

## Review

# (Bio)Tribocorrosion in Dental Implants: Principles and Techniques of Investigation

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**Abstract:** Tribocorrosion is a current and very discussed theme in tribology and medicine for its impact on industrial applications. Currently, the phenomena are mainly oriented to the biological environment and, in particular, to medical devices such as hip prostheses, dental implants, knee joints, etc. The term tribocorrosion underlines the simultaneous action of wear and corrosion in a tribocouple. It has a non-negligible effect on the total loss of contact materials and the potential failure of the bio-couplings. This overview aims to focus firstly on the basic principles of prosthesis tribocorrosion and subsequently to describe the techniques and the analytical models developed to quantify this phenomenon, reporting the most relevant results achieved in the last 20 years, proposed in chronological order, in order to discuss and to depict the future research developments and tendencies. Despite considerable research efforts, from this investigation come many issues worthy of further investigation, such as how to prevent or minimize tribocorrosion in biological tribopairs, the development of a consolidated protocol for tribological experiments in corrosive environments joined with new biomaterials and composites, the possibility to achieve more and more accurate theoretical models, and how to be able to ensure the success of new implant designs by supporting research and development for the management of implant complications. The above issues certainly constitute a scientific challenge for the next years in the fields of tribology and medicine.

**Keywords:** dental implants; tribocorrosion; experimental; failure



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## 1. Introduction

Currently, tribocorrosion is the process of degradation and irreversibility [1] of various materials due to the combined action of wear (tribo) and the aggressive environment (corrosion). It is capturing the attention of many scientists and engineers because of its dangerous consequences on devices such as valves, pumps, electrochemical instruments and especially medical implants (with the exception of particular fields, such as electrochemical processes, where its impact could be considered positive). Extending the life cycle of these instruments, while ensuring their stability and safety and trying to avoid risky and costly future revisions [2], is a much discussed and studied priority and goal. In the medical field, the term tribocorrosion has been replaced by biotribocorrosion to emphasize the specific environment of this phenomenon, i.e., the human body, animals, plants, or any existing life form. It can involve both natural structures (organs, tissues, cells, etc.) and manufactured ones (hip joints, dental implants, knee implants, etc.) with obvious differences [3] and falls under tribology for its reference to the concepts of friction, contact, wear, etc. One of the first studies on the contact between two metal surfaces with slight movements was conducted by Eden et al. [4], in the early 20th century, and it is still analyzed in all its fundamental aspects. The tribocorrosion process [5] is the function of many variables, such as the kind of material, the contact geometry, chemical composition and external factors,

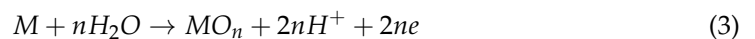
such as environmental pH and temperature and occupies various industrial fields such as biology, chemistry, physics, statistics and so on. Figure 1 represents the degradation process caused by the mechanical wear due to adhesion, abrasion, fatigue and corrosion (redox reaction) between the sample and the environment. Redox is a process involving two semi-reactions [6]; oxidation (Equation (1)) is generally referred to as the anode and reduction (Equation (2)) is referred to as the following cathode:



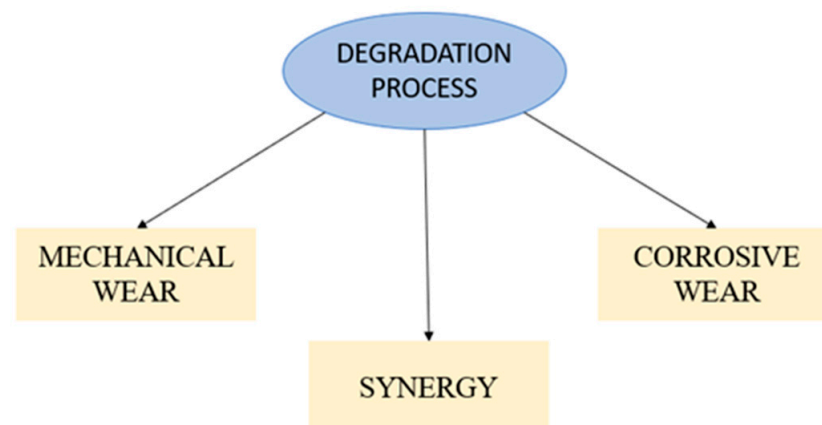
where  $M$  is a general metal,  $n$  is the number of exchanged electrons and  $M^{n+}$  is the ion formed.



Hence, the electrons lost by the metal are acquired by other species such as water, as described in Equation (2), hydrogen ions and dissolved oxygen. The two formulae are considered the main processes but are not the only ones. For example, another reaction, fundamental for avoiding corrosion, regards the formation of a passive layer according to the following:



with  $MO_n$ , the oxide film formed on the surface of the metal (for example, titanium alloy is  $TiO_2$ ) protects the materials from the aggressivity of reagents.



