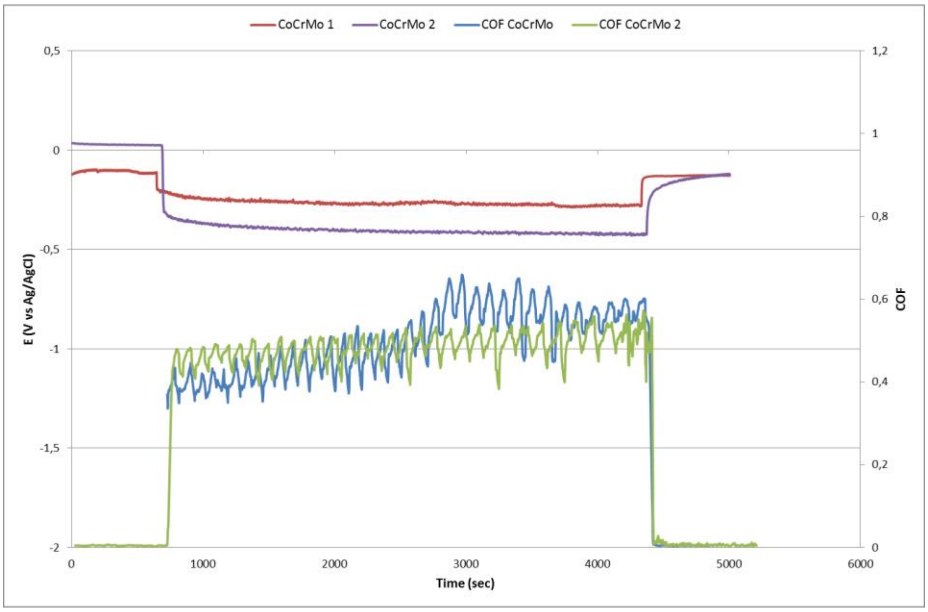


Figure 47 Potential and COF vs Time of CoCrMo OCP PBS

For the CoCrMo sample (Figure 47), the regions with or without rubbing are clearly distinguished, the behaviour is the same than with the NaCl electrolyte, with different values of the OCP as seen in the polarization curves and higher value of the COF.

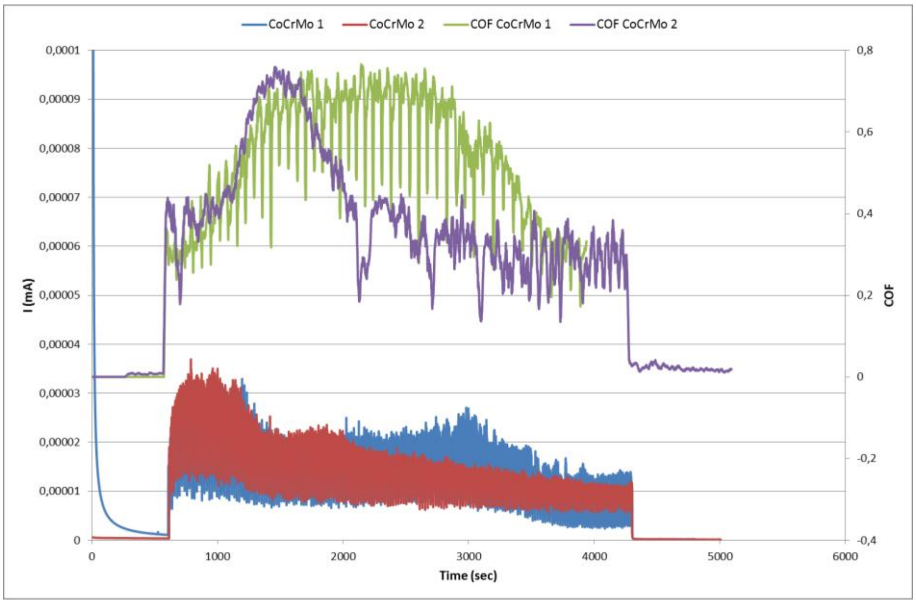


Figure 48 Potential and COF vs Time of CoCrMo +0.3V PBS

For the anodic potential (Figure 48) the current behaves as expected, an increase of it when the rubbing starts, which means that the material will be less resistant to the corrosion, it will start to oxide before.
For the friction coefficient plot, the repeatability is not as clear as in the other tests but the tendency is similar, with an increase of the friction until high values, and then a decrease until more reasonable values; this could be because in presence of this electrolyte it is harder for the material to create a protective layer and in the cases displayed the first one was able to create it before. That is why the high and the values after that are very similar in both tests.

Below, the results obtained for both potential for the hydrogenated sample are shown.
Again, the potential/current values are not very helpful. For OCP potential (Figure 47) it can be seen a slight tendency decreasing the potential. For the anodic potential (Figure 49), current was measured but it is basically zero.
To the extent of the friction coefficient, the OCP test has a difference in both tests carried out with the same patterns but this must be due to the same reasons that are explained in the CoCrMo PBS at +0.3V. In the case of the tetragonal test at +0.3V, the pattern is also the same, high values at the beginning and a recovery after some period of time. In both tests, the COF is pretty similar.

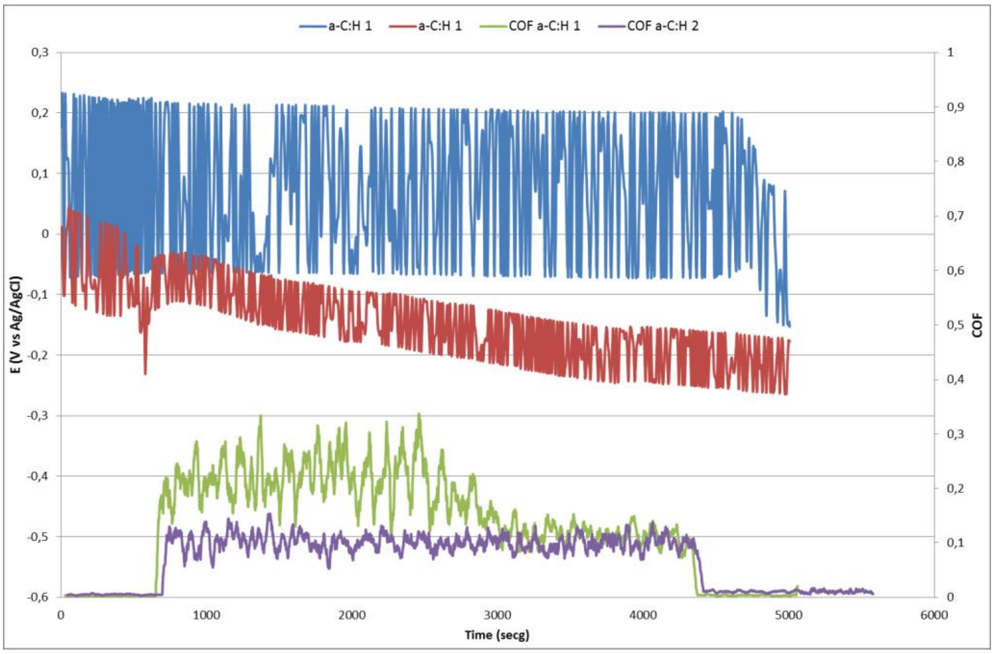


Figure 49 Potential and COF vs Time of a-C:H OCP PBS

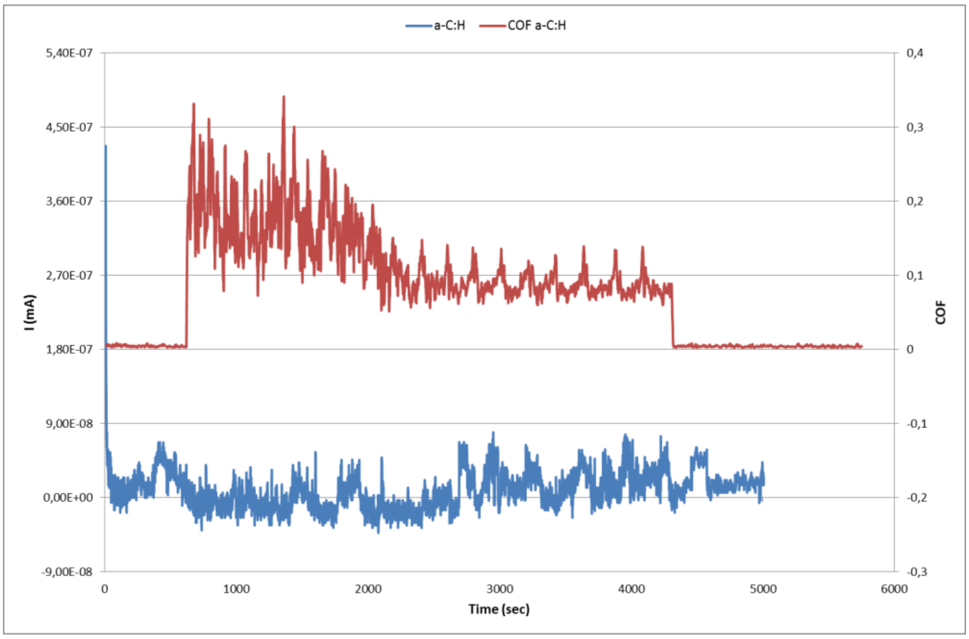


Figure 50 Potential and COF vs Time of a-C:H +0.3V PBS

For the ta-C at PBS electrolyte, at OCP (Figure 51) the results are positive, the corrosion does not affect the tribology process so the friction coefficient values do not increase.

It is remarkable that at the anodic potential (Figure 52), the effect of the rubbing in the current is visible, even though the current is almost zero, when the rubbing starts the current increases and that concurs with higher values of the COF which means both the corrosion and the friction are gathering their consequences.

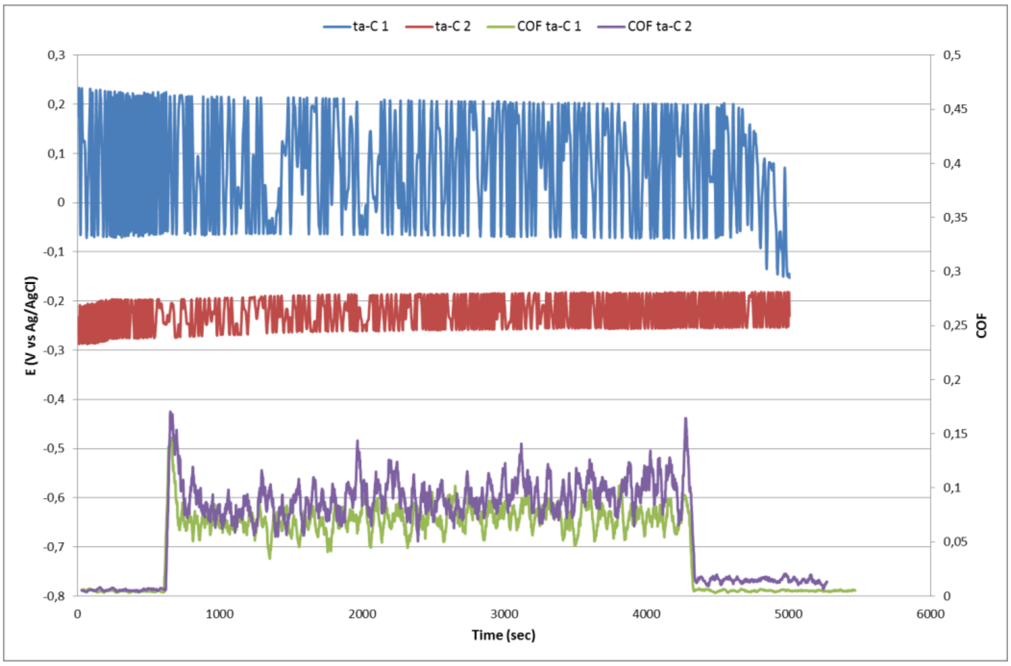


Figure 51 Potential and COF vs Time of ta-C OCP PBS

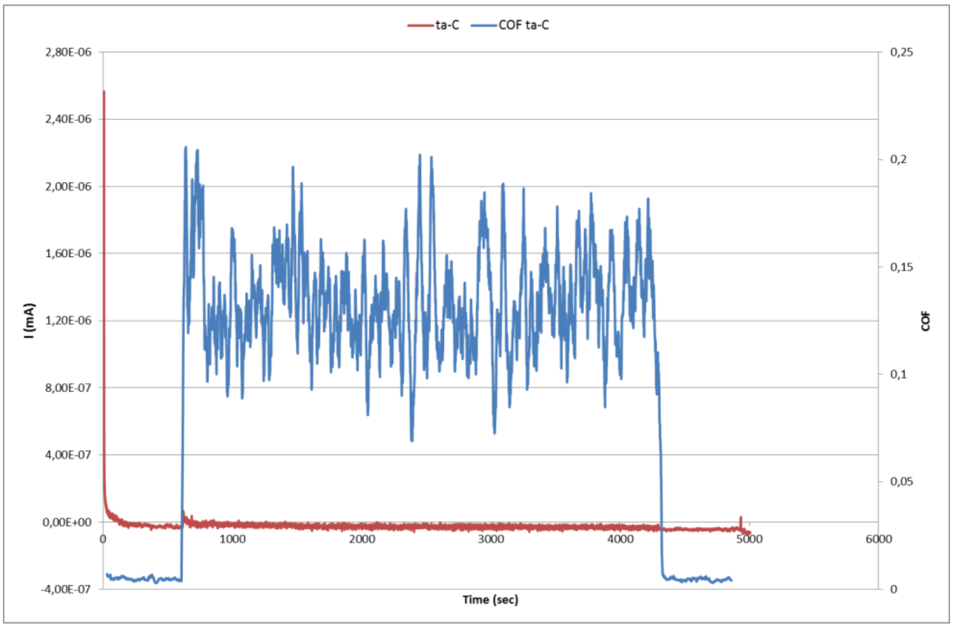


Figure 52 Potential and COF vs Time of ta-C +0.3V PBS

✓ Albumin Electrolyte

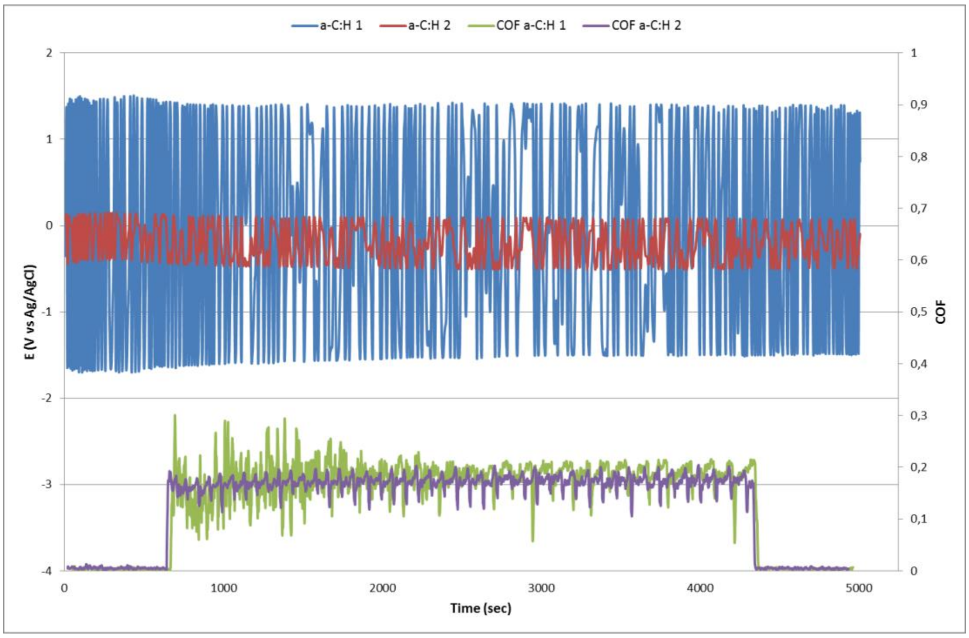


Figure 53 Potential and COF vs Time of a-C:H OCP Albumin

The tendency of the potential in both samples is the same but with a higher variation in the first one.

