

Wear and Corrosion at the Titanium-Zirconia Implant Abutment Interface

BY

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LIST OF ABBREVIATIONS

BCC	Body Centered Cubic Crystal
CoF	Coefficient of Friction
cpTi	Commercially Pure Titanium (Grade Four Titanium)
HCP	Hexagonal Closed Packed
Rox	Roxolid™ (Straumann braded Titanium-Zirconium Alloy)
SEM	Scanning electron microscopy
Ti	Titanium
Ti/Ti	Titanium abutment (ball) / Titanium implant alloy (disc) coupling
Ti/Rox	Titanium abutment (ball) / Roxolid™ implant alloy (disc) coupling
TiV	Titanium Grade Five (aka Ti6Al4V)
TiZr	Titanium-Zirconium Alloy
Y-TZP	Yttria-stabilized tetragonal zirconia polycrystal
Zr/Ti	Zirconia abutment (ball) / Titanium implant alloy (disc) coupling
Zr/Rox	Zirconia abutment (ball) / Roxolid™ implant alloy (disc) coupling
Zr	Zirconia

SUMMARY

A study of the wear and corrosion characteristics between two abutment materials against two implant alloy materials was carried out to evaluate the clinical implications of material selection. Utilizing a simulated oral tribocorrosive environment, titanium (Ti) and zirconia (Zr) abutment materials were slid against titanium and Roxolid™ implant alloys. The testing was conducted for 25K cycles, and the coefficient of friction (CoF) and voltage evolution were recorded simultaneously. Following the tribocorrosion assays, the wear volume loss was calculated, and surface characterization was performed with white light interferometry and scanning electron microscopy.

The coefficient of friction in the titanium groups was higher than in the coefficient of friction in the zirconia groups indicating that more mechanical damage occurred in the titanium groups. Less corrosion occurred in the zirconia abutment groups, as evident from the lower voltage drops observed. The zirconia abutment groups exhibited less total wear volume loss compared to the titanium abutment groups.

Wear and corrosion were found to act synergistically. Overall, the zirconia groups outperformed the titanium groups. In fact, the titanium groups generated 5-6 times more wear to the implant alloys as compared with the zirconia counterparts. The best performing group was zirconia coupled with titanium, and the worst performing group was titanium coupled with titanium.

1. INTRODUCTION

Dental implants have been shown to have predictable success,^{1, 2} but esthetic complications often arise.³⁻⁵ To reduce tissue shadowing from titanium, zirconia abutments may be used.⁶⁻¹¹ However, the literature suggests that the use of zirconia leads to greater destruction of the implant interface,^{12, 13} which may be the result of micromotion-induced component wear. A black ring of titanium debris is commonly observed around zirconia abutments, which is a visual representation of the damage that occurs between implants and abutments.¹² The displaced wear particles may also diffuse into adjacent soft tissues, leading to clinically observed undesirable tissue discoloration.¹⁴

Potential biological and mechanical implications from wear have sparked interest and investigation.^{12, 13} One study used digital photography and scanning electron microscopy (SEM) to evaluate the mechanical wear of implants loaded with zirconia versus titanium abutments.¹² The SEM images were used to quantify the wear based on the measured area of the implant. A similar study added microCT to better visualize the specific patterns of wear that occur at the implant-abutment interface.¹³ Both studies reported that zirconia abutments caused significantly more mechanical damage than their titanium counterparts.^{12, 13} However, their wear loss calculations were obtained from surface area, and they did not account for the volumetric loss. In addition, these studies did not consider the electrochemical interaction that occurs in the oral environment.

Saliva, acting as a weak electrolyte, has been documented *in vitro* to contribute to electrochemical degradation of titanium at physiological pH levels.¹⁵⁻¹⁷ Titanium is a passive metal well known for biocompatibility, primarily due to the oxide layer that spontaneously

forms on its surface. When this passive film is disrupted, the underlying raw metal becomes exposed and susceptible to corrosion.¹⁸⁻²⁰ This process typically occurs in cycles: the oxide layer is damaged and removed, corrosive attack occurs, and the surface recovers, reforming a new protective passivation layer.^{21, 22}

Micromotion from masticatory activity is a contributing factor, causing repeated destruction and removal of surface oxides^{23, 24} Repeated damage at the implant interface from the combined effects of wear and corrosion may ultimately lead to component misfit, titanium fatigue, and potentially implant failure. The released metal ions/debris (Ti and Ti alloys) from the degradation process have been documented to cause local inflammation and titanium tattoos in adjacent tissues.¹⁴ These mechanical and biologic processes affect prosthesis longevity and potentially compromise the patient's esthetic result.

Traditionally, dental implants have been made of commercially pure titanium (cpTi),^{25, 26} but more recently type V titanium (TiV) alloys have become more widely utilized for their increased strength. While the mechanical properties of TiV are superior, its biocompatibility has been questioned.²⁷⁻³¹ As a result, alloys have evolved to incorporate elements like zirconium, which is nontoxic.³² Titanium-zirconium (TiZr) implant alloys, such as Roxolid™ (Straumann), consist of approximately ~15% zirconium, giving them superior strength to cpTi while maintaining a similar corrosion resistance to the traditional material. These TiZr alloys must be able to withstand the intense mechanical and corrosive environment of the oral cavity.³²⁻³⁵

The limited literature on the complex relationship between implants and abutments has focused singularly on either the mechanical or the corrosive aspects of the interface interaction.^{12, 13, 22, 36} No studies have evaluated the effect on implants and abutments from the

combination of both electrochemical and frictional degradation. Tribocorrosion, an area of material science that examines the synergistic effects of both wear and corrosion, has evolved specifically to fill these gaps in the literature.^{21, 37, 38} Therefore, a study utilizing a tribocorrosive system in a simulated oral environment will provide a broader understanding of the complex material interactions occurring at the implant-abutment interface. The purpose of this study was to evaluate the combined effects of mechanical wear and corrosion on the materials at the implant-abutment interface for both TiV and Roxolid™ implant alloys and TiV and zirconia abutment materials. The hypothesis was that zirconia would cause greater damage to the implant alloys than titanium.

2. Literature Review

A. Dental Implants

The use of dental implants to replace missing teeth has become increasingly popular in modern dentistry. Historically endosteal dental implants have been made in a variety of shapes, from blades, to tripods.²⁵ Modern designs are known as root form implants and typically screw into bone.^{25, 26, 39} Over the past decade tremendous research and technology has been invested into improving upon original root form implants that had a machined surface.²⁶ Roughened implant surfaces have shown increased success, and the survival rates of roughened surface implants has been reported around 96%.^{1, 2} Clinician's expectations for osseointegration have correlated with the advances in implant surface technology. High implant survival rates are expected from both clinicians and patients. However, survival does not indicate success. While the implant may survive and maintain intimate contact with the bone, esthetic and soft tissue failures remain more common.^{4, 5}

The most critical area for esthetic success in the oral cavity is the anterior maxilla.^{3, 10} Restoring implants in this area, which is referred to as the esthetic zone, presents unique challenges due to the high visibility. Esthetic complications often arise, especially in patients with a thin tissue biotype.⁷ The underlying titanium has been shown to cast a shadow through the tissue, leaving the marginal gingiva dark and discolored.^{7, 40, 41} In an effort to reduce the blue-gray hue of titanium, clinicians may choose an abutment material that more closely mimics the natural tooth shade.^{6, 9, 10} Manufactures have produced all-ceramic abutments from a multitude of materials, but the most common in the market is zirconia.^{8, 11, 40}

Zirconia's white appearance, high strength and biocompatibility make it desirable for abutment applications;^{11, 42, 43} however, its use has become a topic for discussion.⁴⁴⁻⁴⁶ Upon removal of a zirconia abutment that has been in function, it is common to see a dark band of titanium debris approximating the implant interface.^{12, 13} The stark contrast of titanium particles against the brilliant white of the zirconia brought to light the wear that may be occurring between implants and abutments that was not readily observed with prior use of traditional titanium abutments. Titanium tattoos as a result of the increased wear between zirconia and titanium abutments have been described and documented.¹⁴ The increase of wear of the titanium implant at the interface from the harder zirconia material has been suggested to increase implant complications from destruction of the anti-rotational component of the connection, pre-mature screw loosening, and implant failure, to released metallic particles induced local soft tissue inflammation, and finding its way into the circulatory system, resulting in heavy metal toxicity.^{12-14, 27, 30, 47, 48}