**Figure 1.** Schematic of tribocorrosion phenomena.

The last one is exactly the synergy, i.e., the union, the combination of them, that can be positive (the formation of a passive and hard layer on the surface, capable of protecting the material from wear) or negative (significant loss of material) according to the specific working conditions [7].

The potential disadvantages of tribocorrosion are not only related to the possible loss of function but also to people's health. Indeed, corrosive products could migrate from the implant to the nearby tissues, causing histopathologic problems [8]. Released particles could also cause inflammation (the first sign of discomfort for the patient), followed by the spread of macrophages, which, being cells of the immune system, phagocytize and digest foreign particles [9]. The particles can vary in dimensions and size, extremely complicating their investigation, although the range is about 50–100 nm [10].

In particular, material debris is dangerous because it can trigger a biological response [11], resulting in metallosis, the deposition of metals in human organs and tissues; cytotoxicity-necrosis, in which cells can digest very small particles (not large enough to activate macrophage action) that corrode them and, in some cases, cause their death; hypersensitivity, which is closely related to the patient and which is the biological and immunological response of B and T lymphocytes to the presence of metals; pseudotumor, which is the formation of a huge mass of tissue, probably not aggressive, originating

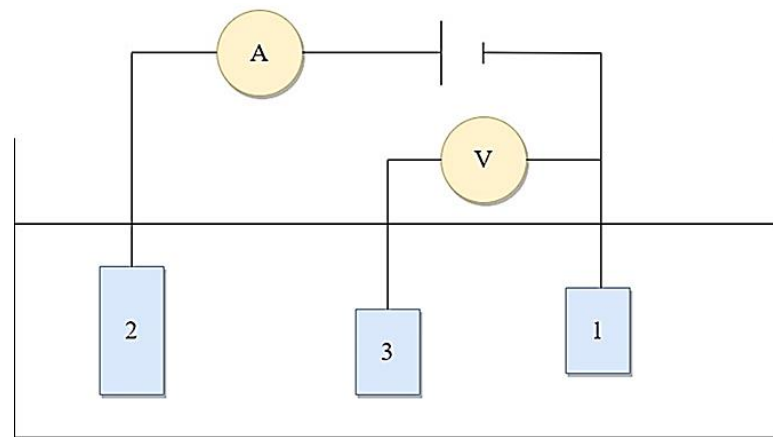
from wear and tear that, although not a true cancer, can cause symptoms such as pain, paralysis, etc.; osteolysis and osteopenia, respectively, the former being the complete destruction of bone, while the latter is the loss of bone mass associated with its density and not its protein aspect. According to Wolff's law [12], bone mass varies continuously as a function of external loads and static and dynamic mechanical stresses. This means that bone needs incentives to maintain its form and density; genetic effects, that is, potential genetic damage to DNA and chromosomes in terms of alterations in structure and number. Chromium and cobalt appear to be potentially mutagenic metals; moreover, some studies have shown an increased tendency for cancer development in patients undergoing surgery with metal and polyethylene implants [13]. Other studies confirmed [14] that there is a correlation between tribocorrosion and biological problems in that the chemical-mechanical degradation results in the release of ions that attack human cells, impairing osseointegration. This process is amplified when the patient has diseases such as diabetes and surface modifications are applied to the implant to promote macrophage activity [15]. Werny et al. [16] stated, however, that vitamin D deficiency has a greater tendency for failure as determined by incomplete osseointegration. According to the study by Gibreel et al. [17], aging and potential osteoporosis are also risk factors for osseointegration. Therefore, tribocorrosion, implant failure and biological activity are all related, as the main factor leading to implant loosening is immunologically mediated rejection [18], and this is facilitated by the former. The long-term success of oral implants depends on maintaining healthy tissues around them. Accumulation of bacterial plaque induces inflammatory changes in the soft tissues surrounding oral implants and can lead to their progressive destruction (peri-implantitis) and, ultimately, to implant failure. According to Albrektsson et al. [19], implant success is assessed by considering aspects of implant stability, peri-implant bone loss after one year of use, the health of peri-implant hard and soft tissues and patient-related factors, including pain or infection due to peri-implantitis, a pathological condition that occurs in the tissues surrounding dental implants. This infectious condition affects about two out of 10 patients [20,21]. With approximately 12 million implants placed worldwide each year by a growing number of physicians with varying skills, there is concern that peri-implantitis is a growing complication in dentistry [22]. Numerous treatment protocols for peri-implantitis have been proposed, including non-surgical, surgical and combined approaches. The stability and retention of the prostheses remains a major challenge for these complex defects.

This review discussed the phenomena of biotribocorrosion, conceptualized and defined the process, then illustrated the investigation techniques and analytical models. Finally, it focused on the case of dental implants, highlighting the most relevant recent investigations.