The friction coefficient increases to values close to 0.2; this could be due to either reasons, or the effect of the rubbing and the corrosion that worsens the resistance of the material or the effect of the albumin and its adsorption. It is harsh to figure out which one is the reason or if both act at the same time since we cannot see the effect of the corrosion in the potential plot against time.

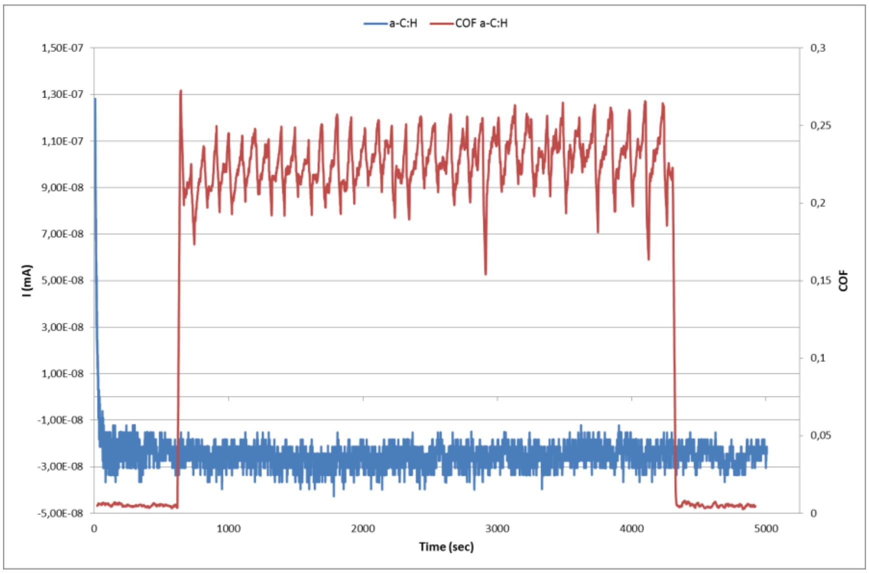


Figure 54 Potential and COF vs Time of a-C:H +0.3V Albumin

For the anodic test (Figure 54), again the current is almost zero, but here it cannot be seen any influence of the rubbing, might be due to the low conductivity of the material.

The reason why it is not believed that the rubbing is not affecting is that the friction coefficient increases substantially compared to the PBS electrolyte results, or another options would be that the material was not able to create the protective layer, that would explain why the plot is very similar to the PBS electrolyte that could not create the layer.

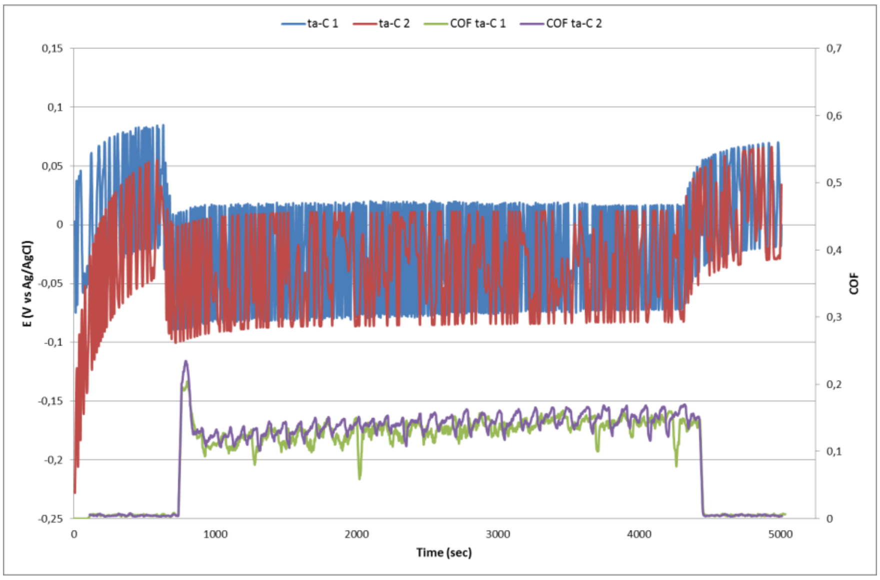


Figure 55 Potential and COF vs Time of ta-C OCP Albumin

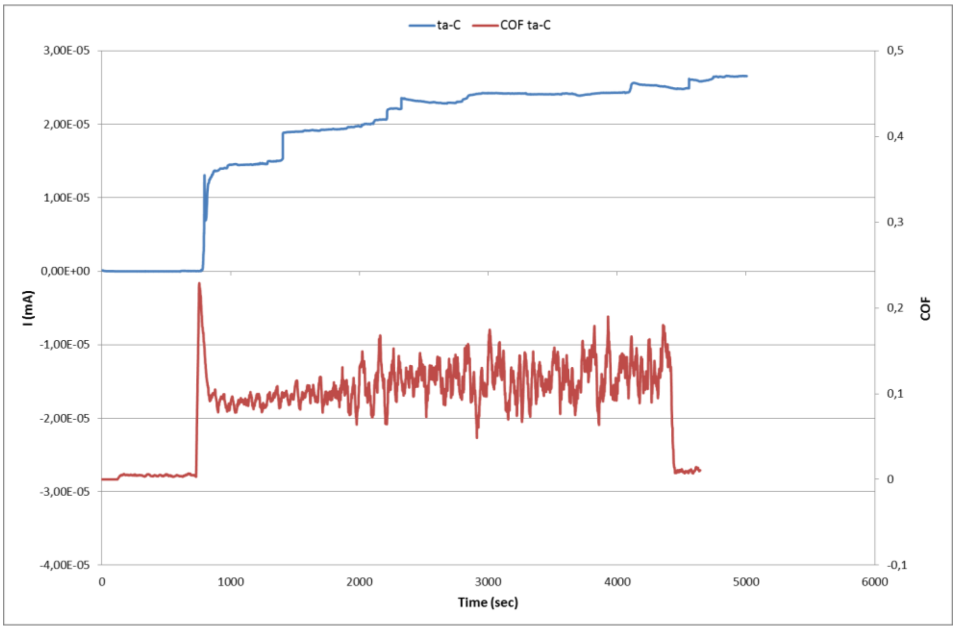


Figure 56 Potential and COF vs Time of ta-C +0.3V Albumin

For tetragonal tests, there is, at OCP (Figure 55), a clear influence of the rubbing and the potential. But still the COF is higher than the one obtained with PBS electrolyte, that’s why we can say this increase is either due to the albumin and the effect of the rubbing that adheres to the corrosion mechanisms.

For the anodic test (Figure 56), seems that there is a correlation of the rubbing and the friction coefficient but the current keeps on increasing and that is not reflected on the COF, so that could be because of the poor conductivity. Again, the current is very close to zero.

4.5 SEM

Once the tribocorrosion tests have been done it was time to analyse the samples. With the scanning electron microscope each sample was observed where the rubbing left a wear track.

Due to the fact that the samples are not good conductive it was harsh to watch in detail everything. Besides, the tests were done with a load of 2N during 1 hour and that did not lead to a big wear track, therefore some of the samples were impossible to find the wear track. Hence, there are not images about it.

Basically, the two wear forms that will be depicted or better say the most common forms of wear expected to be seen are adhesion and abrasion.
In this case, adhesion will occur when due to the rubbing small pieces of the sample will separate and be crushed again to the sample because of the ball.
In the case of abrasion, this will happen when the pieces of the sample are harder than the sample due to the structural deformation and are attached to the ball and rub the sample.

✓ DRY TESTS

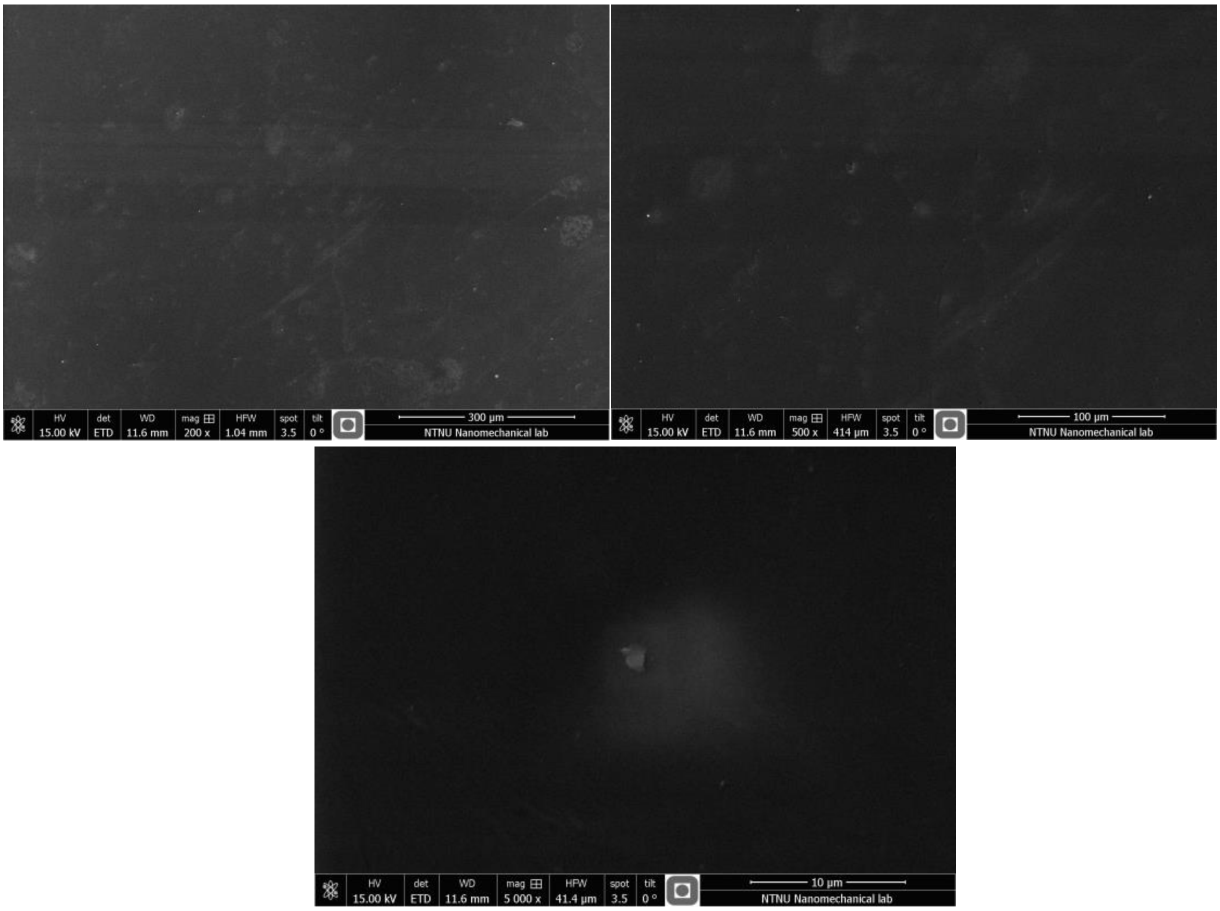


Figure 57 Wear Track Dry Test a-C:H at x200, x500 and x5000 magnification

As it can be seen in Figure 57, for the hydrogenated sample, the wear track can be barely seen; due to the fact that the COF is approximately 0.06 the small wear track makes sense. At the magnification of x5000 there is a flake which shows the adhesion wear mechanism.