B. Titanium Implant Alloys

Traditionally endosseous implants have been manufactured from titanium.^{18, 39} In the past century a wide variety of materials have been used for dental implants, ranging from ceramics to polymers. Titanium has become the gold standard due to its high strength to weight ratio and excellent biocompatibility.⁴⁹ The oxides that readily form on its outer surface provide the metal superior corrosion resistance.⁵⁰ Oxides limit the dissolution of elements and promote the deposition of biological molecules, which allow bone growth to occur in proximity to the surface creating ultimately resulting in so-called osseointegration.^{18, 19, 49, 50}

Titanium is the ninth most abundant element and exists in nature mostly as titanium dioxide. Pure titanium has to be manufactured and is a softer nonmagnetic metal.⁵¹ It exists primarily in two different forms. At room temperature the hexagonal closed packed (HCP) structure predominates and it is known as the alpha phase. The structure shifts to a body centered cubic (BCC) form above 833 °C, which is known as the beta phase. Titanium alloys with carbon, aluminum, nitrogen, and oxygen increase the stability of the alpha phase, whereas alloys with vanadium act to stabilize the beta phase. The beta phase alloys are superior in strength, but have reduced biocompatibility due to fewer surface oxides.^{18, 49, 51}

Thirty-eight grades of titanium alloy are recognized today. Titanium grades 1 to 4 are alpha alloys that are referred to as commercially pure titanium (cpTi). Although called pure, they are actually grades that vary in the amount of interstitial elements that exist. The more oxygen and iron impurities in the metal, the stronger the product metal becomes.¹⁸ Grade 4 cpTi contains the most oxygen (0.40%), is the strongest of the group, and has been used successfully for dental implants dating back to 1965.¹⁸ Commercially pure titanium has a hardness of 258, which is a major advantage because it allows for the critical step of surface roughing.⁵² The micro-rough surfaces dominate the market because they have been documented to generate greater bone-to-implant contact resulting in increased osseointegration.^{25, 26} Most rough surfaces today are manufactured using a subtractive method with grit-blasting and acid etching, which is routinely achieved with cpTi.²⁶ It also has very good strength to weight ratio; however, the ultimate tensile strength of 550MPa can be insufficient.⁵² Modern small diameter implant designs with internal connections have resulted in implants with a relatively thin interface wall. Manufactures began to note narrow cpTi

implants fail due to fracture and began researching alternative alloys with increased strength.^{32,}

52, 53

Titanium grade 5 (TiV, aka Ti6Al4V) is the most common alternative alloy used in implant dentistry today due to its increased strength to weight ratio.⁵¹ It exists as a dual alpha-beta phase, which gains its strength from the 4% addition of the beta stabilizer vanadium, while the 6% addition of aluminum stabilizes the alpha phase (Table 1).^{18, 49, 51} After heat treatment, TiV has an ultimate tensile strength of 864 MPa, which in combination with its corrosion resistance makes it a great choice for implant dentistry.⁴⁹ In addition to the implant itself, because of TiV's strength, it is used in many other components in implant dentistry, including abutments, frameworks, bars, and screws. The high strength and increased hardness (296 VH) of TiV make it resistant to fracture but also renders it more difficult to achieve the roughened surfaces that are known to improve osseointegration. The biocompatibility of the alloy has also come into question due to reports of the corrosion products causing adverse effects.^{52, 54} Vanadium ions in particular have been associated with neurotoxicity, and inhibition of cell differentiation and proliferation.^{29, 55} As a result, attempts have been made to create titanium alloys that lack the toxic elements.

Alternative alloys with non toxic elements such as, niobium (Nb), tantalum (Ta), palladium (Pd), and indium(In) have all been proposed.^{32, 33} One of the most promising of the group is Ti6Al7Nb. Similarly to TiV, it is also a dual alpha-beta alloy, but the beta stabilizer is niobium instead of vanadium. Although this alpha-beta alloy possesses the required strength and biocompatibility that would tend to make a good implant alloy, the surface cannot be etched the same way as cpTi.³² Thus, to achieve the roughened surface that has become so

integral for implant success, new methods would need to be developed. Additionally, niobium has a much higher melting point (2469 C), making it harder to manufacture. Tantalum alloys have also been promising. However, it is much less abundant than the alternative elements, making it economically less attractive to manufactures.³³

More recently, titanium zirconium alloys have been explored. Zirconium is a non-toxic metal, which should not be confused with its ceramic form zirconium dioxide (ZrO₂) also known as zirconia.³² The metal zirconium, is in the same group of the periodic table as titanium, and its properties and behavior is closely resembles titanium. It maintains the same alpha-beta phase transformations and crystal structures, it transforms at similar temperatures, and it is also produced by means of the kroll process. In addition, zirconium is found in similar geographic locations often adjacent to titanium and is relatively abundant making it financially more feasible than the other non toxic alloy elements.^{32, 33}

Zirconium titanium alloys have demonstrated high strength and biocompatibility^{33, 34}. The binary TiZr alloy stands apart from other alloy alternatives because it maintains the same alpha structure as cpTi, allowing it to be modified in the same way, with sand blasting and acid etching.³³ Straumann, an implant manufacture, has produced one such TiZr alloy that it calls Roxolid™. Roxolid™ consist of roughly 85% titanium and 15% zirconium and has a ultimate tensile strength of 987 MPa.³³ That is roughly 10% increase in strength from other alloys. It also had demonstrated to have greater surface oxides compared to cpTi that would suggest superior corrosion resistance and enhanced biocompatibility.⁵³ Overall, Roxolid™ alloy appears to provide the increased strength that modern implants require. This in combination with

increased biocompatibility and its ability to be manufactured similarly to current cpTi implants makes it a promising alloy for the future of dental implants.⁵³

C. Zirconia Implant Abutments

Zirconia is the crystalline oxide (ZrO_2) ceramic form of the metal zirconium. It was first identified in 1789 by Martin Klaproth, but wasn't investigated for biomedical applications until the 1960's. In 1969, Helmer and Driskell first described its use as the ball in total hip replacement operations.⁵⁶ Since the discovery of transformation toughening, zirconia has been under considerable investigation with aims for further biomedical application.⁵⁷

Zirconia is known to exist in three distinct crystalized forms that vary by temperature. Below 1170 °C zirconia's structure is described as monoclinic (M). Between 1170 and 2370 °C it takes on a tetragonal (T) form and above 2370 °C it transforms to a cubic (C) structure. If a cubic or tetragonal zirconia sample is then allowed to cool back down below 1170 °C the transformation will reverse and it will revert back to the monoclinic structure, which is accompanied by a 4% expansion. The significant increase in volume upon cooling results in pure zirconia breaking apart at room temperature.⁵⁶ Alloying pure zirconia with additional oxides such as CaO, MgO, CeO₂, or Y₂O₃ allows stabilization of both cubic and tetragonal phases at room temperature, preventing the ceramic to crack propagation during cooling.⁵⁷

The most common type of zirconia used in biomedical applications contains approximately 3 mol% of yttria (Y₂O₃).⁵⁷ It is referred to as tetragonal zirconia polycrystal (3Y-TZP), because the yttria stabilizes the highest percentage of the strongest tetragonal form of zirconia. The mechanical properties of 3Y-TZP are strongly correlated to the grain size. Above

the critical 1 μ m grain size spontaneous T \rightarrow M transformation can occur resulting in reduced fracture toughness and a potential for catastrophic failures. Higher sintering temperatures and the longer sintering times produce larger grain size in the final product. The optimal microstructure of dental 3Y-TZP consists of small 0.2-0.5 μ m grain, and is achieved by sintering temperatures between 1350-1550 C. The resulting zirconia has great molecular stability with flexural strength ranging from 800-1000 Mpa, fracture toughness of 6-8 MPa x m^{1/2}, and hardness of 1600-2000 (VH).^{43, 57}