## 2. Techniques of Investigation in Tribocorrosion

The most common experimental setup used for experimental activity on tribocorrosion consists of a classical tribometer (for mechanical wear estimation) equipped with a potentiostat (for the chemical component) and a specific chemical cell, which are all connected, operating simultaneously to guarantee the synergistic action of tribocorrosion. The cell is schematically represented in Figure 2 as follows:

The cell is composed of an ammeter (A) and to a voltmeter (V) connected with three electrodes [23] indicated as blocks 1,2,3 follows: the first is referred to as the working electrode (WE), i.e., the sample that will undergo the test; the second is the counter (CE) that provides the current control, essentially made of gold, platinum or carbon; lastly there is the reference electrode (RE) made of copper, hydrogen, calomel, etc., necessary to calculate the potential, since it must be referred to a standard potential [24]. Each one is immersed in a solution of variable composition such as calf bovine serum (similar to the synovial fluid) [25], sulfuric acid [26], artificial seawater [27], NaCl [28], Ringer solution [29], etc. Hence, nowadays, two different methodologies exist for the corrosion approach by considering whether or not the presence of acid can complicate the experimental setup (the way of inserting it in tribological devices) and the aspect of safety.



**Figure 2.** Schematical representation of an electrochemical cell equipped with three electrodes.

As represented in Figure 1, the three factors should be evaluated. Hence, for mechanical wear, the classical investigation is achieved by a classical tribometer, whereas for chemical wear, several techniques should be adopted according to the aim of the investigation [6], involving two or three electrodes. The first and the simplest is the OCP (open-circuit potential), as follows: it is a passive measurement since the counter electrode is bypassed with the passage of current. Hence, OCP is the free potential calculated between the working and reference electrodes [30]. Besides, it is linked with the concentration ratio of the species present in the reaction (Equations (4) and (5)) in the sense that by measuring OCP it is possible to evaluate the following concentrations involved:

$$E_{OCP} = E_{WORKING} - E_{REFERENCE} \quad (4)$$

Measured by voltmeter, but for Nernst formula, as follows:

$$E_{OCP} = E^0 + \left( \frac{RT}{nF} \right) \ln \left( \frac{C_o^n}{C_r^m} \right) \quad (5)$$

where:

- $E^0$  is the standard potential of reduction;
- $R$  and  $F$  respectively the Universal Gas Constant and Faraday Constant;
- $T$  the temperature expressed in Kelvin;
- $n$  the number of electrons exchanged;
- $C_o$  and  $C_r$  raised to the stoichiometric coefficients the molar concentration (or pressure in gas cases) of the species oxidated and reduced.

The main disadvantage of this method is the scarcity of information since there is no mention of the current trend, passivation phenomena, local and total wear, etc. Consequently, it is often replaced by potentiostatic and potentiodynamic techniques. In both, a current flow occurs controlled by a potentiostat but with the following difference [31]: for the former, the potentiostat maintains a fixed potential by varying the current, whereas in the second case, the potential changes at a constant rate (potential sweep rate). This current is formed of the following two components:

$$I_{tot} = \sum I_{Anodic} + I_{Cathodic} \quad (6)$$

The sum is referred to the number of reactions on WE,  $I_{anodic}$  and  $I_{cathodic}$  the currents of the two semi-reactions whose values respect the potential imposed. Relation 6 yields the value of current, which appears in classical Faraday Law as follows [32]:

$$M = \rho V = \left( \frac{C}{F} \right) Q \quad (7)$$

where  $\rho$  is the density,  $M$  and  $V$  mass and volume of material lost during the tribocorrosion,  $Q$  is the charge and  $C$  is the ratio between the molecular mass ( $MM$ ) and electrons exchanged ( $n$ ). Equation (7) can better be specified by considering the charge as the integral of the current in the interval of time  $T$ , as follows:

$$M = \left( \frac{MM}{nF} \right) \int_0^T I(t) dt \quad (8)$$

This reflects the drawback of this approach, i.e., the analysis of current is not constant but a function of time [33]. Here, the current changes strongly during the sliding time and it is sensitive to the potential imposed as shown below. To overcome this kind of problem, usually, average values or empirical formulas [34–36] are used.

Another way is offered by the classical Tafel plot (Figure 3), obtained by the composition of the two Evan's diagrams related to the semi-reactions of oxidation and reduction. It considers on the x-axis the logarithm of current, whereas on the y-axis the potential, as follows: by tracing the slope of the two regions' curves (anodic and cathodic), the point of intersection will give the current that can be inserted in Equation (8) [37].