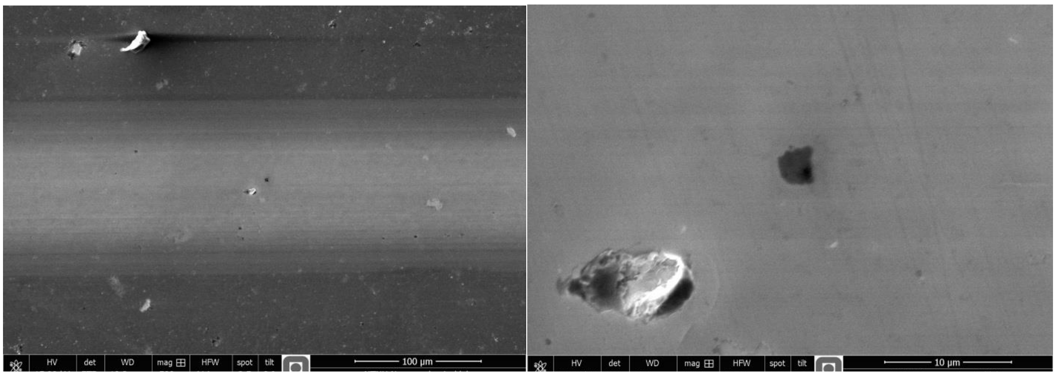


Figure 58 Wear Track Dry Test ta-C at x500 and x5000 magnification

In Figure 58, the tetragonal sample shows higher wear than the hydrogenated one, this coincide with the results obtained, the COF is approx. 0.12. The wear track is more visible and bigger flakes appear and lines in the direction of the rubbing are also visible (hard to see though) and that could explain abrasion

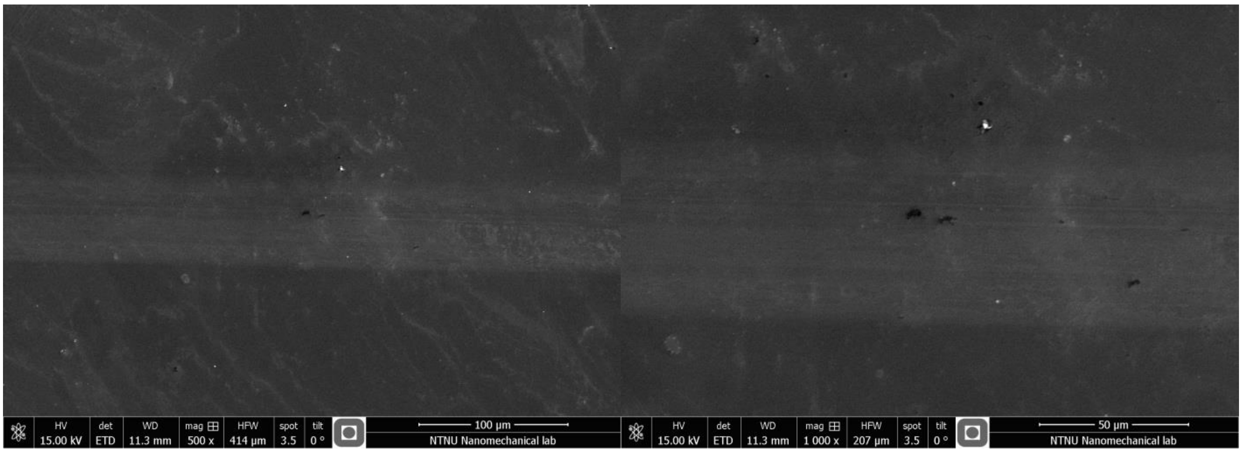


Figure 59 Wear Track Dry Test Ti-doped at x500 and x1000 magnification

For the Ti-doped sample (Figure 59), the wear track is “easily” visible, still harder than the tetragonal sample, this is depicted in the COF plot where the Ti-doped values are between the hydrogenated and the tetragonal samples; this behaviour can be explained by the Ti-doped that decreases the hardness of the coating.

Flakes are visible as well as abrasion; the second one is harder to be seen.

Now, second batch of samples are displayed, the coatings made in Germany.

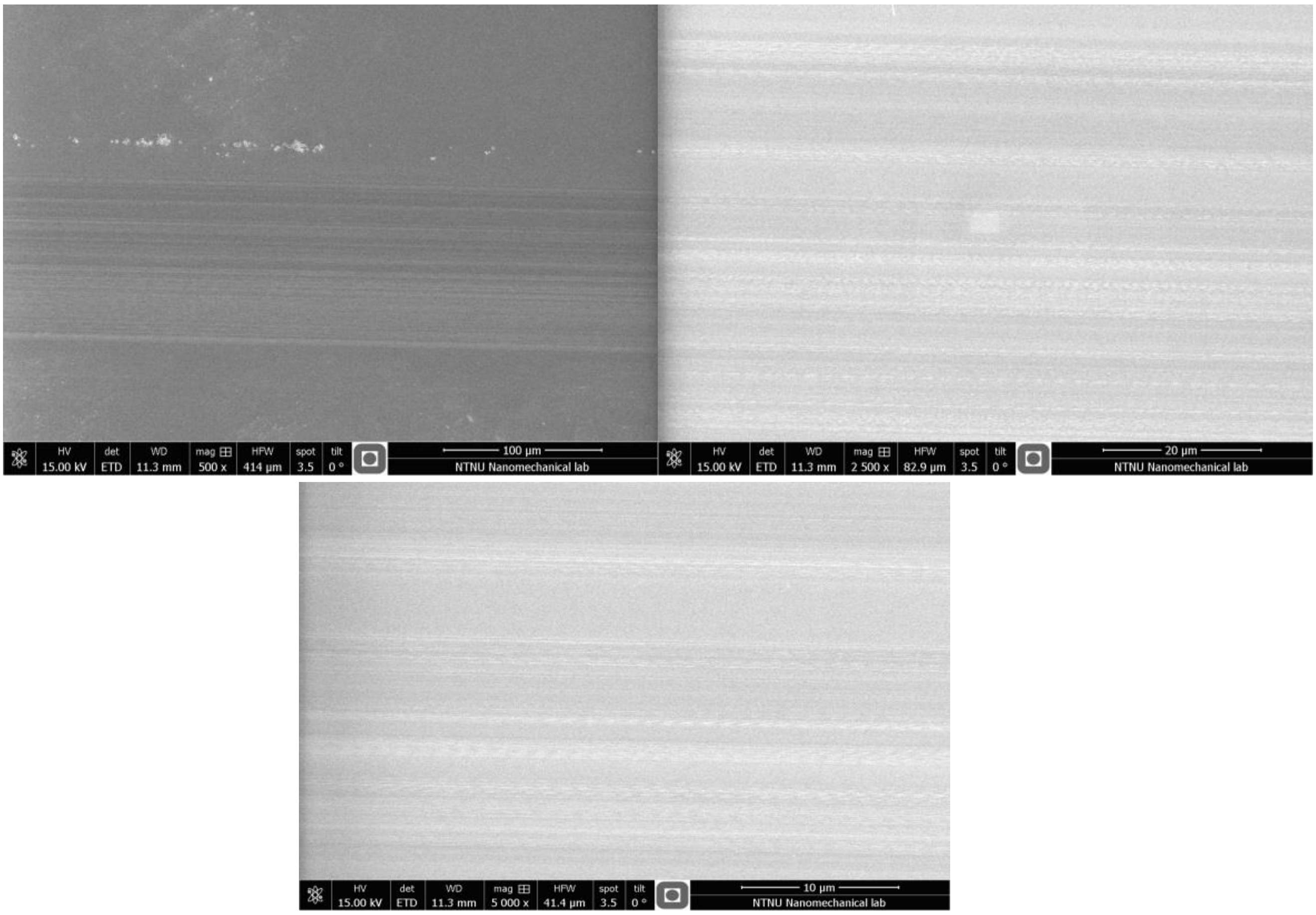


Figure 60 Wear Track Dry Test a-C:H (6micras) at x500, x2500 and x5000 magnification

The a-C:H coating has clear abrasion wear mechanism on its surface, the fact that when two tests were done, one had a COF of approx. 0.3 and the other one of 0.07 shows little repeatability. It will be discuss later the possible reasons.

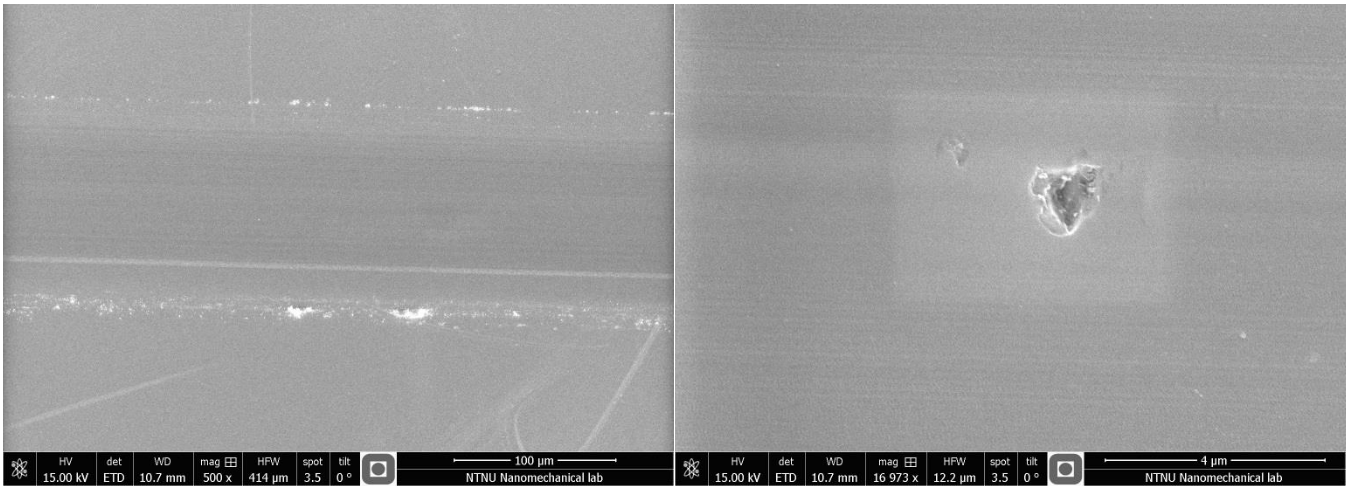


Figure 61 Wear Track Dry Test a-C:H (17.4micras) at x500 and x17000 magnification

With higher thickness (17.4µm) the wear is lower, the abrasion is almost impossible to see and flakes are very small, like the one shown in Figure 57 that was found at a magnification of x17000.

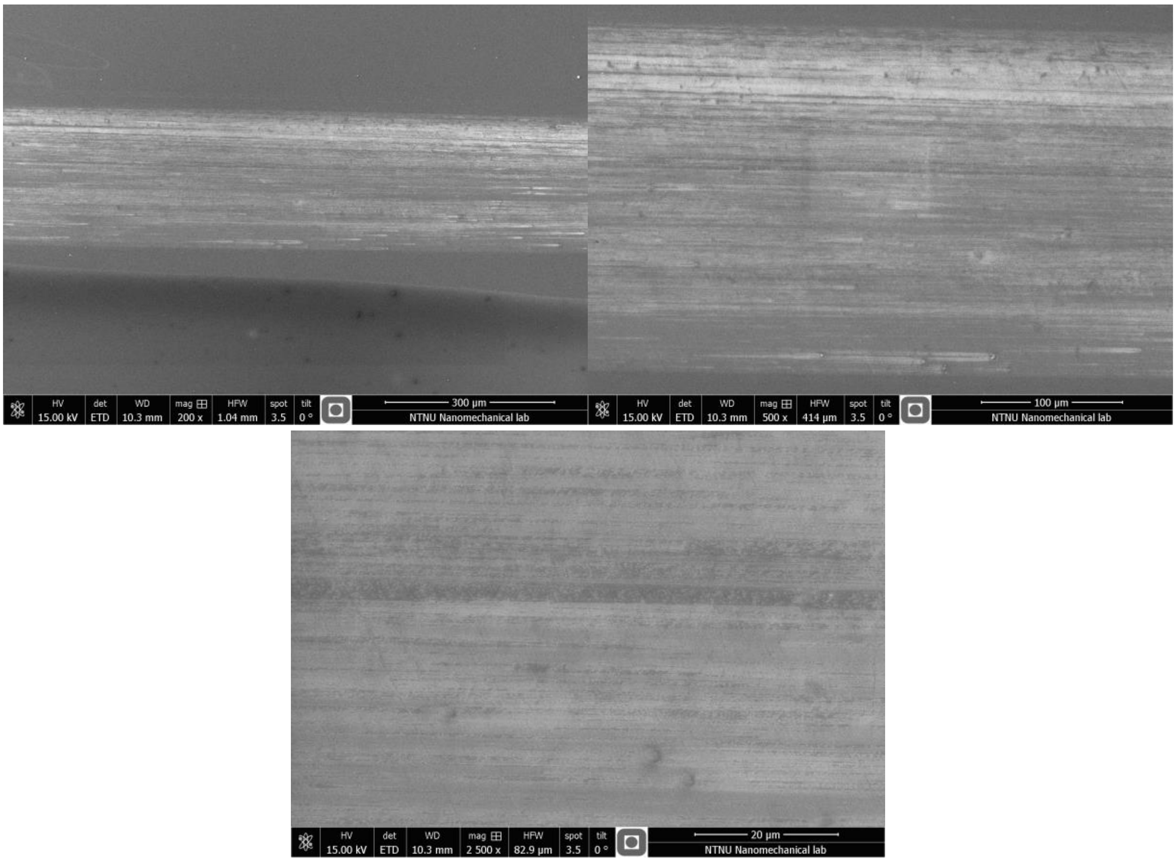


Figure 62 Wear Track Dry Test Si-doped at x200, x500 and x2500 magnification

For the Si-doped (Figure 62) the wear track is much more visible, with a magnification of x200 it has the same size as the a-C:H at 6µm and 17.4µm at x500. The COF vs time plot shows as in the case of the a-C:H (6µm) two behaviours, one with approx. 0.35 COF value and other one with 0.1.
The prevailing wear mechanism is the abrasion but also has some flakes due to adhesion.