The high fracture toughness is unique to zirconia ceramics, and is due to a mechanism to prevent cracks known as transformation toughening. As a crack propagates, stresses become concentrated within the matrix causing a stress-induced T \rightarrow M phase change. The resulting internal 4% expansion generates internal compressive forces oppose the stress from the crack, slowing its growth and increasing the toughness of the material.^{43, 56, 57}

Zirconia's superior mechanical properties and white appearance make it particularly attractive for dental applications, but it wasn't utilized until the 90's due to manufacturing difficulties.⁴² Since the introduction of computer aided design and computer aided milling (CAD/CAM) zirconia has been used to fabricate anything from crowns, bridges, and full-arch restorations to posts, implants, and implant abutments.^{42, 58, 59} Due to its high hardness, CAD/CAM zirconia products are typically manufactured by milling pre-sintered blocks. This process, known as soft machining allows for faster milling with less wear to the milling components. Following the milling, the zirconia is sintered, resulting in a roughly 25% shrinkage that the CAD system must compensate for.⁵⁷

Custom CAD/CAM zirconia abutments have become increasingly utilized in implant dentistry.⁵⁹ Traditionally, implant abutments have been made from titanium (TiV), and until CAD/CAM technology was implemented, custom abutments were fabricated from cast gold. Although cast gold custom abutments are still fabricated, most custom abutment today are manufactured with CAD/CAM technology from either titanium or zirconia.¹¹ Zirconia is often the material of choice when esthetics are of concern.¹⁰ The white material has been documented to reduce the grey shadow of titanium in patients with thin tissue types.^{6, 8, 9}

However, despite zirconia's strength and toughness, its use has come into question after reports of increased complications, such as abutment fracture and screw loosening.^{44, 47, 48, 60-63} Additionally, reports suggest that the mismatch in material properties between zirconia and titanium results in increased wear at the implant abutment interface.¹²⁻¹⁴ It has also been suggested in the literature that these common complications associated zirconia abutments may be due to the design, manufacturing, and sintering processes and not due to the raw material itself.^{61, 62, 64}

D. Biomechanics at the Implant-Abutment Interface

Biomechanics has long been an interest in in implant dentistry. Screw loosening of implant-supported restorations is one of the most common mechanical complications that has been reported in the literature.⁶⁵ Single tooth implants have been shown to have the highest incidence of screw loosening. Reports with external hexagonal connections have indicated screw loosening to occur in as much as 45% of cases.⁶⁶ Modern internal connection designs have improved this significantly reducing the incidence to 8%; however, the problem still

remains.⁶⁵ The screw loosening is thought to be a clinical effect from a combination of other biomechanical complications stemming from the occurrence of micro-motion at the implant abutment interface.²⁴

Stability of the implant abutment interface is required for long term implant success.²³ The implant abutment connection is under constant load in the oral cavity. Although it is very difficult to study micro-motion clinically, it has been quantified in lab studies and is suggested that its occurrence may cause screw loosening and consequently wear and destruction of the implant abutment interface.^{23, 24} The degree of misfit in the connection doesn't appear to have a direct correlation to micro-motion and quantitatively, the movements of titanium vs zirconia abutments are documented to be similar.²³ The force on the screw known as preload is responsible for holding together the implant abutment connection. After a screw is tightened, the threads undergo an elastic deformation that acts to hold the parts together with friction. The torque that a screw is tightened to should correlate with the yield strength of any particular alloy to maintain the clamping force.²⁴ Metal fatigue and wear as a result of small masticatory oscillations may cause settling of this joint, which will result in clinical loosening.²⁴

Modern implant designs have moved away from external butt joint connections that placed significant force on the screw itself. Newer tapered internal connections reduce the stress on the screw and improve the mechanics at the implant abutment connection by instead transferring the lateral forces to the walls of the implant.⁶⁷ Based on the principles of Morse taper, 8 degree tapered internal connections also aim to create a so-called cold weld between abutment and implant alloys.⁶⁸ These principles work very well for titanium implant-titanium abutment connections because the metallic properties for elastic deformation, however

principles of Morse taper create internal stresses in ceramics that may be responsible for the increase fracture rate of zirconia abutments.^{44, 45}

Internal connections may reduce screw loosening and improve mechanics, but it does not completely eliminate the motion that occurs at the implant abutment interface.^{23, 69, 70} Even with precision fit components, inevitable microgaps are still present between implants and abutments.⁷¹ The microgap while present prior to loading then becomes larger with cyclic loading as wear occurs.⁷² These gaps are present with both zirconia and titanium abutments and have been shown to harbor bacteria. The resultant microleakage in and out of the microgaps have been proposed to induce inflammation leading to peri-implant pathology.⁷¹ In addition to becoming a reservoir for bacteria, corresponding with micromotion, these microgaps allow a constant flow of saliva and wear products into and out of the implant abutment interface that may potentially increase the wear at the junction.⁷³

E. Previous Studies of Titanium Implant Wear with Zirconia Abutments

Ceramic implant abutments have been used successfully as support for anterior single crown since the 1990's.^{74, 75} The use of zirconia as an abutment material was introduced in 1997 as a way to improve esthetics but maintain the strength of titanium.⁷⁶ Since then, zirconia abutments have become increasingly more prevalent along with the progression of CAD/CAM technology, which made design and fabrication assessable and achievable without great effort.⁷⁷ The interaction between zirconia abutments and titanium implants has been investigated previously, but the literature is extremely limited. Studies have focused singularly on either the mechanical or corrosion aspects of the interaction.

The first mechanical wear related article was published in 2003 and highlights the visual observation of displaced titanium debris from an implant that was noted on a white zirconia abutment after cyclic loading.⁷⁸ The visualization of similar phenomenon occurring clinically has sparked interest due to the potential biological and mechanical implications.¹⁴ In 2011 a pilot study directly investigated the wear at the implant abutment interface associated with zirconia abutments.¹² Zirconia abutments were placed in titanium abutments and cyclically loaded for 1,000,000 cycles. The specimens were examined at periodic intervals during the testing in an effort to track wear progression. During the examinations the interface was evaluated and the surface area of the wear was quantified using digital photography and scanning electron microscopy (SEM). Based on the surface area, it was determined that zirconia abutments generated 8.3 times greater wear than titanium abutments. Additionally, the rate of wear of zirconia abutments showed a peak at 250,000 cycles, after which it continually decreased.

In 2012, a similar study was performed except microCT was added to better visualize the specific patterns of wear that occur at the implant-abutment interface.¹³ Based on the surface area, this study also concluded that zirconia abutments cause significantly more wear than titanium abutments. Although insightful, these studies only report surface area and not the volumetric loss of material. In addition, these studies did not consider the electrochemical interaction that occurs in the oral environment.

Titanium, as described above, has been used as the gold standard for dental implants due to its biocompatibility, however, it is not completely inert to corrosive attack.²⁰ Titanium is a passive metal primarily due to the oxide layer that spontaneously forms on its surface. When this passive film is disrupted, the underlying raw metal becomes exposed and susceptible to

corrosion.¹⁸⁻²⁰ This process typically occurs in cycles: the oxide layer is damaged and removed, corrosive attack occurs, and the surface recovers, reforming a new protective passivation layer.^{21, 22} Many studies have demonstrated the corrosive potential of titanium in biological systems.^{20, 22, 79, 80} In fact, there are numerous reports that show the electrochemical degradation of titanium in the presence of saliva.^{15, 16, 36}

The effect of salivary pH on the corrosion of titanium has also been investigated and it was found that lower pH values increase titanium degradation.³⁶ However, a similar study found that titanium corrosion resistance was lowest in saliva of neutral pH, specifically at pH 7.5.¹⁵ Saliva of physiological pH can act as a weak electrolyte, which may increase the overall material break down at the implant abutment interface. To date, no literature has been published in which the combined effect from both electrochemical (corrosion) and frictional degradation (tribology) was evaluated between implants and abutments.