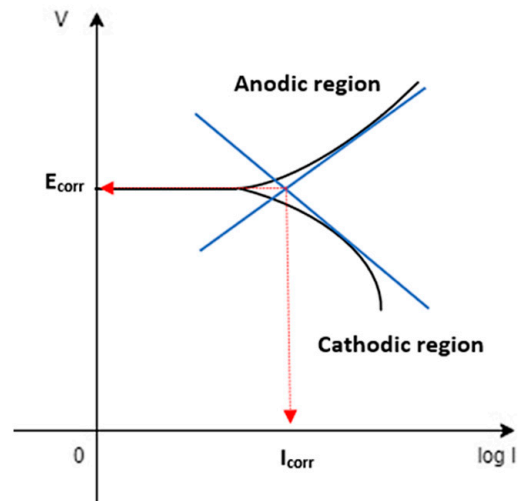


Figure 3. Tafel plot.

Lastly, the method as indicated by ASTM G-59 (Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements) involves the following main steps:

1. Calculation of Stern–Geary coefficient  $B$  as follows:

$$B = \frac{(b_a \cdot b_c)}{(2.303 \cdot b_a + b_c)} \quad (9)$$

where  $b_a$  and  $b_c$  are the anodic and cathodic slopes in volts.

2. Evaluation of  $I_{Corr}$  as follows:

$$I_{Corr} = 10^6 \cdot \left( \frac{B}{R_p} \right) \quad (10)$$

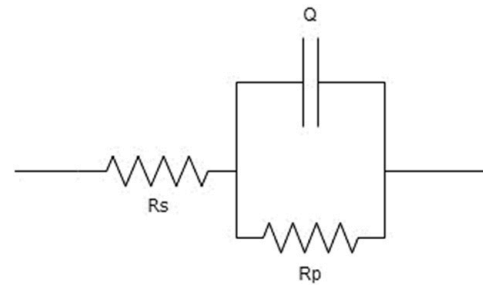
with  $R_p$  (polarization resistance) slope of the potential versus current density plot taken at 20 mV.

3. Corrosion rate measurement as follows:

$$CR = 3.27 \cdot 10^{-3} \cdot I_{Corr} \cdot \left( \frac{E_W}{\rho} \right) \quad (11)$$

where  $E_W$  is the equivalent weight in grams,  $\rho$  the density in  $\text{g}/\text{cm}^3$  and  $CR$  is the corrosion rate in mm per year.

Finally, the EIS (*Electrochemical Impedance Spectroscopy*) approach is also valid. Indeed, it is very diffused in the literature, and it regards the evaluation of system answers after an external perturbation of small amplitude [38]. The EIS method also permits the equivalent modeling of a tribocorrosive system as shown in Figure 4.



**Figure 4.** Equivalent circuit model: Randle's circuit.

By analyzing the spectra and their trends, it is possible to model the system with its properties (time constant and circuit elements). In Figure 4, it is reported that a simple circuit [39], known as the Randle circuit, is composed of two resistors ( $R_s$  for the solution) and one capacitor for the charge transfer between sample and electrolyte, so that the total impedance is given by a parallel and a series. Obviously, it cannot be a general scheme, being strongly dependent on the conditions of the electrochemical cell but, at the same time, particularly useful for mathematical description.

### 3. Synergistic Approach

Since tribocorrosion involves numerous variables with a not yet well-understood behavior, much research was conducted to provide theoretical models [40–49] capable of predicting the total wear for precise input conditions to be used at the occurrence. In this manuscript, only the synergistic approach was discussed (since it is one of the simplest) as an example of tribocorrosion evaluation, but the references inserted can be used by the readers for further detailed studies. Hence, Watson in 1995 [50] introduced a simple model, in which is observable the absence of chemical and mechanical valuations as follows:

$$W_{tot} = A + B + C \quad (12)$$

where  $W_{tot}$  is the total loss volume of material,  $A$  is the loss induced by mechanical wear,  $B$  is induced by corrosion and  $C$  is the synergy contributes. Equation (12) can be further explored by better specifying the last term ( $C$ ), being the most crucial factor in the formula. Diomidis et al. [34], followed by Ponthiaux et al. [35], proposed the (13), according to the standard ASTM G 119–04 (Guide for Determining Synergism Between Wear and Corrosion) as follows:

$$W_{tr} = W_{act}^m + W_{act}^c + W_{repass}^m + W_{repass}^c \quad (13)$$

with  $W_{tr}$  material loss in the sliding track equals to the sum of 4 components respectively due to the following two zones: one named active and the other one re-passivated, the former obtained after the rupture of passive layer, that, as explained before, protects the sample from tribocorrosion and the latter where the film is not completely destroyed, or it had time to restore. More precisely, the synergistic effect is provided by  $W_{act}^c$  and  $W_{repass}^m$  which represent, respectively, the loss of corrosion after the removal of the passive layer caused by mechanical interaction and loss of mechanical wear of the re-passivated material. The last two are  $W_{act}^m$  and  $W_{repass}^c$ , i.e., respectively, the contribution for mechanical wear

of active layer and corrosion of re-passivated sample. After calculating the four factors, it could be useful to use the parameter  $K$  defined as followings:

$$K = \frac{W_{act}^c + W_{repass}^c}{W_{act}^m + W_{repass}^m} \quad (14)$$

That can be rewritten in the following way [51]:

$$K = \frac{K_c}{K_m} \quad (15)$$

Depending on the value assumed by  $K$ , the mechanism of degradation can be established as follows (Table 1):