✓ 0.9% NaCl Electrolyte

• Open Circuit Potential

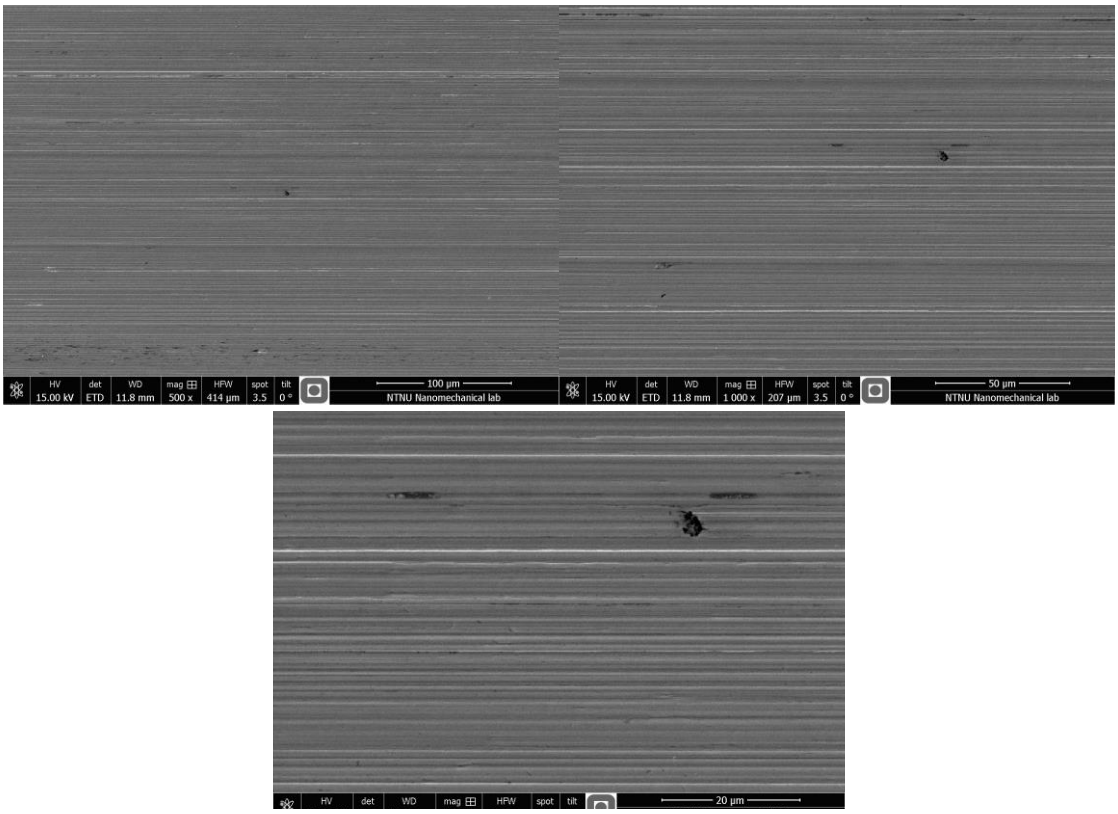
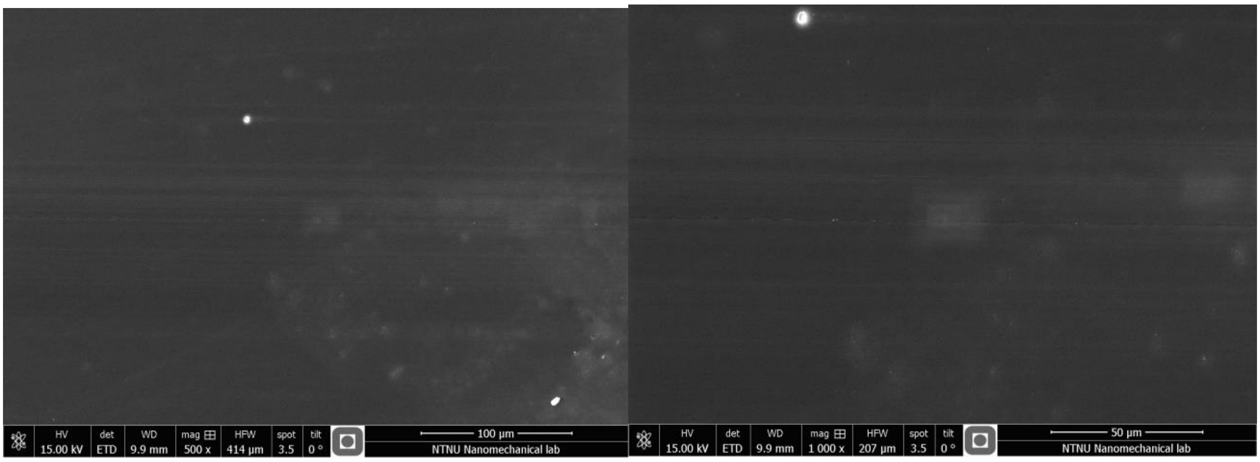


Figure 63 Wear Track 0.9% NaCl OCP CoCrMo Electrolyte at x500, x1000 and x2500 magnification

For the un-coated sample, the abrasion is more evident, with a COF of 0.35 it makes sense, there are also flakes and small holes that can be formed due to pitting corrosion.



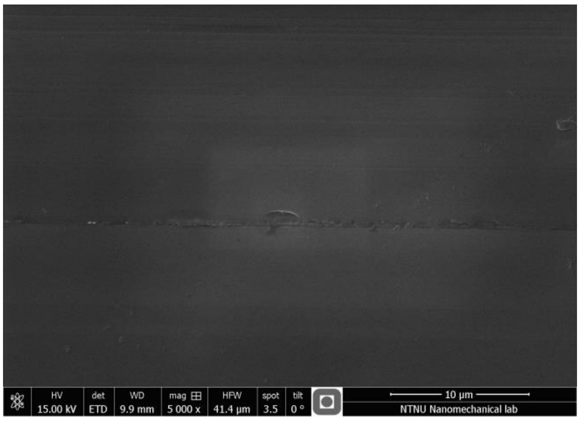


Figure 64 Wear Track 0.9% NaCl OCP a-C:H at x500, x1000 and x2500 magnification

For the a-C:H sample (Figure 64), the wear is less evident, the E vs time plot is useless but the COF increases compared to the dry test.
It can be seen an imperfection along the rubbing direction which could be due to abrasion but with higher magnification there is also visible a flake, due to adhesion presumably.

For the ta-C coating (Figure 65), the wear track is easier to see than the a-C:H coating, this could be due to several reasons, taking into account that the COF is lower, could be due to worse focus using the SEM or because of the electrical conductivity that allow better images.
Anyhow, there are flakes and some type of lines.

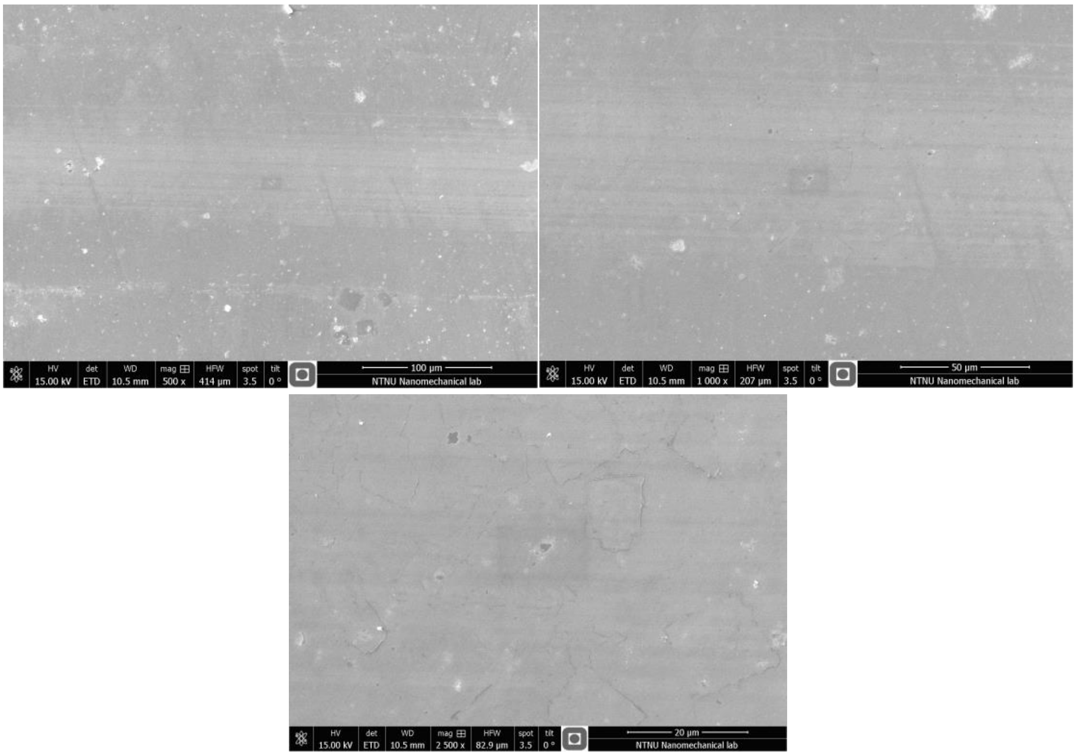


Figure 65 Wear Track 0.9% NaCl OCP ta-C at x500, x1000 and x2500 magnification

The samples with the coating deposited in Germany were also tested under OCP potential and 0.9% NaCl electrolyte. Another tests belonging to this batch were performed due to lack of time (except for the dry tests already shown). Despite this, it was impossible to find the wear track with the scanning electron microscope, most probably due to the low electrical conductivity, this is the best hypothesis considering that the COF was higher than the other samples and for these ones it was possible to find the wear track.

- **Anodic Potential**

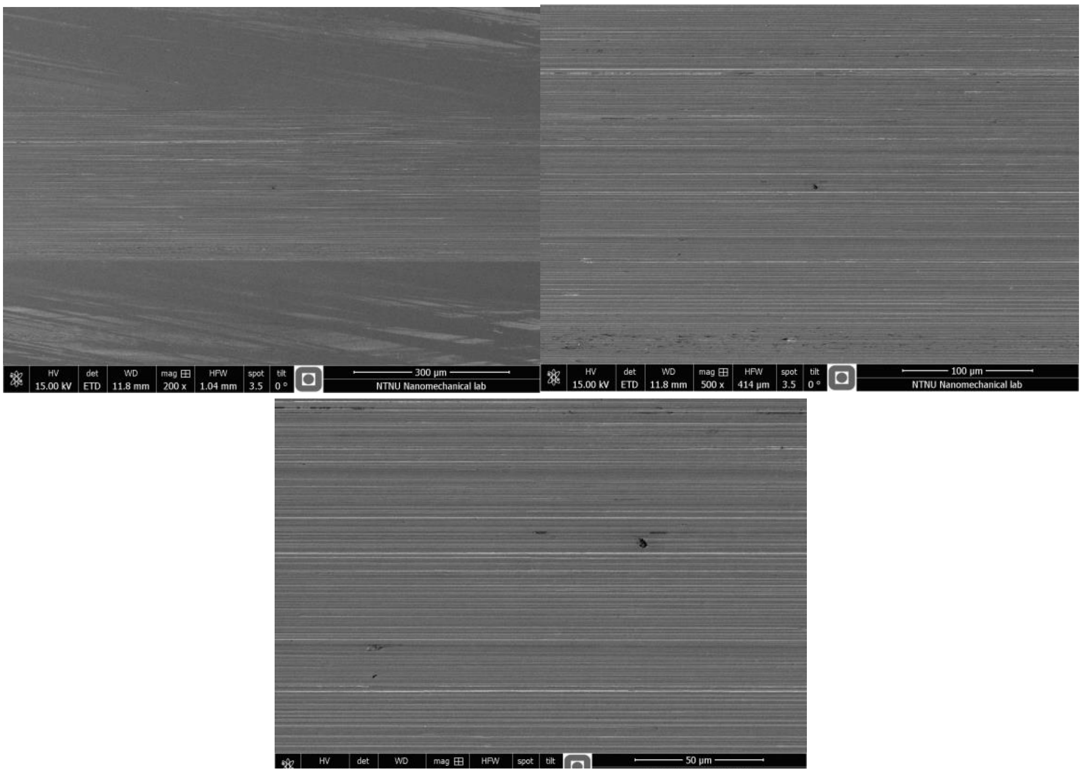
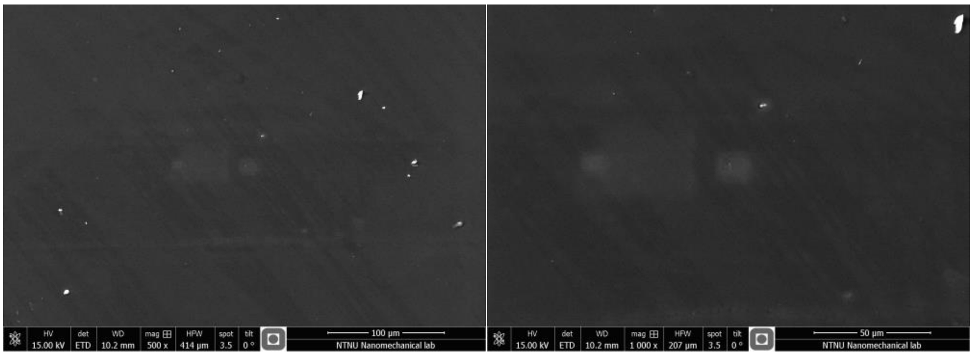


Figure 66 Wear Track 0.9% NaCl +0.3V CoCrMo at x500, x1000 and x2500 magnification

For the un-coated sample, the abrasion is the most important mechanism, but pitting corrosion can be seen also as well as adhesion wear (in lower measure).



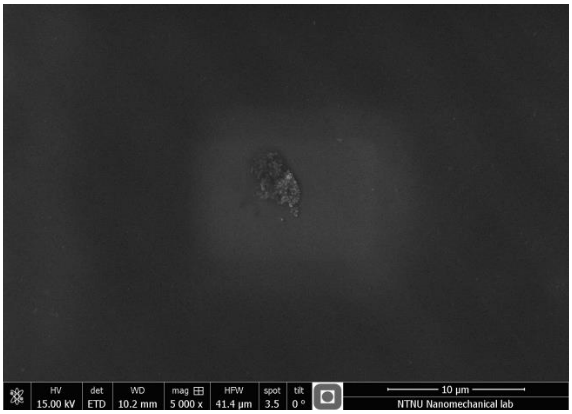


Figure 67 Wear Track 0.9% NaCl +0.3V a-C:H at x500, x1000 and x5000 magnification

For the hydrogenated coating (Figure 67), nothing can be seen with the SEM, only a small flake.

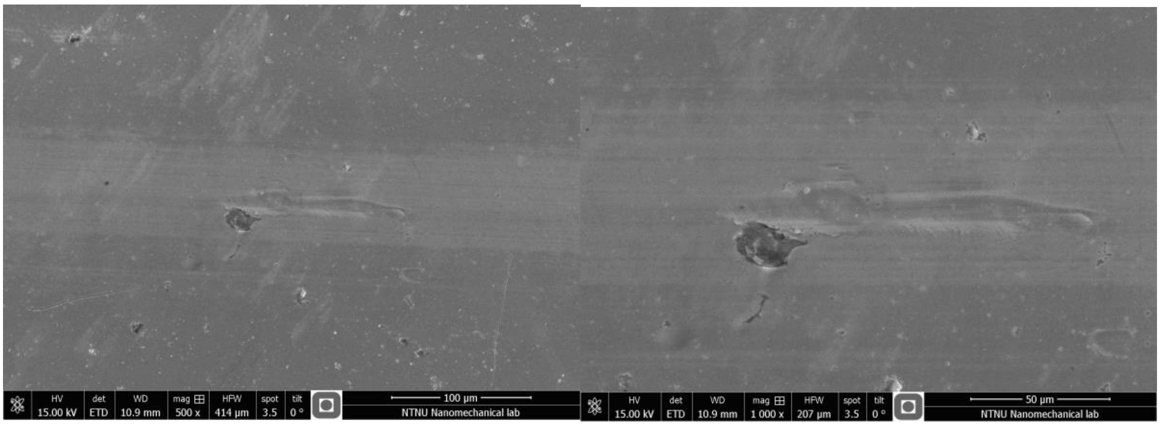


Figure 68 Wear Track 0.9% NaCl +0.3V ta-C at x500 and x1000 magnification

The tetragonal coating is dominated by adhesion wear, flakes can be seen (Figure 68).
The behaviour almost vary when using OCP or +0.3V potential.