Tribocorrosion, an area of material science that examines the synergistic effects of both wear and corrosion, has evolved specifically to fill these gaps in the literature. Simply understanding the tribological (mechanical) effects of an interaction lacking a corrosive environment or the electrochemical behavior lacking mechanical wear is not sufficient to predict the tribocorrosive performance.³⁷ In a biological system, the mechanical and electrochemical behaviors act in a true synergy resulting in an increase in overall wear of articulated materials.²¹

Tribocorrosion studies aim to replicate the biological environment to more accurately predict outcomes.²¹ Studies with these designs have been carried out extensively in orthopedic sciences in an effort to increase the life spans of total hip and knee replacements.⁸¹

Tribocorrosive investigation has also been implemented in implant dentistry, primarily looking at the effects of implant-bone interface.^{15, 38, 81} Additionally, the tribocorrosive effects of titanium and titanium alloys (TiV and TiZr) in the presence of saliva and LPS have been completed with alumina counter bodies.^{15, 17, 34, 82, 83} Presently, there are not any tribocorrosion studies that aim to investigate the materials of the implants abutment interface. Additionally, zirconia counterbodies are rarely used in tribocorrosion studies, and most use alumina. The limiting factor for tribocorrosion designs is that due to the testing equipment and apparatus set up, only material samples can be tested as opposed to implants and abutments themselves.

3. Materials and Methods

A. Experimental Apparatus:

A custom-made ball-on-disc tribocorrosion set-up was used for this study (Figure 1). The ball representing the abutment, articulated against a disc, representing the implant. The testing occurred in an electrochemical cell that sits on top of the linear reciprocating tribometer (DUCOM- Material Characterization Systems, Evanston, IL). As the ball slid against the disc, the tribometer recorded the frictional data, and the potentiostat (SP-240 Bio-Logic, LLC, Knoxville, TN) recorded the corrosive data simultaneously. All tests were conducted using the standard 3-electrodesystem in a bath of artificial saliva at pH 6.5 and at physiological temperature 37° C (Figure 2). During the testing, the abutment material (ball), slid against the implant alloy (disc) with 8N load at a frequency of 2Hz and a 2mm stroke for 25,000 cycles. A saturated calomel electrode (SCE) was used as the reference electrode (RE), a graphite rod as the counter electrode (CE), and a copper electrode placed underneath the sample functioned as a working electrode (WE).

B. Experimental Design:

Testing was completed using a standard tribocorrosive design known as “Free Potential” (Figure 3). Two abutment materials, zirconia (Zr) and TiV (Ti), were tested against two implant alloys, TiV (Ti) and Roxolid™ (Rox), creating a total of four material couplings (ball/disc). The four couplings (Ti/Ti, Ti/Rox, Zr/Ti, Zr/Rox) were selected for the tribocorrosion tests (N=3), and the following output parameters were monitored and recorded: 1) the evolution of coefficient of friction (CoF), which represents expected mechanical damage, 2) the evolution of voltage,

which describes the corrosive tendency, and 3) the wear volume loss, representing the overall wear-corrosion synergistic effect.

C. Sample Preparation:

Disc:

A total of 12 discs were prepared. Six discs were made of TiV (Mc-Master Carr, Elmhurst, IL), and six were made of Roxolid™ (Straumann USA LLC, Andover, MA). The alloy compositions are shown in Tables 1 and 2. The TiV discs were 15mm in diameter and 2mm thick. The Roxolid™ discs measured 15mm in diameter and 1mm thick. All 12 discs were mounted into acrylic resin bases (Caulk Orthodontic Resin, Dentsply) and were polished to a mirror finish following the standard metallographic methods. The specimens were initially wet ground with 240-800 grit sandpapers (Carbimet 2, Buehler, Lake Buff, IL). After sanding, the discs were polished with diamond paste (MetaDi 9-micron, Buehler) on a lubricated (MetaDi Fluid, Buehler) microfiber cloth (TextMet Polishing Cloth, Buehler). The final polish was achieved using a colloidal silica suspension (MasterMed, Buehler) on a lubricated (Distilled water) Chemomet polishing cloth (Chemomet I, Buehler). After the polishing, the discs were removed from the acrylic bases, and they were ultrasonically cleaned (FS 20, Fisher Scientific, Pittsburg, PA) in deionized water and 70% isopropanol for 15 minutes.

Ball:

A total of four balls were prepared, one for each material coupling. Two of the balls were made of TiV, and two balls were made of zirconia (ZrO₂). The balls measured 3/8" in diameter and were polished to a smooth finish by the manufacturer (Mc-Master Carr, Elmhurst,

IL). Before tribocorrosive testing, the balls were cleaned with 70% isopropanol and oriented so that a fresh contact point was used in every trial.

Artificial Saliva:

Artificial saliva was made and set at a physiologic pH of 6.5. The components listed in Table 3 were individually measured and added to the solution, and the pH was verified with a pH meter.

D. Tribocorrosion Testing Protocol:

The tribocorrosion testing consisted of three phases: initial stabilization, tribocorrosion testing (sliding phase), and final stabilization (Figure 4). After the specimens were cleaned, they were mounted in the tribocorrosion cell, the cell was filled with artificial saliva, and the temperature was maintained at 37°C. The initial stabilization was started, and an electrochemical cleaning phase at a constant cathodic voltage of -0.9 V. SCE was applied. Consequently, an open circuit potential (OCP) test was conducted to measure the free potential (E_{oc}) of the exposed surface. This was followed by electrochemical impedance spectroscopy (EIS) measurements at a range from 100 KHz to 5 mHz with a 10 mV of scan amplitude. Following the initial stabilization, the ball was lowered into contact with the disc, 8N load was applied, and the sliding phase started. The free potential tribocorrosion was conducted for 25,000 cycles with sliding frequency (2Hz) and amplitude of 2mm. During the testing, the coefficient of friction and the evolution of voltage (corrosive potential) were monitored and recorded. Following the sliding phase, the load was released, and the ball was raised from the contact zone on the disc. Final stabilization (EIS test and OCP measurement) was then completed. After the test, the samples were cleaned with deionized water and sonicated for

15min in 70% isopropanol before being put into a storage chamber. Groups for tribocorrosion testing were defined by their ball/disc coupling. For example, Ti/Ti represented a titanium ball/titanium disc coupling.

E. Surface Characterization:

Following the testing, the worn surface was examined. A white light interferometry microscopy (Zygo New View 6300, Middlefield, CT) was used to determine the total volumetric loss encountered by each specimen. The Zygo was also used to measure the surface roughness, and the average roughness R_a was plotted. Two areas were chosen for investigation: inside the damaged wear scar and the untouched or undamaged area adjacent to the wear scar. The discs were also examined with a scanning electron microscope (SEM, Joel JSM-6490 LV, Japan) and damage was qualitatively compared among groups. Energy dispersive x-ray spectroscopy (EDX) was used to evaluate the chemical composition of the materials on the damaged surface.

F. Statistical Analysis:

Data were analyzed using one-way between-groups analysis of variance to explore the impact of the material on the coefficient of friction, voltage drop, volume loss, and surface roughness. *Post-hoc* comparisons Bonferroni test was performed to evaluate the significant differences among groups. A mean difference significance at the 0.05 level was used for all comparisons. All statistical analyses were performed using standard statistical software (SPSS 22.0, IBM Corp. Armonk, NY, USA).

4. Results

A. Coefficient of Friction:

The CoF is representative of the mechanical damage and degradation that are expected in the system (Figure 5). For each group, as the tribocorrosion sliding started, the CoF increased significantly and then stabilized. The Ti ball groups had lower overall CoF and displayed less variability of fluctuations (Figure 5). The groups with Zr ball had higher CoF and displayed greater variability in the CoF fluctuations. The Ti/Ti group had the lowest average CoF ($0.5033 \pm 0.091\mu$), which was found to be significantly lower ($p=0.021$) than the Zr/Rox group ($0.9531 \pm 0.135\mu$) (Figure 6). Thus, the Ti/Ti group had significantly less mechanical damage.