**Table 1.** Regime of wear according to  $K$  value.

$K$	Mechanism of Degradation
<0.1	Wear
0.1–1	Wear-Induced Corrosion
1–10	Corrosion-Induced Wear
>10	Corrosion

When  $K$  is greater than 1, the prevalent mechanism is corrosion, whereas when it is lower than 1, wear dominates. Obviously, the remaining parameters can be compared as shown below as follows:

$$K_m = \frac{W_{act}^m}{W_{repass}^m} \quad (16)$$

In this case, the expression underlines the strength of the passive layer for corrosion protection as follows: if it is >1, the film is efficient, otherwise not.

Zhang et al. [27], instead, proposed a different relationship from the following Equation (12):

$$W_{tot} = C_o + W_o + S \quad (17)$$

That becomes the following:

$$W_{tot} = C_o + W_o + \Delta C_w + \Delta W_c \quad (18)$$

with  $\Delta C_w$  and  $\Delta W_c$ , the volume of corrosion aggravated by wear and the volume of wear aggravated by corrosion, respectively. Consequently, the factor  $T$  is, by grouping the following common terms:

$$W_{tot} = (C_o + \Delta C_w) + (W_o + \Delta W_c) \quad (19)$$

That can be rewritten as follows:

$$W_{tot} = C_w + W_c \quad (20)$$

- $C_w$  = total loss for corrosion;
- $W_c$  = total loss for wear.

Overall, the global comprehension of tribocorrosion phenomena is almost complicated both for mechanical issues in terms of the definition of the correct input variables as well as the definition of the kind of wear and for the chemical aspects that are not fully defined, since many scenarios could be present, such as the type of growth of the films [52] (partial or uniform), current law (Tafel, high-field conduction), wear model (Faraday or empirical models), influential external variables, etc. Moreover, each approach has its pros and cons, together with its basis hypothesis, that must be kept in mind for future



developments. Finally, other models [41,53] are also available in the literature, often very specific, varying from the presence of lubrication [54], protein concentration [55], third body [56], the multiphysics modeling [57], confirming the depth of this field in all its variables and key points.

#### 4. Dental Implant

Tribocorrosive effects assume a key role in artificial dental implants and therefore deserve to be studied within the experimental and theoretical approaches outlined in the previous sections. Dental implant surgery (arches, implants, plates) is a widespread technique, which has achieved an almost 90% success rate in terms of stability of the prosthesis, bone loss and presence of bacteria [19]. Thus, it is an ordinary procedure with high reliability, which is missing teeth and supporting oral tissues have traditionally been replaced with removable or fixed prostheses that allow the restoration of chewing function, phonetics and aesthetics, improving the quality of life of many patients and increasing demand for them in recent years. On the other hand, they are subjected to failure or dangerous events that could compromise the proper functioning of the prosthesis. Their study is therefore necessary, especially considering that the dental environment has its own characteristics and peculiarities that profoundly affect tribocorrosion, often making the analysis very difficult to perform.

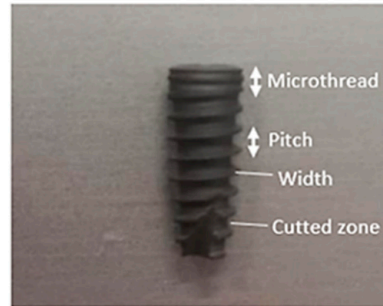
##### 4.1. Implant Structure

The implant is formed of a fixture that is a cylindrical screw, acting as an artificial root in contact with the bone; the crown or dental prosthesis, corresponding to the upper zone, represents the visible area of the total implant and the abutment, which connects the last two. In addition, the implant can provide, to fix beyond the components, a junction screw or can be cemented. The former is, currently, preferred because of the likely destruction of the cement layer and colonization of bacteria and because of less stress distribution to the implant [58]. Moreover, it can be monophasic or biphasic according to the number of operations realized as follows: for the first, all the implants will be installed in one operation, whereas for the second, the fixture and the remaining parts are collocated in different periods of time. The choice depends on the patient as well as on the distribution of the deformations [59]. Regarding the geometry, instead, the implants can assume the following many configurations:

In Figure 5, a biphasic implant with a head diameter of 4.4 mm and a length of 13 mm with the presence of a cutted zone is shown. The cutting area is an interesting zone because the incision has the function of facilitating the formation of the bone and reinforcing its stability. The surface topography [60] and the specific dimensions of the thread, as well as its type (buttress, reverse buttress, V-shape, sinusoidal, square), play a key role, as well as the upper diameter and the total length of the implant, in the contact conditions and stress/strain field [61]. The last impact on the life span of a prosthesis is as follows: the magnitude of the transmitted forces and the resulted contact pressures should be investigated in the different areas of the implant and in the surrounding bone and comparing the values with the ones coming from the adopted failure criteria. More precisely, the value of the forces should be not too high to avoid a potential overload and the rupture of implant/bone, and not too low according to the cited above Wolff law. Indeed, the bone remodels in response to the external load as follows: it means that if the forces are not big enough, stress shielding will occur with the reduction of bone density, causing issues such as inhibition of bone development, inflammation, or, in the worst case, the failure of the prosthesis [62]. Regarding, instead, the topographical properties, numerous studies confirmed the relationship between  $R_a$  (arithmetical roughness) and osseointegration as follows: an *ideal* range for the implantable surfaces was found to be between 1 and 2  $\mu\text{m}$  [63,64]. Hence, a not completely smooth surface could be preferred, as follows: treatments such as acid etching, shot blasting and plasma spraying are all valid processes impacting the topography of the surface [65]. On the contrary, greater roughness



determines a lower real contact area [66] and consequently higher pressures in localized zones. In addition, the probability of bacterial adhesion is higher [67] than that which can develop a biofilm, i.e., a complex structure of microbiological cells enclosed essentially in a polysaccharide matrix [68], with variable chemical nature.



**Figure 5.** Example of a dental implant with cutted zone.

#### 4.2. Literature Overview in Dental Tribocorrosion

Although tribocorrosion is a relatively recent research field, many scientists have carried out different tests from experimental, numerical and clinical points of view. In the dental case, many mechanical and chemical variables should be considered, such as the contact load, the frequency, the environment's chemical composition and pH, the contact surfaces topography and properties and the influence of eventual external microorganisms [7]. In this manuscript, the aim was to drive the readers through the available and recent investigation approaches, focusing on tribology in dentistry [69]. In the next sub-chapters are underlined the influence of the main involved operating parameters in the tribocorrosive process.

##### 4.2.1. The Effect of the Regime of Sliding

Firstly, dental tribocorrosion occurs because of the continuous exchange of load, for example during mastication and the corrosion due to the oral environment causes teeth to wear. The tribochemical-involved are very complex and not fully understood and modeled, even if some interesting investigations are found in the scientific literature. Barril et al. [70] in 2002, by using an experimental procedure focused on fretting corrosion; they were interested in the main affecting variables, both electrochemical and mechanical, such as potential, normal force, frequency and so on the wear phenomena acting in the analyzed tribosystems. The interesting aspect of their research was the study of these properties according to specific fretting regimes as well as the kind of wear established (for instance, the presence of a third body referred to as localized current peaks). They found that the dependence on the slip amplitude was crucial since it affects the potential formation of an oxide protective layer as follows: a large slip amplitude ( $>10\ \mu\text{m}$ ) is obviously associated with an increased chemical reactivity and, in addition, the coefficient of friction and wear are correlated especially with applied potential. This approach highlights an innovative point of view, i.e., to analyze the change in the tribological response of materials to different fretting regimes and external conditions.

##### 4.2.2. The Influence of the Solution Chemical Composition

Two years later, Contu et al. [71] focused their attention during an abrasion test, analyzing the potential and repassivation occurrence of pure titanium and  $\text{Ti}_6\text{Al}_4\text{V}$  alloy in a bovine calf serum with variable pH. The aim was to investigate the different behaviors of materials, which are very common in dentistry, for a precise solution type. The results showed similar electrochemical behavior between the materials, but the commercially pure titanium exhibited a faster propensity to repassivation. In any case, it is important to underline that each experiment strongly influences the chemical composition of the working solution, affecting the tribocorrosive behavior of the studied coupling. A clear example