As said before, any tests were done with the second batch under these conditions because of a lack of time.

✓ PBS Electrolyte

• OCP Potential

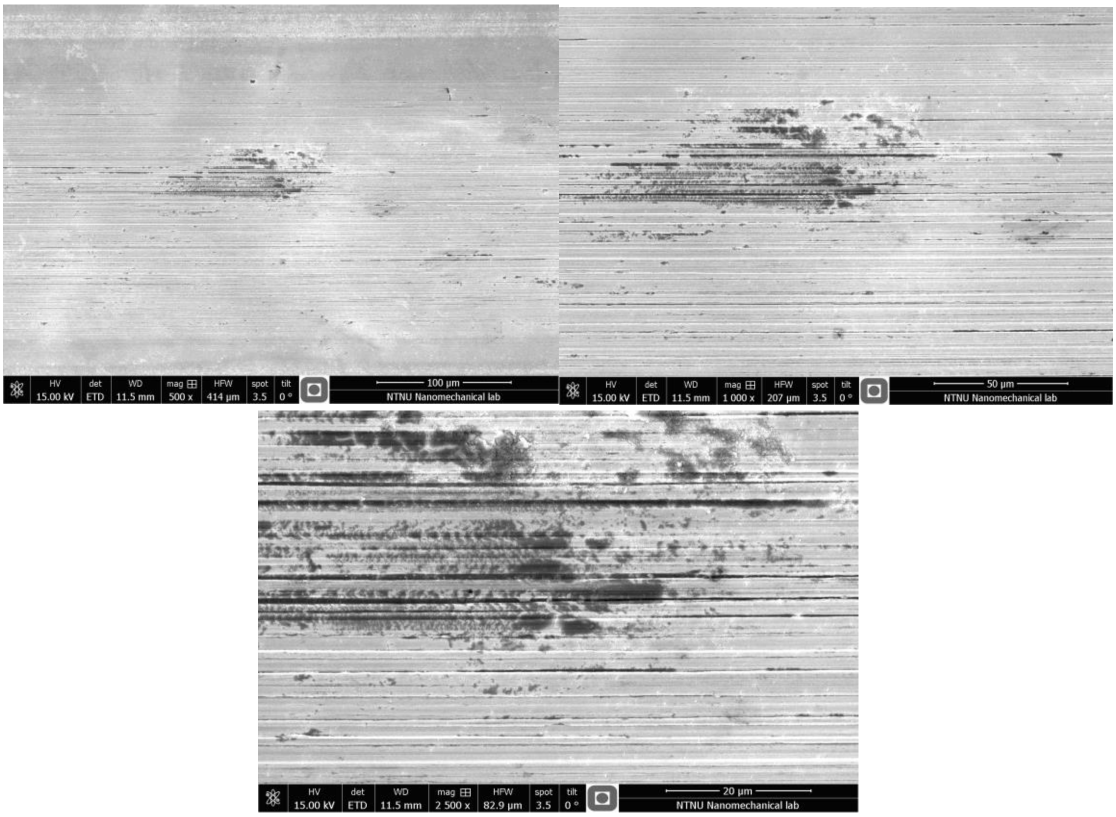


Figure 619 Wear Track PBS OCP CoCrMo at x500,x1000 and x2500 magnification

For the un-coated sample (Figure 69), the predominant wear mechanism is the abrasion but also with a big influence of adhesion.

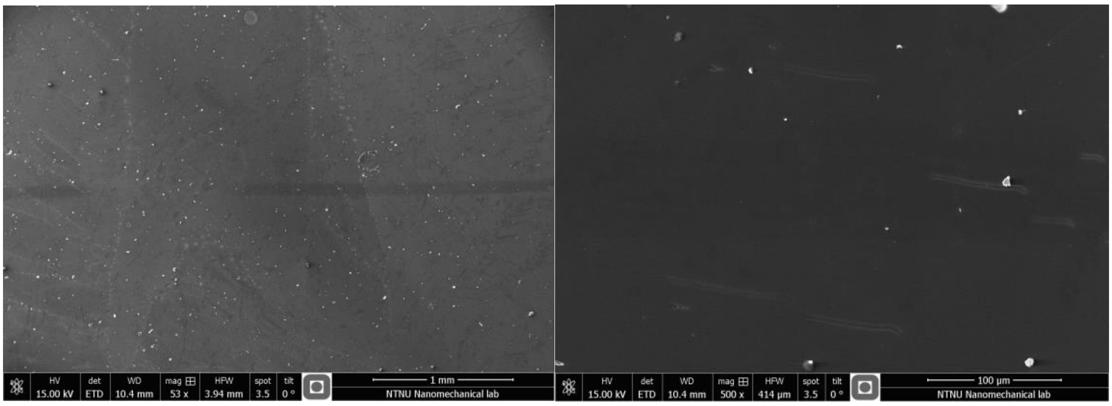


Figure 70 Wear Track PBS OCP a-C:H at 50 and 500 magnification

For the a-C:H coating (Figure 70), the wear track is almost non-existent and with a magnification of x500 non imperfections are able to be seen. Despite the fact that the COF is around 0.15, which is approx. three times bigger than the one obtained in the dry test.

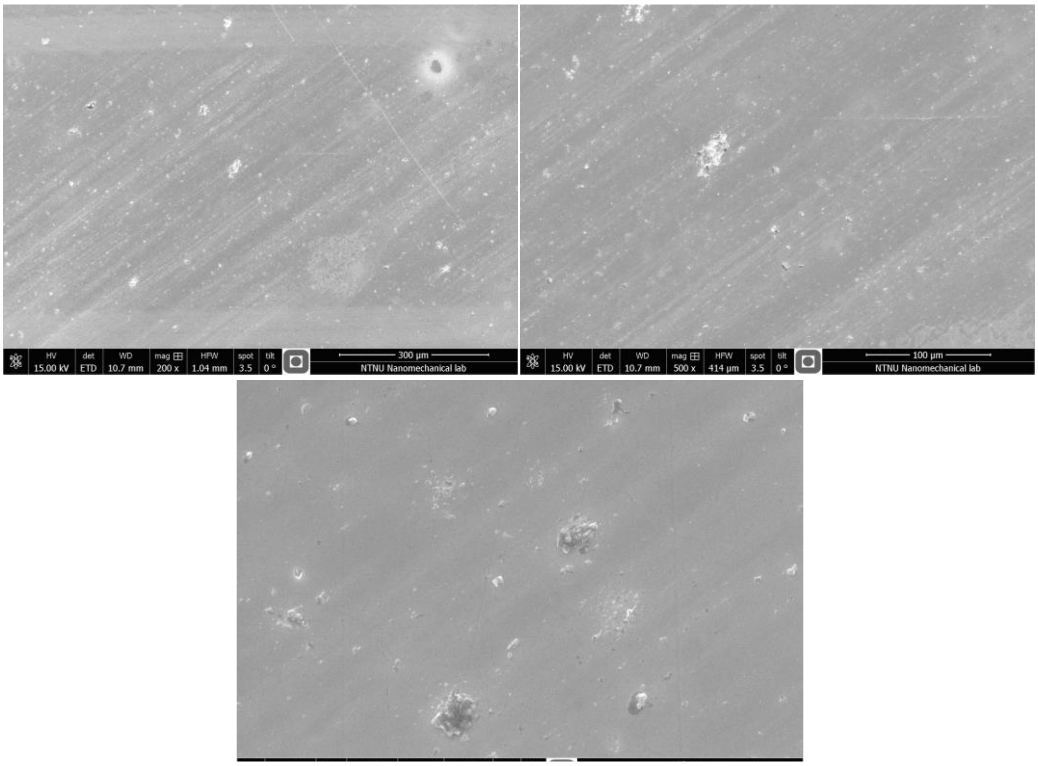


Figure 71 Wear Track PBS OCP ta-C at x200, x500 and x5000

For the ta-C coating (Figure 71), the wear track has lines crossing it at a 45º angle but no adhesion wear mechanism. There are imperfections but they do not seem to be due to the rubbing.

- **Anodic Potential**

In the case of the un-coated sample (Figure 72), the abrasion mechanism leads the wear, there are also black holes that seem to be pitting corrosion.
There is also one rectangle in the highest magnificated image, but that one is where the window of the focus was aiming and the sample got extra charged with the electrons, that rectangle has to be neglected since it does not belong to the rubbing imperfections.

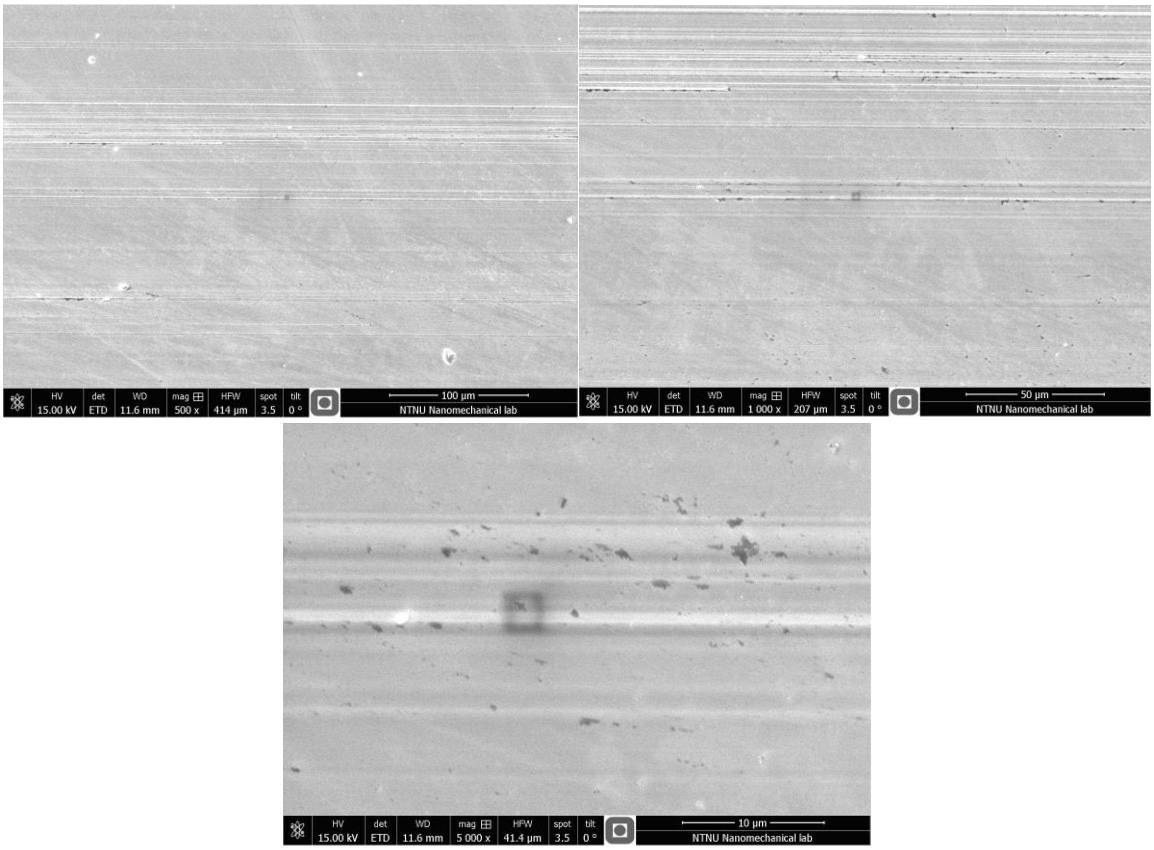


Figure 633 Wear Track PBS +0.3V CoCrMo at x500, x1000 and x5000 magnification

For the hydrogenated coating (Figure 73), the wear track couldn't be found, thus an image of the surface was taken in order to see the deposition of the electrolyte.

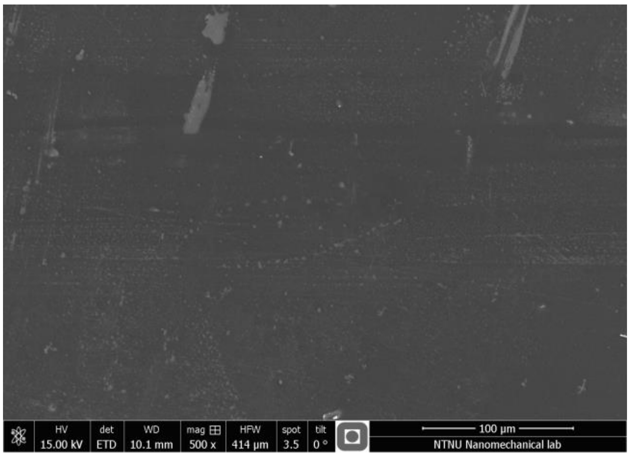


Figure 64 Wear Track PBS +0.3V a-C:H at x500 magnification

For the ta-C coating (Figure 74), the wear tack was easy to find, but the wear mechanism that can be found is adhesion, because of small flakes that can be seen with a magnification of 5000. There are lines also at 60º from the horizontal. This could be due to the roughness of the coating that wasn't mirror surface quality.