B. Evolution of Voltage:

Figure 7 illustrates the evolution of voltage (potential) that occurred during the sliding. A significant voltage drop was observed immediately following the start of the sliding, and this drop reflected greater electrochemical or corrosive potential in the system. Voltage fluctuations occur during the tribocorrosion testing and when the sliding stops, the voltage recovers to the initial values. The voltage drops were measured, and the average values were plotted in Figure 8. The Ti/Ti group had the greatest voltage drop (0.802 ± 0.059 V), which was found to be significantly higher ($p=0.019$) than the Zr/Rox group. The Zr/Rox group had the lowest voltage drop (0.628 ± 0.053 V). Thus, the Ti/Ti group had significantly more corrosion.

C. Wear Volume Loss:

Wear scars formed at the contact zone of each disc were measured with white light interferometry and the wear volume loss was calculated (Figure 9). The Ti ball groups had significantly larger wear scars than the zirconia ball groups (Figure 10). Overall, the Ti/Ti group

had the largest wear volume loss ($15.1 \times 10^7 \pm 2.25 \times 10^7 \mu\text{m}^3$), while the Zr/Ti group had the least volume loss ($2.26 \times 10^7 \pm 4.15 \times 10^6 \mu\text{m}^3$). Ultimately, both zirconia couplings had significantly less wear volume loss than the titanium couplings ($p < 0.001$).

D. Surface Roughness:

White light interferometry was used to calculate the surface roughness (Ra) of the discs inside the wear scar and on the outside polished surfaces (Figure 11). In all groups, the areas outside of the wear scar are smooth due to the mirror polish that was achieved during the specimen preparation. The Zr/Rox group was found to have the highest internal surface roughness, and the Zr/Ti had the lowest ($p < 0.001$).

E. Surface Characterization:

Scanning electron microscopy (SEM) was used to evaluate the worn surface (Figure 12). The first column of images was captured at a low magnification of 30x to yield a visual representation of the whole wear scar. To investigate the breakdown and deterioration of the surfaces, the images at high magnification are shown. The 3000x image of the Ti/Ti group in the right column shows very characteristic wear patterns with rows of light grooving. In the Zr/Rox group, several features of the wear process, coupled with corrosion attack, can be observed, for example the crack in the surface (Figure 12). Evaluation of the chemical composition of the worn surfaces was completed using energy dispersive x-ray (EDX) spectroscopy (Figure 13). When evaluating the Ti/Rox group, vanadium was detected on the Rox disc, showing the transfer of particles.

5. Discussion

Zirconia abutment materials, represented by the Zr ball, generated significantly less wear and corrosion damage to both implant alloys as compared to the Ti abutment group, and thus our hypothesis was rejected. In fact, titanium created over five times more wear to both implants alloys. These tribocorrosion results suggest a different thought process regarding zirconia abutments compared with the previous reports. Studies with off-access cyclic loading have been used to assess the effect of zirconia abutments at the implant interface.^{12, 13} The results were limited to observation of the mechanical damage, and these studies concluded that zirconia abutments generated significantly more wear to dental implants. In addition to the variation in study design and testing methods, the disparity in findings compared to this study is likely a consequence of not incorporating corrosion into the system.

The tribocorrosion model used in this study provides a highly controlled testing environment to investigate corrosion and wear simultaneously. This provides a better understanding of the details of the interaction that could occur between materials in a clinical setting. However, there are limitations due to the nature of the testing equipment: only material specimens can be tested and not actual implant and abutment components as previous cyclical loading studies have done. In addition, the tribometer used was originally designed for larger movements, and the smallest reproducible stroke was 2mm, which was used for the testing in this study. This linear movement is much larger and less complex than the micromotion or fretting process that occurs between implants and abutments in a clinical setting.

Taking the limitations into consideration, the tribocorrosion methodology has been widely accepted in material sciences. It allows the addition of electrochemical investigation, which isn't possible in other study designs but is essential to gaining a complete understanding of the complex relationship between materials at the implant-abutment interface. The methodology used in the current study allows for a magnified view of the interaction at the microscopic level between implant alloys and abutment materials.

A. Mechanical Influence at the Implant-Abutment Interface:

The coefficient of friction (CoF) was used as a surrogate measure to investigate the mechanical wear that occurred at the material interface during tribocorrosion testing. When testing started, CoF increased as the ball began to scrape against the disc, resulting in mechanical degradation. The higher the CoF, the more wear occurred. Oscillations in the CoF were observed during the tribocorrosion testing in all groups. These fluctuations may be the result of third-body particles that have entered the system.³⁷ The abrasion from the abutment material rubbing on the disc likely caused oxide layer detachment, surface deformation, and material shearing.^{17, 21, 38} Eventually the released wear particles become trapped in the contact zone. These third-body particles can act as a lubricant or as an abrasive component, resulting in CoF oscillations.^{82, 84}

The Ti ball (abutment) groups both had lower average CoF with more stable patterns, indicating less third-body interaction. This is evident from the light grooving pattern in the contact zone of the titanium discs (Figure 12). The groups with the Zr ball had higher average CoF and more fluctuations in the evolution of CoF, likely due to the increased hardness of the Zr material and mechanical property mismatch at the contact zone.⁸⁵⁻⁸⁷ Such conditions

potentially produced more shearing damage to the disc surface, resulting in third bodies and transitioning the wear process from a two-body to a third-body mechanism.^{81, 82}

The SEM images of Zr groups show scales that are likely to delaminate and detach from the surface (Figure 12), and the EDC data (Figure 13) confirmed that the transfer of particles occurred with vanadium from TiV being present on the Rox disc. The shearing and detachment of wear particles would not only cause mechanical damage to the surface but would also cause wear-accelerated-corrosion.^{17, 37} After the harder material penetrated into the metal below and removed particles, it would leave behind a bare surface wear track, which is more prone to corrosive attack.³⁷ Thus, wear accelerated corrosion occurred until the oxide layer reformed.⁸⁸ A schematic of the possible mechanisms occurring at the contact zone is illustrated in Figure 14.

B. Electrochemical Influence at the Implant-Abutment Interface:

The evolution of voltage (potential) was used to evaluate the corrosion susceptibility of the materials at the implant-abutment interface (Figure 7). With lower voltage, more metal dissolution occurred that reflected greater corrosive attack.¹⁷ A significant voltage drop was observed in all groups immediately following the start of the tribological sliding, indicating the removal of the passivation layer and the exposure of an unprotected raw alloy that was prone to corrode.^{37, 81, 84} The passive oxide layer was constantly altered and reformed due to the electrochemical interactions with the electrolyte (artificial saliva), and the fluctuations of the voltage (Figure 9) correspond to these recurrent passivation cycles.²⁰

It was found that the Ti/Ti coupling had the greatest corrosion and the Zr/Rox coupling had the least. Corrosion studies with titanium have shown that at neutral pH (6-6.5), titanium has the highest corrosion due to an increased current flow that may be adding to the corrosive

activity in the test.^{17, 36} Both of the zirconia couplings had better corrosion resistance likely due to zirconia's inert ceramic nature.

In this study, Roxolid™ couplings showed less corrosive potential than the TiV disc couplings, which is similar to the limited number of reports that have investigated the TiZr-based alloys.^{29, 34} Corrosion resistance is dependent on the rate of passive layer reformation; thus, the Roxolid™ material would likely reform the oxide layer faster than TiV (see the schematic diagram- Figure 14).⁷⁹ In addition, the superior corrosion resistance is likely result of increased surface oxides due to the physical composition and grain structure.