in dentistry is our saliva, which is chemically variable according to human habits (food assumed, smoking, etc.). In 2005, Ribeiro et al. [72] were interested in recreating the oral area with artificial saliva combined with some additives (citric acid, organic inhibitors) and analyzing the tribocorrosion behavior. The tests were performed for more than 10,000 cycles and in environmental conditions very close to the oral cavity, where the implants are constantly submitted to mechanical stress. The different additives and solutions influenced the material loss (the citric acid was the worst), confirming the great influence of the chemical composition of the solution on wear phenomena. On the contrary, Vieira et al. in 2006 [73], by electromechanical tests on pure titanium in artificial saliva solutions, varied in compositions thanks to specific inhibitors, found the opposite, as follows: the tribolayers with citric acid or anodic inhibitor became more stable with a lower coefficient of friction and lower current. This underlines the absence of a unique trend in the results, caused by the many variables involved, which requires a more intensive experimental investigation. Moreover, pH is another relevant variable and it is known that it is generally in the range of 6.2–7.4 (neutral solution), different from patient to patient and from different zones of the oral cavity but, in any case, strongly influencing the tribocorrosion occurrence. In fact, Mathew et al. in 2012 [74] evaluated the combined effect of corrosion and mechanical wear for the following three pH values: between 3–6 and 9, finding that the worst, because of the incomplete formation of a protective passive layer, is exactly the second. This result is almost surprising since the worst conditions did not occur when the solution was acidic (under 2 pH), but when it was neutral, which is the typical value of our mouth. The direct consequence is the high probability of tribocorrosion occurrence in the oral cavity. Together with pH, the fluoride concentration derived from common toothpaste can also have a negative effect on tribocorrosion resistance, as confirmed by Golvano et al. [75] and on the active dissolution of titanium alloys, as confirmed by Licausi et al. [76]. This demonstrates the aggressivity of the external area to biological objects such as the dental prosthesis. In Golvano et al. work, a near- $\beta$  Ti13Nb13Zr alloy was investigated in place of the common pure titanium or Ti<sub>6</sub>Al<sub>4</sub>V alloy. The choice depends on the diffusion of toxic elements of these samples and therefore the necessity of the development new titanium samples as  $\beta$  and near- $\beta$  titanium alloys, whose strength-to-weight ratio and excellent biocompatibility determined their diffusion in the orthodontic field. Nevertheless, their wear behavior is not so excellent and not away from the titanium samples. Lastly, Teixeira et al. [77] detected the change in solution viscosity, which is an important factor from both a mechanical point of view, for the lubrication regime imposed and chemical, for the corrosion reactions, derived from the effect of particular biomolecules such as albumin, urea and mucin in artificial saliva, as well as the tribocorrosion response of the samples, with the result that the presence of the mucin leads to the lowest wear coefficients.

#### 4.2.3. The Impact of Specific Surface Treatments

An alternative approach could be driven by contact surface treatment. Regarding this, Alves et al. in 2013 [78] stated that, by applying an anodizing treatment on titanium surfaces, a homogenous oxide film capable of protecting the sample was formed. From a chemical point of view, the anodizing was performed in an electrolyte containing  $\beta$ -glycerophosphate and calcium acetate. The latter, in terms of concentration, was evaluated as relevant for tribocorrosion behavior because of microstructural changes. The porous structure, obtained after the treatment, not only resulted in lower mechanical damage but also can be crucial for better osteointegration allowing, the bone to build inside the pores. In any case, to achieve complete acceptability, the modified implants should be inserted into real systems where, more likely, other aspects like bacterial attack (*Streptococcus Mutans*) or cellular response, adhesion and proliferation, should be also considered. Alves, in another article published in 2015 [79], confirmed the beneficial effects of calcium and phosphorus Ti-oxide films again for wear contrast and osteoblast interactions. The same was formulated by Geringer et al. [80] regarding the acid etching technique adopted for improving sample properties, by Vilhena et al. [81] for the Selective Laser Melting Technique, which

showed lower passive current density and by Mindivian et al. [82] about the pulsed Plasma Nitriding Process and its direct consequences on the lower coefficient of friction, higher OCP and lower wear volume loss. It is almost clear that a direct correlation between sample treatment and wear effects does not occur as follows: Some conditions impact chemical wear, in correspondence to lower current values, others on mechanical wear and on the friction of the tribosystem. Moreover, the type of wear established (abrasion, adhesion, fretting, three-body) is also crucial for correct tribocorrosion estimation. Overall, the surface preparation, in terms of topography, roughness and coatings, becomes crucial for a long-life implant, precluding postoperative complications and expenses [83] since tribocorrosion was considered one of the most possible failure causes [84] since the long-term production of toxic ions and local/global inflammation in the oral cavity cumulate their impact on the implant and the surrounding bone, causing, in the worst cases, the failure.