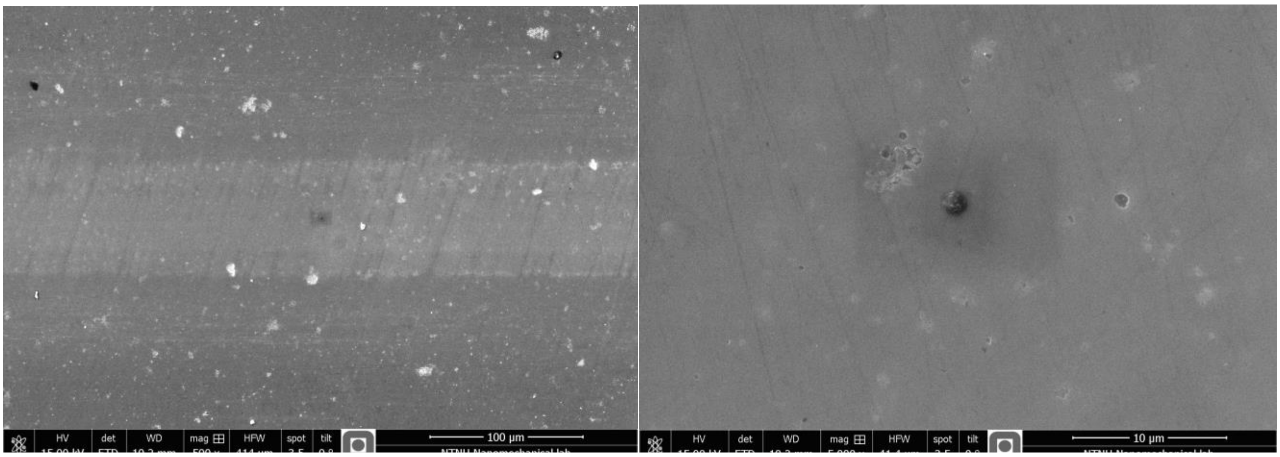


Figure 65 Wear Track PBS +0.3V ta-C at x500 and x5000 magnification

- ✓ **Albumin Electrolyte**
    - **OCP Potential**

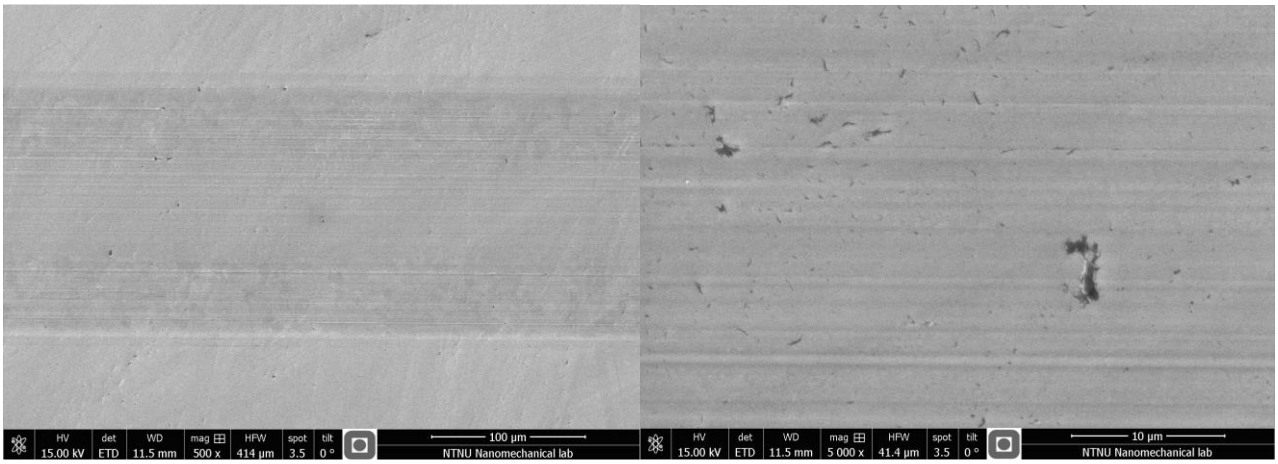


Figure 66 Wear Track Albumin OCP CoCrMo at x500 and x5000 magnification

For the un-coated sample (Figure 75), the abrasion dominates the wear but it is also visible the flakes belonging to adhesion wear. The wear is as always more visible in the case of the un-coated samples.

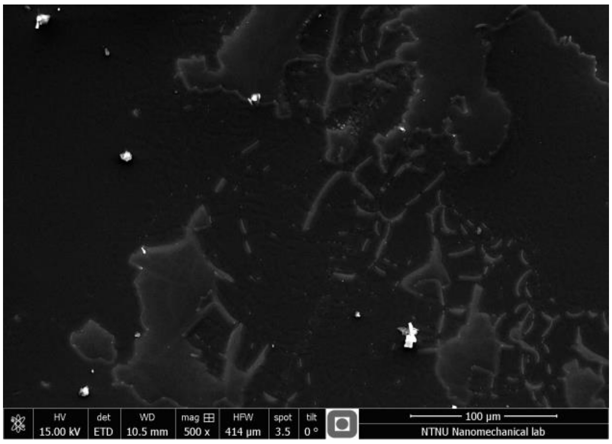


Figure 67 Albumin OCP a-C:H at x500 magnification

For the a-C:H coating (Figure 76), it was not possible to find the wear track, therefore an image of the surface was taken in order to see the deposition of the electrolyte.

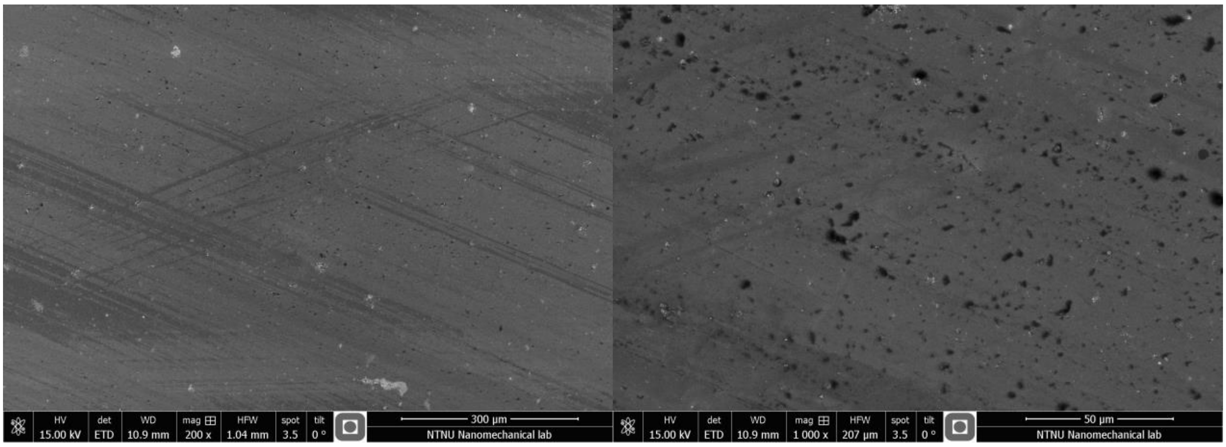


Figure 68 Albumin OCP ta-C at x200 and x1000 magnification

In the ta-C case (Figure 77), the wear track was also not possible to find and centred images were taken. Here there are holes that could be either pitting corrosion or porosity of the coating.

- **Anodic Potential**

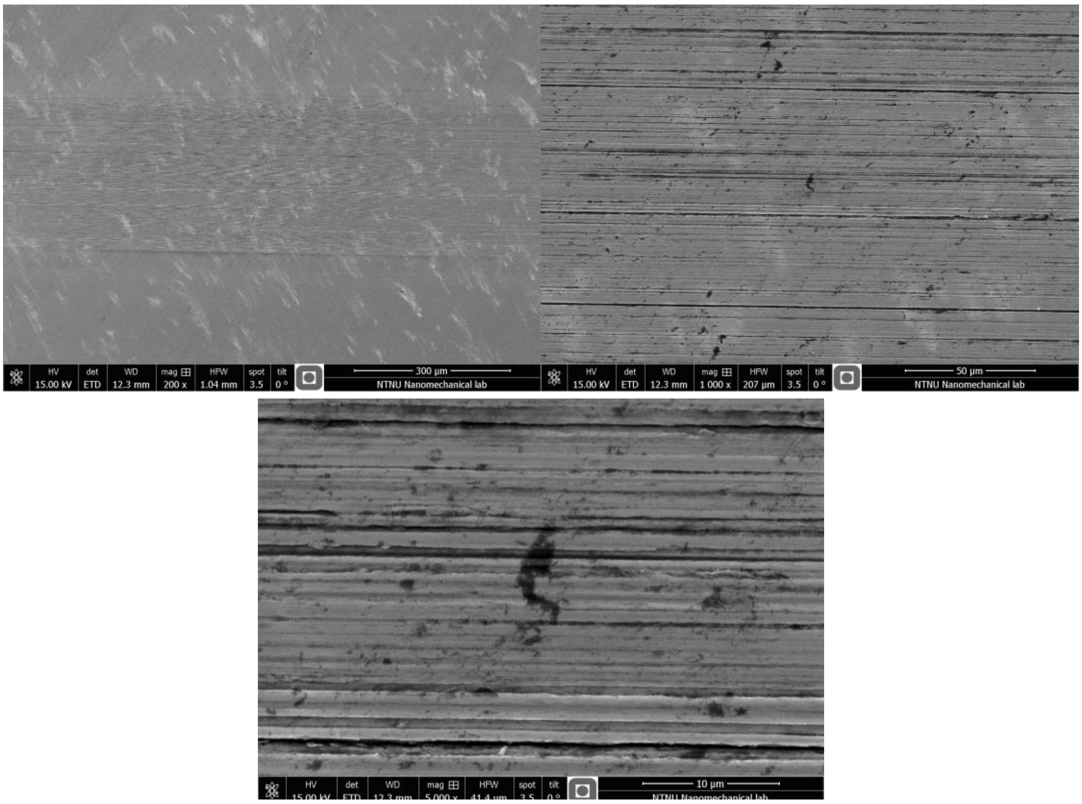


Figure 69 Wear Track Albumin +0.3V CoCrMo at x200, x1000 and x5000 magnification

For the un-coated sample (Figure 78), the wear is as expected, high, it can be seen abrasion along the rubbing direction as well as flakes at higher magnification denoting adhesion wear.

For the a-C:H coating (Figure 79), it was not possible again to find the wear track that is why images of the centre of the surface were taken to see the deposition of the electrolyte.

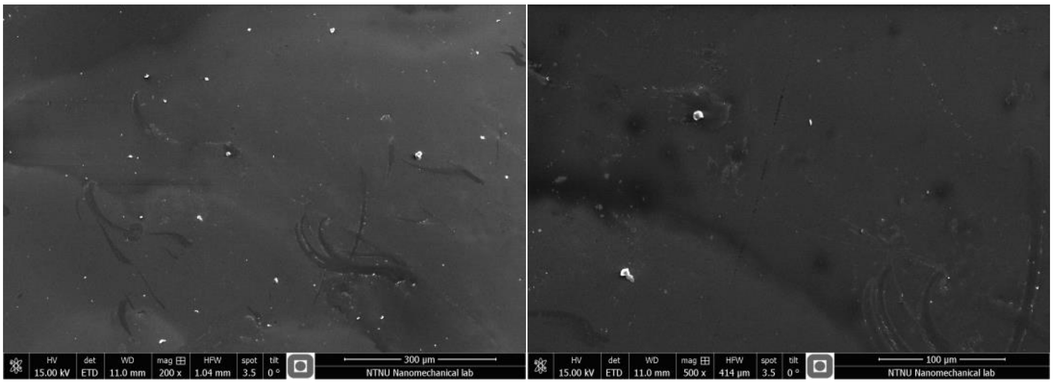


Figure 70 Albumin +0.3V a-C:H at x200 and x500 magnification

For the tetragonal coating (Figure 80), again it was not possible to find the wear track, therefore images of the centre of the surface were taken to see how the electrolyte gets attached.

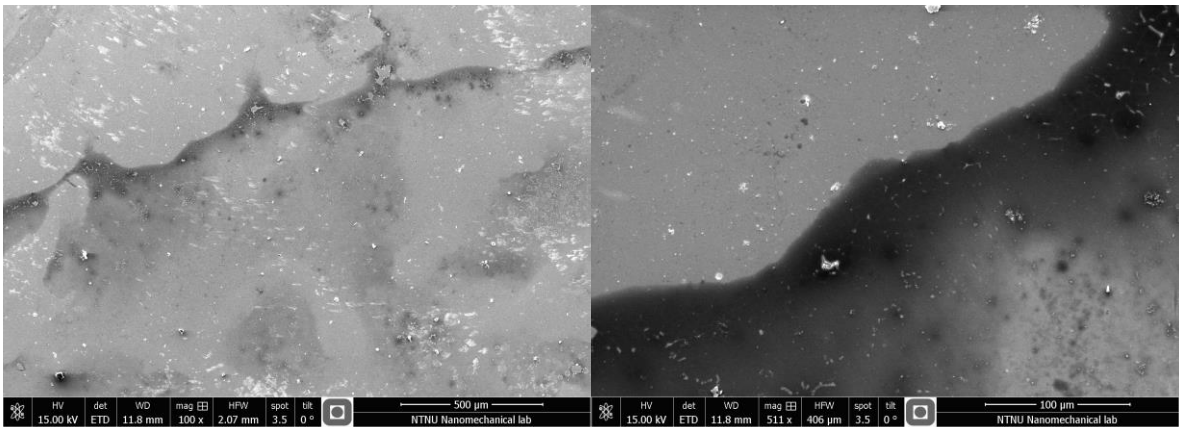


Figure 71 Albumin +0.3V ta-C at x100 and x500 magnification

4.6. HARDNESS VICKERS

After the tribocorrosion tests, hardness tests were done. On each sample, it was measured the hardness 3 times outside and inside the wear track and calculated the average value.

Some of the samples were impossible to find the wear track due to its small size, therefore there are empty gaps.

For the second batch of samples, the test was done at 0.1N and the HV was 1000 (inside and outside of the wear track) but then it was done at 0.3N (outside) and obtained 502.8 and 434.3 at 2N. Because of this discrepancy, the tests were carried out at 0.1N same as the ones done before. The different values could be because the indentation is able to go through the coating and then the obtained value corresponds to the CoCrMo.

All the samples that were measured their hardness were tested before to tribology or tribocorrosion experiments, therefore they will be gathered by the test performed before, in order to see how the material behaves differently to the test.