Titanium exists primarily in two different forms. At room temperature the hexagonal closed packed (HCP) structure predominates, which is known as the alpha phase, and above 833 °C the phase shifts to a body centered cubic (BCC), which is known as the beta phase. The alpha structure is known for superior biocompatibility due to increased surface oxides, while the beta phase alloys are superior in strength, but decreased surface oxides.^{18, 49, 51}

Commercially pure titanium (grade 1-4) is primarily composed of alpha phase grains, which spontaneously form a TiO₂ surface layer, rendering it biocompatible.⁸⁰ The Ti6Al4V alloy (grade 5) is a dual alpha/beta phase alloy, in which vanadium is added to stabilize the larger beta phase, thus improving the physical properties.¹⁸ Although, it has been shown that Ti6Al4V alloy is sufficiently biocompatible, inherently it has less abundant surface oxides to protect against corrosion.²⁰ TiZr alloys on the other hand are composed of a binary alpha structure. Because zirconium has identical allotropic transformation and very similar phase transition temperature to titanium, its alloys create an alloy of only alpha grains.^{32, 35} The result for alloys like Roxolid™ is a smaller grain size with increased surface oxides, which likely explains why we

observed improved corrosion resistance as compared to the Ti6AL4V alloy tested.^{33, 53} Further studies should be completed to evaluate the specific corrosive properties of the Roxolid™ alloy.

C. Synergistic Behavior of Wear and Corrosion at the Implant-Abutment Interface:

The combined effect of both wear and corrosion was evaluated through the wear volume loss from the tribocorrosion tests and surface characterization of worn surfaces. The wear volume loss depicted the total degradation of the materials due to the interplay of the wear and corrosion processes, which are directly/indirectly influenced by the mechanical and environmental effects. Previous studies have shown that the effect of tribocorrosion on material degradation is not simply the addition of the individual contributions from wear and corrosion. Rather, the total weight loss is much greater than the expected individual components. According to Stack et al., the synergistic interaction of the wear and corrosion leads to several mechanistic transitions at the contact zone.⁸⁹ The synergistic ratio, (K_c : weight loss due to corrosion / K_w : weight loss due to wear) could assist in determining the dominating tribocorrosion mechanism. The tribocorrosion system, with “wear dominated corrosion” as the major driving mechanism, could lead to a high degree of unexpected degradation loss (Figure 14).

In this study, titanium ball (abutment) groups had significantly more volume loss compared to the zirconia ball groups. Based on the volume loss, the best overall performing group was Zr/Ti, and the worst performing group was Ti/Ti, which had over 6.5x more material displaced. Hence, the observed wear volume loss demonstrated that synergistic interaction is thought to be the dominating mechanism for destruction.¹⁷ It is also worth noting that the high degree of passivation of Ti in pH 6.5 could enhance the rate of material removal (self-sacrificing

effect), resulting in high wear volume loss.¹⁵ However, the future tribocorrosion test in potentiostatic mode would need to be completed to confirm the dominating mechanisms for each of the material pairings. The findings also indicate the major influence of saliva on the destruction and degradation of materials in the oral cavity. The inert nature of the zirconia resulted in low wear volume loss, which is important in minimizing metal ion liberation.

D. Clinical Significance:

This *in vitro* study clarified the mechanical and chemical relationship that could occur between materials at the implant-abutment interface. Roxolid™ implant alloy had improved corrosion characteristics, which combined with its mechanical properties and lack of toxic elements makes it a promising implant alloy. Zirconia abutment materials resulted in significantly less damage to implant alloys. In fact, the zirconia groups generated 5-6 times less wear of the implant alloys as compared with the titanium counterparts. Clinically, zirconia abutments may result in less deterioration at the implant-abutment interface, potentially leading to less metal release, less tissue tattooing, and superior long-term outcomes. Future clinical studies could confirm these concepts. Clinical complications that have been reported with zirconia abutments may be attributed to design flaws and fabrication errors and not the material itself.⁶⁴

6. Conclusions

This study investigated the complex interaction between the materials of the implant-abutment interface. Within the limitations of this study, the following conclusions could be drawn.

- Wear and corrosion interact synergistically in the oral environment
- Zirconia abutment groups had significantly less volume loss compared to titanium
- Roxolid™ implant alloy showed superior corrosion resistance
- Zirconia abutment / titanium implant pairing had the best overall performance