#### 4.2.4. The Tribocorrosion: A Multivariable Phenomenon

Many investigations [85] tried to depict wear maps, describing them as a very useful tool to provide a reference for wear predictions in dental implants. Wang et al. [86] in 2018 analyzed the trend of volume loss with load and noticed that the material loss increased in the presence of corrosion proportionally to the load applied. This can be easily demonstrated by considering the relation between load and potential as follows: the higher the load, the lower the potential and the greater the corrosion wear. As well as the former, the potential also impacts the propagation of wear, as analyzed by Borrás et al. in 2019 as follows [87]: for low passive conditions, the wear was low, whereas for high passive conditions it was the opposite, as expected, since the latter compromises the protection of the oxide layer. An interesting outcome is the capacity of the compacted wear debris, at open circuit conditions, of supporting the external load, reducing in this way the total wear of the coupling. Another key variable is the masticatory frequency, as analyzed by Alfaro et al. [88] in 2019; they found that it has a relationship with oxide layer stability, understanding that the lower frequencies (1–2 Hz) allow for greater repassivation, in contrast to the higher ones at 4 Hz, where the passive film resulted in interruption. The effect is the drastic drop of potential toward negative values. The results can be easily explained by considering that, for high frequencies, the available time for repassivation is shorter and, probably, not sufficient. In reference to the dental environment, where the load and the frequencies of mastication or bruxism are variable and the loads multidirectional, these results become relevant for implant longevity. Regarding the choice of the material instead, Mehkri et al. [1] tried, in 2021, to compare the very common grade 2 or 4 or 5 titanium implants with Zirconia Toughened Alumina and Ytria Stabilized Zirconia. The tests pointed out that the latter behaves better against wear and, therefore, can be considered a valid alternative accounting for the that titanium implants, which have the drawback of dangerous ion diffusion [89]. Another study, always in 2021 and referred to as the material choice, conducted by Ramachandran et al. [90], focalized on the ideal combination of titanium and zirconium as Ti + 5% Zr, which exhibited improved corrosion and wear resistance behavior. This does not happen for 10–15% of zirconium, where the tribocorrosion response was worst. The reason comes from the function performed by Zr as follows: it increases the hardness of the alloy, but a higher value causes microstructural changes characterized by an irregular topography, which does not permit the formation of a uniform oxide layer. Therefore, each aspect should be kept in mind when a new sample is realized. The same comparison was performed by Sikora et al. [91] with the following equal outcomes: the best performing were the Zr/Ti ones, i.e., zirconium for the abutment and titanium for the implant. Interesting is also the potential application of TiO<sub>2</sub> nanotubes (NTs), adopted for the improvement of osteointegration and reduction of infection released. Regarding this, Rossi et al., study [92] showed an enhanced tribocorrosion performance (in terms of adhesion strength and hardness) due to the growth of a nano-thick oxide film. Certainly, other particular elements [93] can also be chosen (as a coating, for example), such as niobium-based thin films, which, combined with carbon (NiC), provide optimal

protective efficiency (anti-wear and anti-corrosion) and osteogenic potential (bioactivity in terms of cellular attachment, mineralization and differentiation) as stated by Xu et al.

#### 4.2.5. The Future Tendencies

Most of these studies were performed by experimental techniques, but other approaches are also adopted similar to the numerical ones, regarding, for instance, the changes in bone according to specified loads [94] or clinical regarding bone loss evaluation [95] in a long-term evaluation by radiographic image. Interesting and innovative is the method suggested by Barao et al. [96] for the use of the acoustic emission technique, a non-destructive and non-intrusive approach, instead of the classical test rig, providing results with the same efficiency and accuracy. Moreover, the procedures and the models explained above should be coupled with instruments such as SEM [97] (Scanning electron microscope) or confocal microscopy. Indeed, they guarantee a deeper investigation regarding the topography and the chemical structure of the implant. For example, by SEM it is possible to evaluate the potential osteointegration of an implant removed (different zones of bone anchorage) or the element composition of the oxide layer (partial or complete passivation) and other important analyses. More specific studies are carried out on the surface wear [98–102] in order to estimate the wear type, chemical elements and composites formed after the tribocorrosion impact. In particular, the comparison between natural teeth and artificial samples could be resulted very interesting for validating a specific material. What was discussed underlines the abundance of aspects which can be developed, experimentally, numerically and especially clinically, representing, in this way, the new future tendencies.

### 5. Conclusions

In this work, the bio tribocorrosion phenomena were overviewed, starting from the conceptualization and the definition of the process, followed by the techniques of investigation and the analytical models. Finally, we focused on the case of dental implants, highlighting related recent and relevant investigations. This review points out the novelty and the fascination of this field because of its strong interdisciplinarity among engineering subjects (chemistry, physics, biology), applied directly to the biological environment of the mouth, where risk factors such as poor oral hygiene, smoking, systemic factors and occlusal overload may be associated with the development of peri-implantitis, implying possible failure of the implant itself. Unfortunately, patients have the mistaken belief that implants are similar to natural teeth, and this results in the medical-legal implications being magnified. It should be clear from the signing of the consent and the information provided before and during treatment planning by the dentist that implants are not equal to natural teeth; indeed, implants often require more attention than their natural counterparts with regard to maintenance and monitoring. Over the past two decades, despite considerable research efforts, many questions remain unanswered, such as how to prevent tribocorrosion (statistical analysis on main influent variables), a general protocol for tribocorrosion experiments, what materials might be considered the best choice or innovative ones such as composites and rigorous models for synergy estimation, including other processes such as protein adsorption and how to be able to ensure the success of new implant designs by supporting research and development for the management of implant complications. All these concerns outline future developments and trends in tribocorrosion.

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