✓ Dry Tests

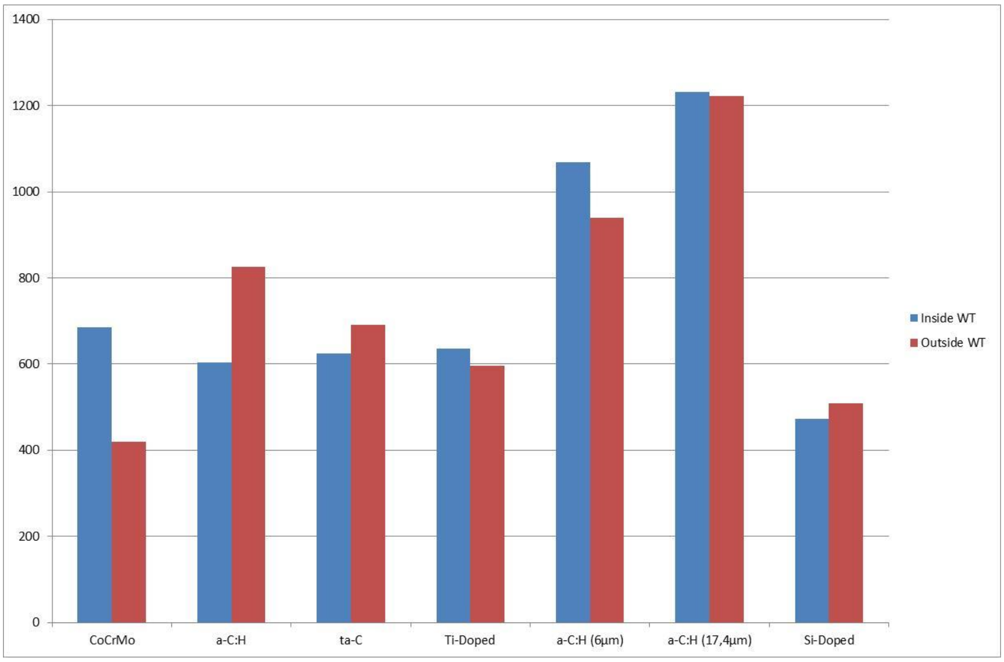


Figure 72 Hardness Test for Dry Tested Samples

The expected results are an enhancement of the hardness inside the wear track due to the plastic deformation of the material. Although, it did not happen as expected in every sample.

First of all, it is remarkable how the second batch of samples have double hardness values than the first batch. This could be due to the thickness of the coating but no evidence was observed during the hardness tests that could show that the coating was broken and the values measured were the ones belonging to the CoCrMo.

It is also interesting, this was expected to happen, that the doped coatings have less hardness than the normal diamond like carbon coatings; and better in the case of the Ti-doped than the Si-doped.

There are also some samples that the hypothesis of higher values inside the wear track does not occur like the a-C:H, ta-C (from the first batch) and the Si-doped. In the case of the non-doped samples one reason for this could be the low wear which would not be strong enough to enhance the material. For the Si-doped, this theory does not fit since there was considerable abrasion in the wear track.

The un-coated samples is the best example of this behaviour, because its hardness increases in a proportion of 1,75.

- ✓ **NaCl Electrolyte, OCP Potential**

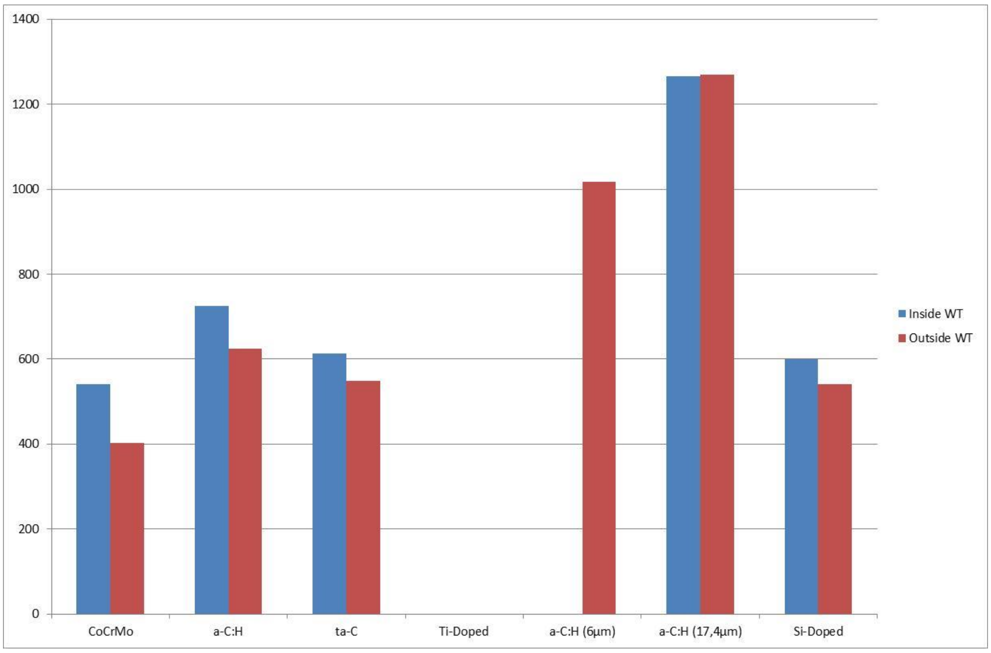


Figure 73 Hardness Test for NaCl Electrolyte under OCP Potential Tribocorrosion Test

Several things before analysing the results; the Ti-doped wasn’t tested due to lack of samples and the a-C:H (6µm) coating does not have values inside the wear track because it was not possible to find the wear track due to its small size.

In this case (Figure 78), the expected behaviour was better fulfilled and inside the wear track the material was enhanced due to plastic deformation.

The un-coated sample increases its hardness inside the wear track, compared to the dry test, this fits with the theory that the corrosion plus the tribology does not occur independently but they increase their rate.

Same for the a-C:H and the ta-C coatings, which would confirm that in the dry test the wear was so little that it didn't enhance the material but in this case where the COF was almost double, it does.

- ✓ **NaCl Electrolyte, Anodic Potential**

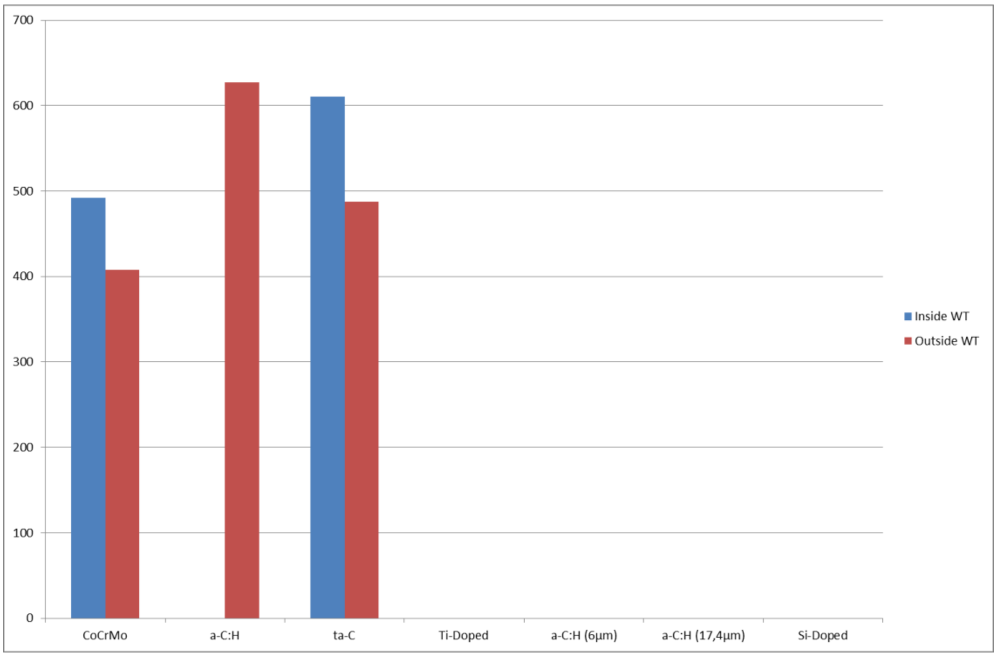


Figure 74 Hardness Test for NaCl Electrolyte under +0.3V Potential Tribocorrosion Test

From this point, only samples belonging to the first batch will be shown since the other ones weren't tested due to a lack of time. Besides, in this case, the a-C:H sample does not have a hardness value inside the wear track, again, because it was not possible to find it.

Little things can be said about this experiment, it shows practically the same results as the open circuit test. Which is at the same time something good, because it shows that even though the test are carried out on the anodic region of the material, the corrosion is not high and does not increase wear mechanisms which would enhance the material but at the same time would increase the volume loss.

- ✓ **PBS Electrolyte, OCP Potential**

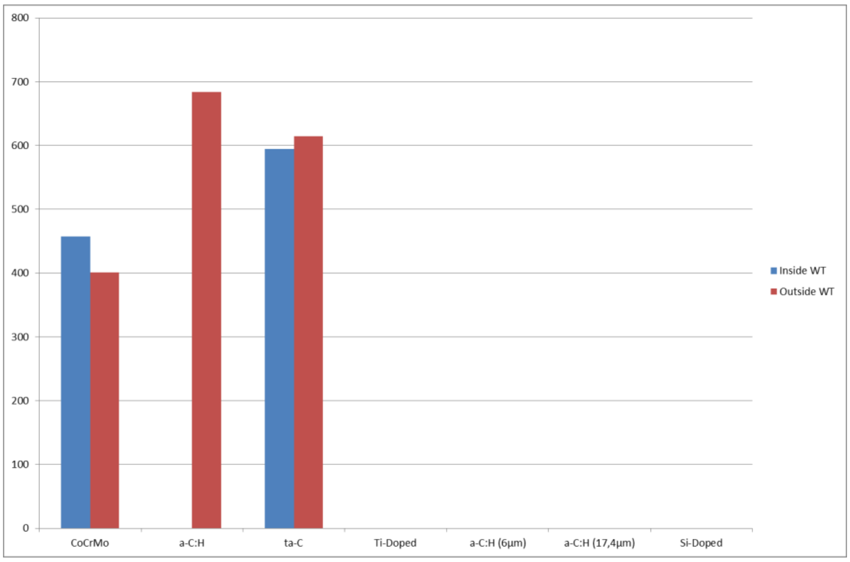


Figure 75 Hardness Test for PBS Electrolyte under OCP Potential Tribocorrosion Test

Again, non-possible to find the a-C:H wear track to measure the hardness value.

Higher values of the hardness outside the wear track which could mean that both inside and outside the enhance has been increased, but there are not proves of that.
The COF increased but the potential vs time plot cannot be used to figure out the corrosion due to its poor electrical conductivity.

For the ta-C coating, the hardness inside and outside the wear track is barely the same.

- ✓ **<u>PBS Electrolyte, Anodic Potential</u>**

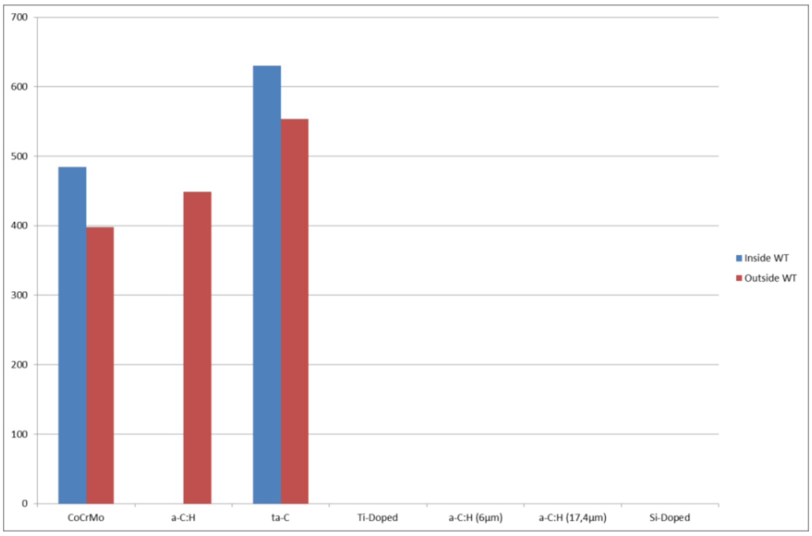


Figure 76 Hardness Test for PBS Electrolyte under Anodic Potential Tribocorrosion Test

Nothing remarkable about this results, which makes sense since PBS is just NaCl with a stabilizer, just notice that the values at anodic potential are almost the same as with OCP potential, has it happened with the NaCl electrolyte.

✓ **Albumin Electrolyte, OCP Potential**

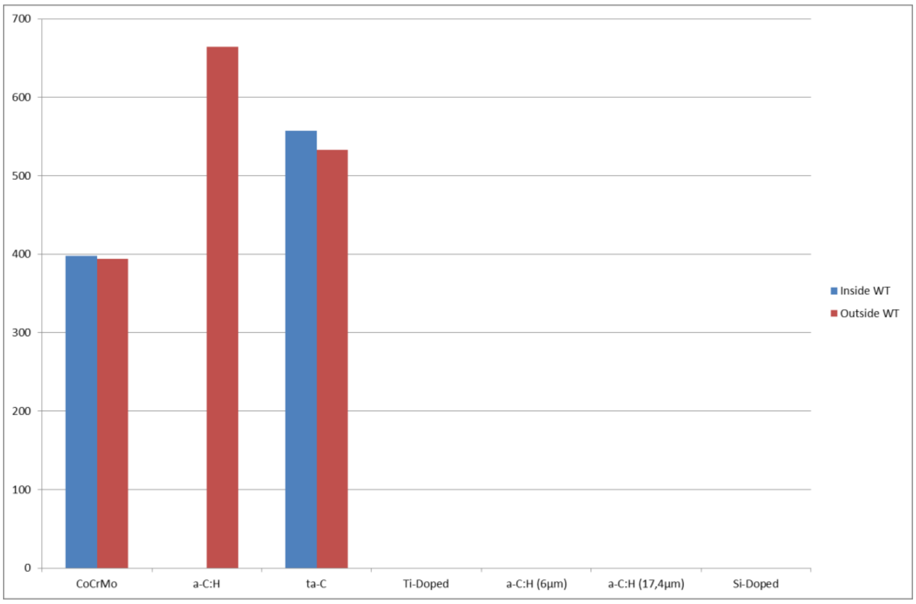


Figure 77 Hardness Test for Albumin Electrolyte under OCP Potential Tribocorrosion Test

There is one interesting result here, the CoCrMo sample increases its hardness outside the wear track, this could be due to the deposition of the albumin on the surface of the sample. The rest of the values remain almost constant.