FIGURES

Figure 1: Experimental Apparatus

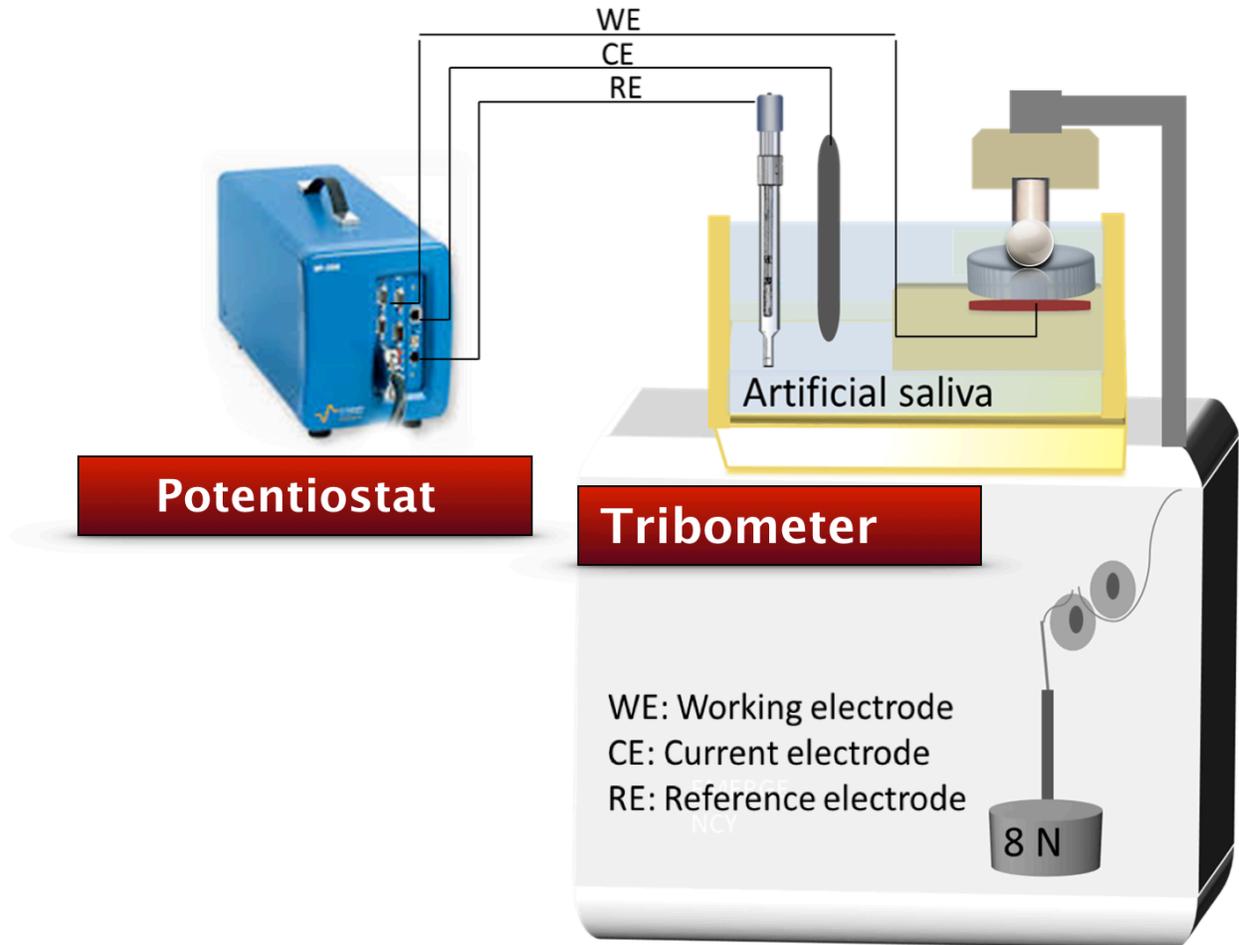


Figure 2: Testing Chamber

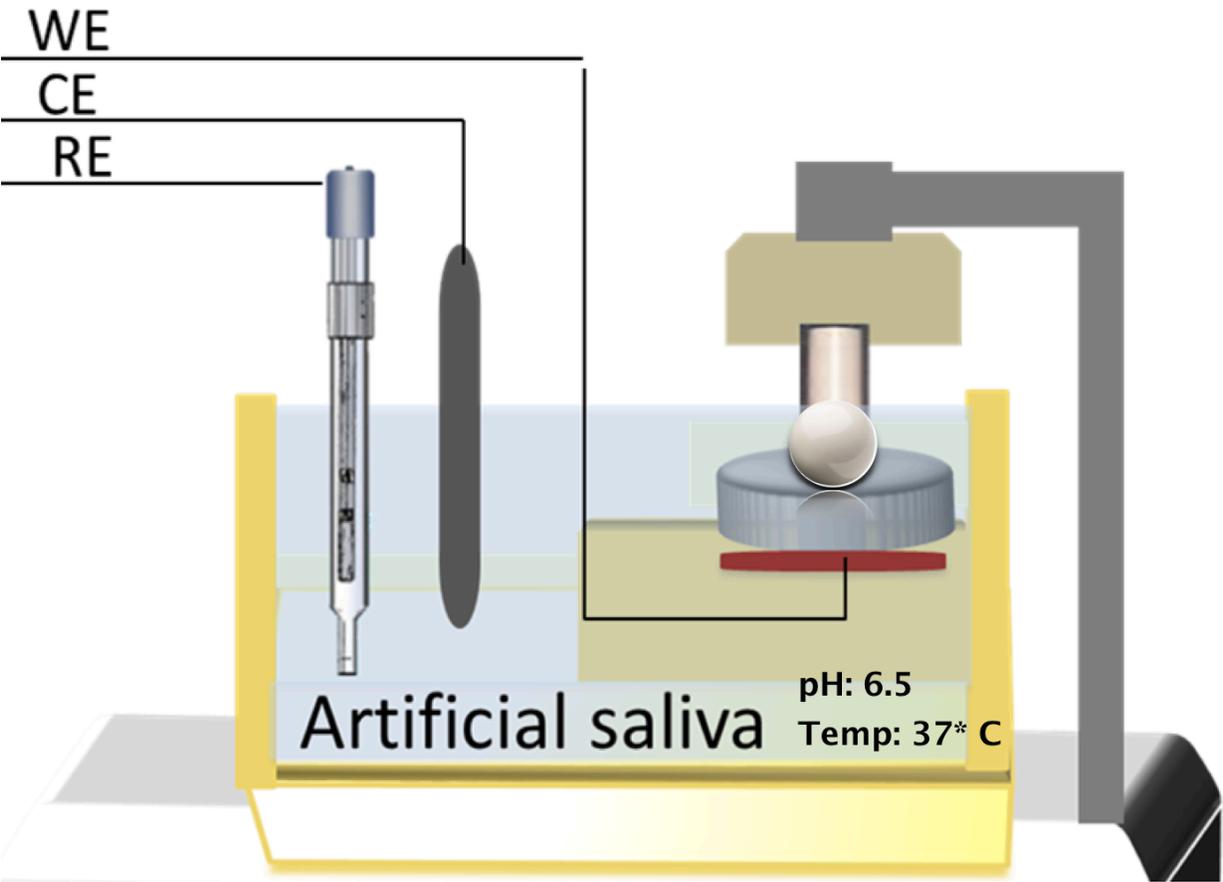


Figure 3: Experimental Design

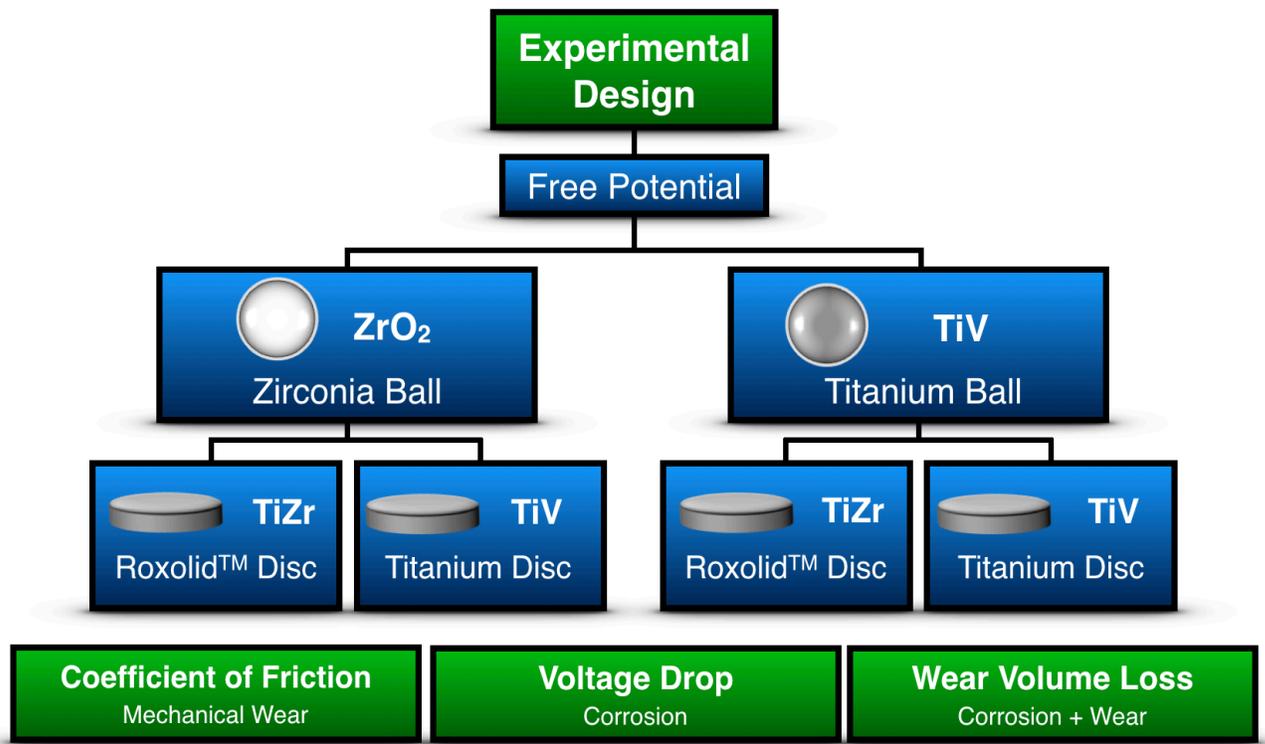


Figure 4: Experimental Protocol