✓ **Albumin Electrolyte, Anodic Potential**

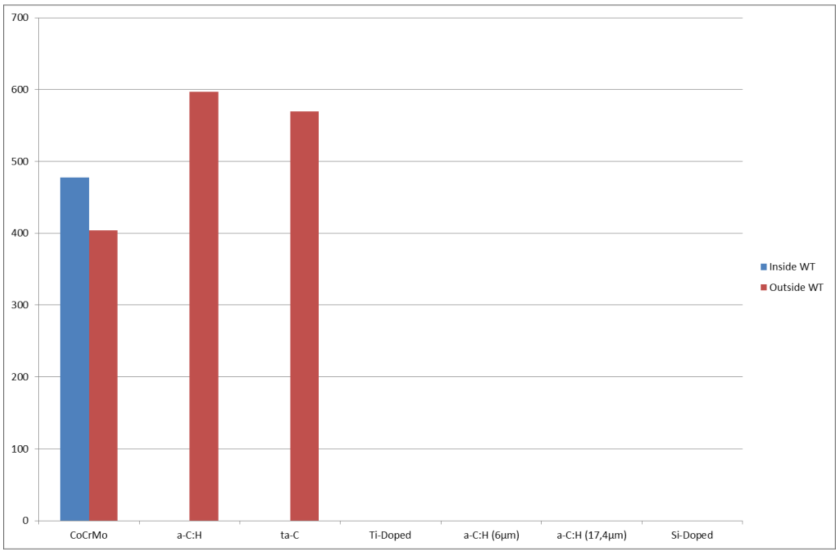


Figure 78 Hardness Test for Albumin Electrolyte under Anodic Potential Tribocorrosion Test

In this case (Figure 83), none of the DLC coatings wear tracks were possible to find, the deposition of the albumin on the surface complicates it.

The un-coated sample its hardness outside of the wear track due to higher wear caused by the anodic potential addition, which allows both the tribology and the corrosion mechanisms work together.

For the other samples there are not remarkable differences.

✓ **All Hardness Tests Together**

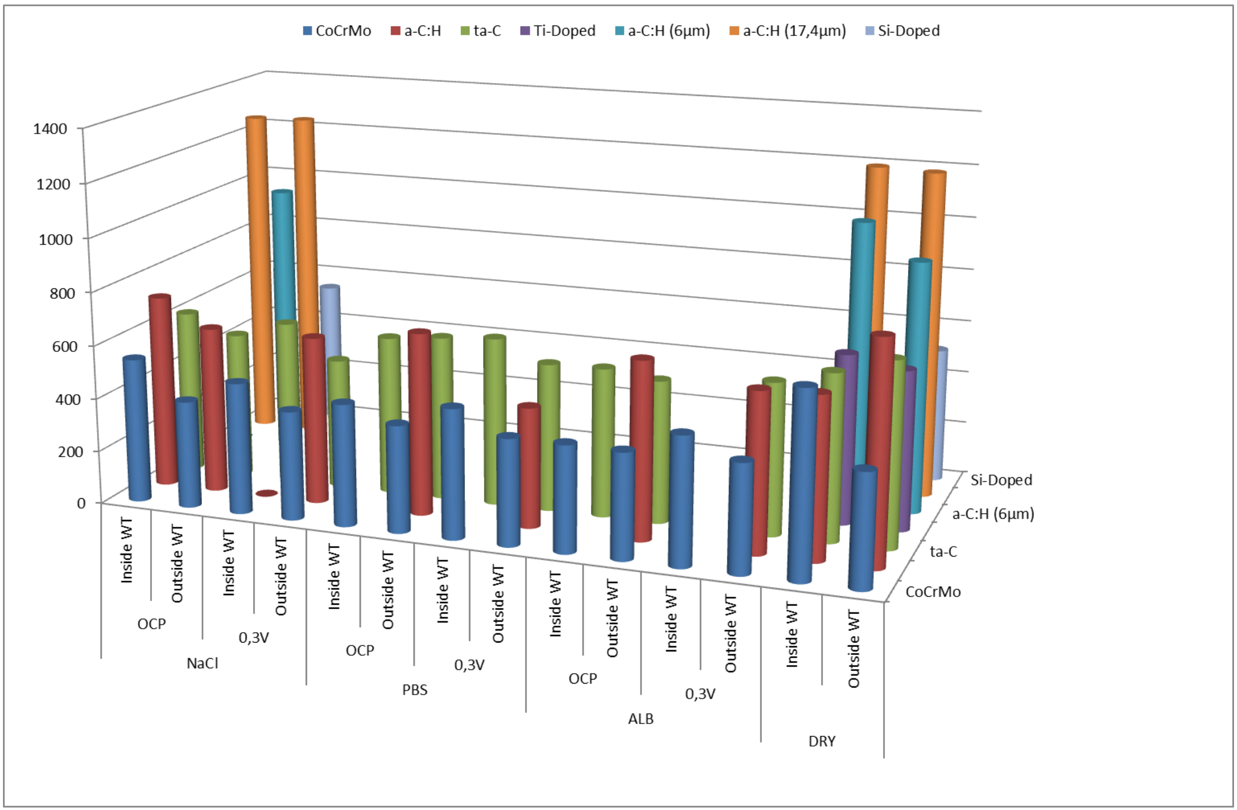


Figure 79 All Hardness Tests Together

4.7 CONFOCAL MICROSCOPE

With the help of the confocal microscope, the size of the wear track was tried to be measured, for the un-coated samples there wasn’t big problems at this point but the wear track of the DLC coated samples was too small to be measured with the microscope.

That’s why this method to analyse the results was worthless and there are no results.

5. DISCUSSION

- CORROSION

Factors that may influence the behaviour of DLC coatings are diverse, from the electrolyte to the deposition method to create the coating and also the parameters used to deposit the coatings.

Hydrogenated coatings show the best behaviour to corrosion, one of the reasons presumably is the lower porosity that protects better the coating.

All the coatings have better corrosion resistance than the CoCrMo alloy and this tendency appears with all the electrolytes. Thus, related to corrosion, the improvement of DLC coatings is out of doubt, it is expected this improvement due to the chemical inertness of the DLC.

Related to the electrolyte influence, the phosphate ions present in the PBS solution tends to move the polarization curves, of all the samples, to more anodic potentials; this behaviour was already observed with CoCrMo samples [23] [24].
The effect of the albumin is a complex process, hard to predict, it is observed a displacement of the polarization curves to more cathodic potentials, again for all the samples; which was also observed for the CoCrMo alloy before [1] [2]. Besides, the passivation region gets shortened and in the active region for all the samples there are peaks, presumably because a passivation layer is trying to be made.
The effect of these displacements is higher in presence of proteins than phosphate ions.

Different DLC coatings have similar OCP values, all of them better ones than the un-coated sample; standing above the rest it is the hydrogenated coating with better resistance to corrosion (lower current density).

Both ta-C and Ti-doped (PVC and PECVD) showed pitting on their surfaces after the polarization curve test in presence of 0.9 WT% NaCl

- TRIBOLOGY

The outstanding properties of the DLC are present in the tribology tests; with friction coefficients from 0.05(a-C:H PECVD), though 0.10 (ta-C PVD) to 0.3 (a-C:H PECVD).
The big differences are due to the high amount of characteristics that can influence its behaviour.

Being ta-C the hardest material (theoretically, hardness tests didn’t show this results) due to its higher amount of sp^3 bonds, it has higher friction coefficient than hydrogenated (PECVD), this could be due to the graphite debris formed because of the wear that ‘lubricates’ the surface [25].
Hydrogenated DLC (PECVD) showed COF of 0.07 and 0.28, for the 0.07 the beginning of the rubbing starts with higher values but after a period of time the COF decreases to 0.07 this could be due to the formation of this graphite layer that protects the surface. It is remarkable to say that it happens the same with different thickness of a-C:H coatings (high values at the beginning followed by a decrease).
The creation or not of this layer could be due to several factors such as the deposition method, its characteristics (like bias voltage, pressure deposition, etc.), hydrogen content, roughness, etc. More research on the creation of this layer should be carried out.

Ti-a-C:H show variable values, from 0.1 to 0.02 (during the same test), which are very good values, taking into account that it was expected to increase considerably the COF. Actually it has better values than ta-C (PVD) coating.
Si-a-C:H coating shows the same variability as the a-C:H (PECVD) which suggests that the formation of the protective layer is not always possible. If this layer is not created then the improvement, compared to the CoCrMo alloy, is negligible.

- TRIBOCORROSION

Under corrosion and tribology processes occurring at the same time, the material whose response is better is the ta-C (PVD). It is going to be compared gathering results by electrolyte.

  - NaCl Electrolyte

For the OCP tests, comparing with the dry tests:
CoCrMo improves its COF from 0.45 to 0.35
a-C:H (PECVD, smallest thickness) goes from 0.05 to 0.11
ta-C (PVD) goes from 0.11 to 0.07
a-C:H (PECVD, 6µm) goes from 0.07 (if the protective layer is created) to 0.18
a-C:H (PECVD, 17.4µm) from 0.06 (if the protective layer is created to 0.21

Under tribocorrosion effects, responses are diverse, while CoCrMo and ta-C improves their behaviour, the rest worsen it.
This could be because in presence of the electrolyte, the graphite debris mentioned before is not able to form this protective layer, for the hydrogenated coatings. In the case of the ta-C, the content of sp^2 bonds (related to graphite) are lower that is why this protective layer was not created or not so strong in the

dry tests and thus in presence of the electrolyte the missing of this layer is not so decisive.

At the beginning of the tribocorrosion tests, it is observed higher values of COF, it is normal that the statistic friction coefficient is higher than the dynamic but it is important to control how the protective layer is created, otherwise the improvement is negligible.

Si-doped tests have COF around 0.2, which is close to the results obtained for the hydrogenated coatings created by PECVD, same as Ti-doped; thus the high values of COF (compared to the other deposition methods) it is not clear if they are that high due to the deposition method or the doped effect.

For the anodic tests, the results are almost the same obtained at OCP. It is important to say that during this test the current measured was practically zero, with three orders of magnitude lower in the case of a-C:H (PECVD) and one in the case of ta-C (PVD) compared to the CoCrMo.

The measurement of the current density against the time was not very helpful because the current does not show any effect when the rub starts, in opposition to the CoCrMo tests.

- PBS Electrolyte

PBS solution gives more diverse results because of the phosphate ions that are more unpredictable.

- For the OCP tests:

In the CoCrMo tests, where the NaCl is the electrolyte when the rubbing starts the potential decreases until -0.3V with a COF of 0.35, in the PBS tests, the potential goes to -0.25V or -0.4V and the COF increases until 0.47, with peaks up to 0.6.

For the ta-C (PVD) and the a-C:H (PECVD) this worsen is not that obvious, the ta-C COF remains almost steady (compared to NaCl electrolyte) while the a-C:H has more problems to maintain the protective layer healthy, that is why there are peaks up to 0.2 and other values of 0.1.

- For the anodic tests:

The difficulty to create a passive layer increases at anodic potentials, there are peaks of 0.7 (COF) for the CoCrMo, the a-C:H (PECVD) shows also problems to maintain this layer but if it does, the COF is below 0.1 and the ta-C increases its COF to 0.15, which could be due to its inability to create it, because of the higher corrosion that and the rubbing that destroys or doesn't allow its creation.

Again, the resistance to allow the current go through them, a-C:H and ta-C coatings, is very high, having current values of almost zero.

- Albumin Electrolyte

The adsorption of the protein, present in the albumin solution, is very complex that is why it is hard to predict and to understand.

- For the OCP tests:

CoCrMo COF decreases until 0.3 and the potential when rubbing starts stabilizes at -0.4V, this decrease of the friction coefficient is because of the adsorption of the protein that protects the surface.

The a-C:H (PECVD) has almost half the COF value of the CoCrMo while the ta-C (PVD) has even lower.

It is remarkable than during this tests, ta-C showed the beginning of the rubbing by decreasing its potential when it started, this is the only OCP DLC test that did it.

- For the anodic tests:

The a-C:H (PECVD) and the ta-C (PVD) increase their COF while their current is practically zero.

Analysing the hardness Vickers tests, un-coated sample has an increase of the hardness inside the wear track due to the plastic deformation suffered during the rub; by scanning electron microscope it is clear to see abrasion. This behaviour can be observed for every single test, dry and in presence with the electrolyte.

For the DLC coated samples, this fact is not so clear; no patterns are observed, that is why it is not possible to say that one coating always suffers plastic deformation besides there is the additional problem of finding the wear track to analyse it, and because of that there is a lack of information at this point.

Hydrogen free coatings have clearer tendency at this point, in spite of being the coating that worst behaves under dry tests (highest COF values), in presence of an electrolyte it is the one that best behaves, with an enhancement of its properties after the deformation.

6. CONCLUSION

A comparison between un-coated CoCrMo and coated, with different types of DLC coatings and deposition methods, samples behaviour under tribocorrosion environment were carried out in simulated body fluids. For this aim, polarization curves, electrochemical and hardness tests were done, as well as scanning electron microscope for analysing the results.

The outstanding properties of DLC coatings remain under tribocorrosion processes, with remarkable differences between hydrogenated or not coatings, or doped ones, apart from the deposition method, and all of them improve the behaviour than the CoCrMo.

Tetragonal DLC coatings (PVD) show the best response, with friction coefficients from 0.35 (CoCrMo, 0.9 WT% NaCl at OCP) to 0.0.7 (ta-C, 0.9 WT% NaCl at OCP) or 0.12 (ta-C, Albumin, anodic potential). This is because either the sp^3 bonds or deposition method advantages, to tribocorrosion processes, but it was impossible to compare different methods of deposition for the tetragonal coatings.

Hydrogenated coatings show worse results than ta-C (PVD) but still a good improvement compared to CoCrMo.
With worse response from thicker coatings; with friction coefficient, in 0.9 WT% NaCl at OCP potential, of 0.35 (CoCrMo) 0.012 (a-C:H smallest thickness) 0.175 (a-C:H 6µm thickness) and 0.23 (a-C:H 17µm thickness).
Remembering that the one that show better results was deposited in a different laboratory with different characteristics (same deposition method). That is why the difference has to be the way it was deposited, characteristics like bias voltage, pressure, etc. since no influence of the thickness has been observed before, apart from the fact than a minimum thickness has to be created in order to be able to form sp^3 bonds.

Doped a-C:H coatings with Ti and Si shows similar results but with higher difficulties from the Si-doped coatings to form a protective layer, difficulties also noticed at thicker a-C:H.

With all the results, to sum up, the tetragonal coatings deposited by PVD method show the best behaviour under tribocorrosion processes; a-C:H coatings show big differences depending on the characteristics of the deposition method (being for all of them, PECVD) and this differences on the behaviour were also observed with Ti and Si doped which could be due to the metal used to dope or due to the characteristics as said before.

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