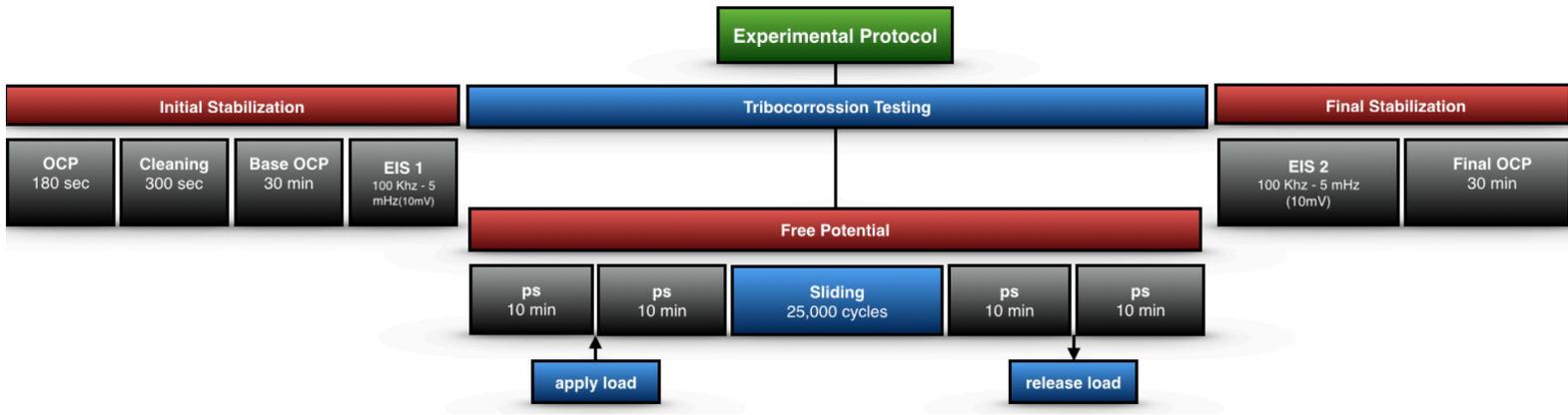


Figure 5: Evolution of Coefficient of Friction

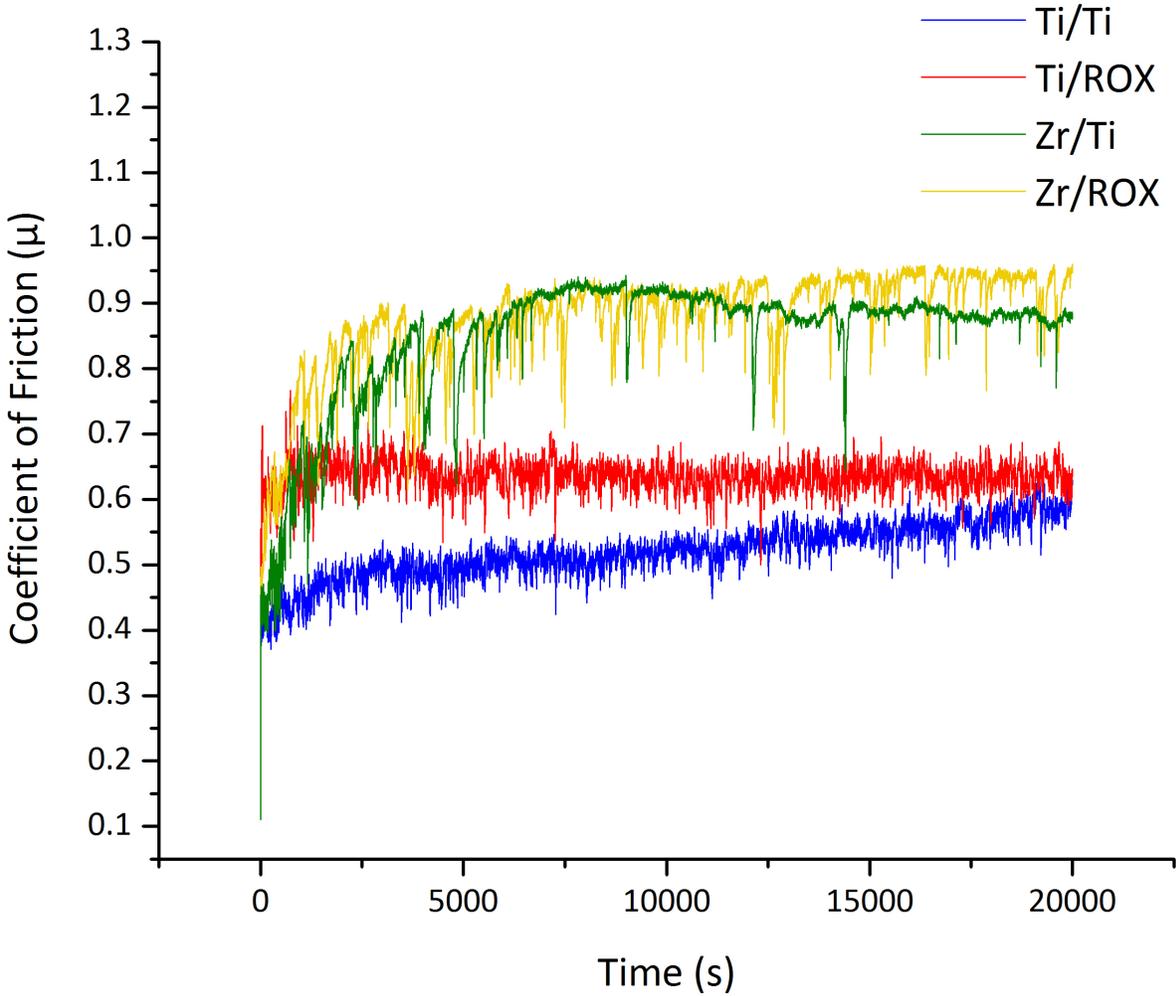


Figure 6: Average Coefficient of Friction

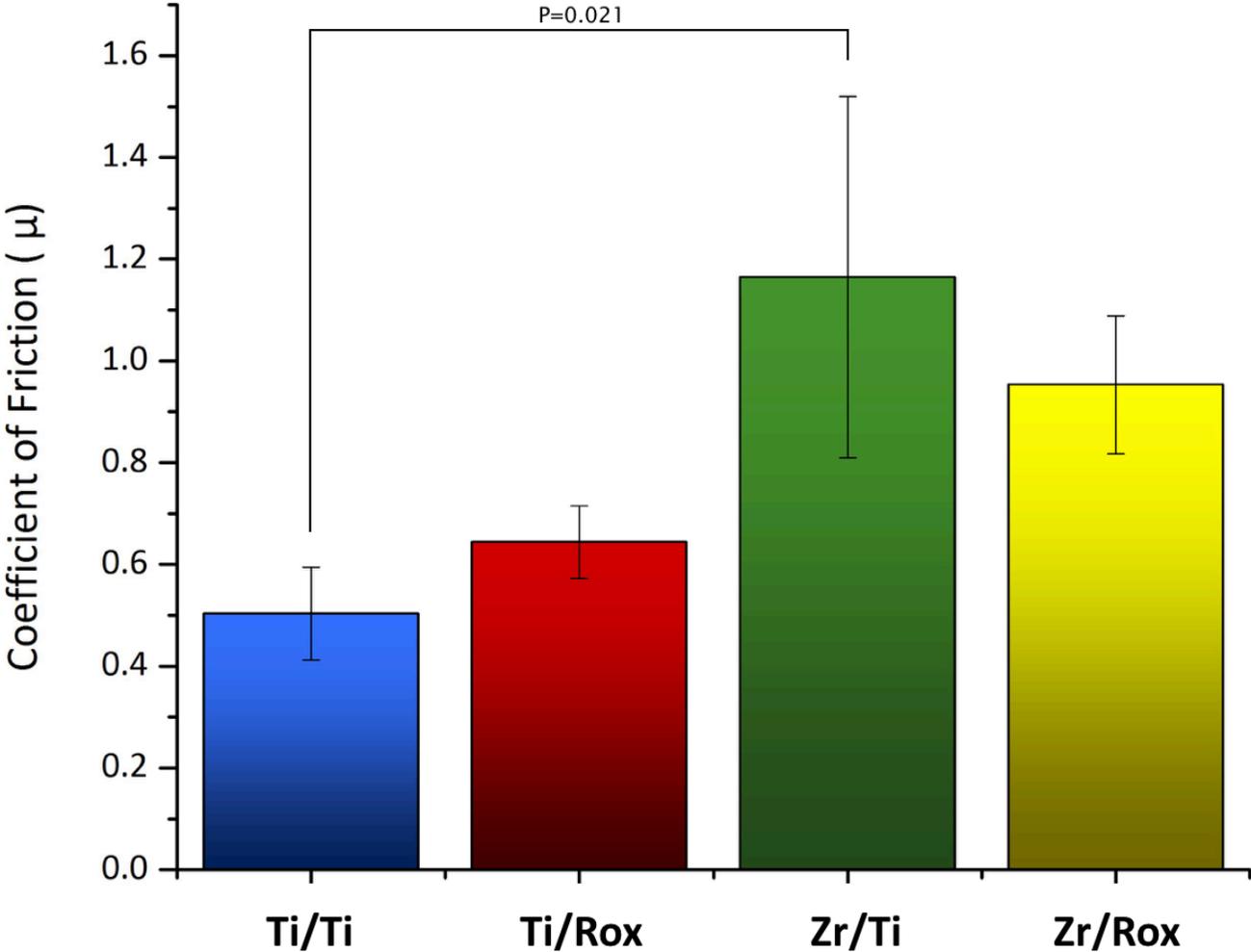


Figure 7: Evolution of Voltage (potential)

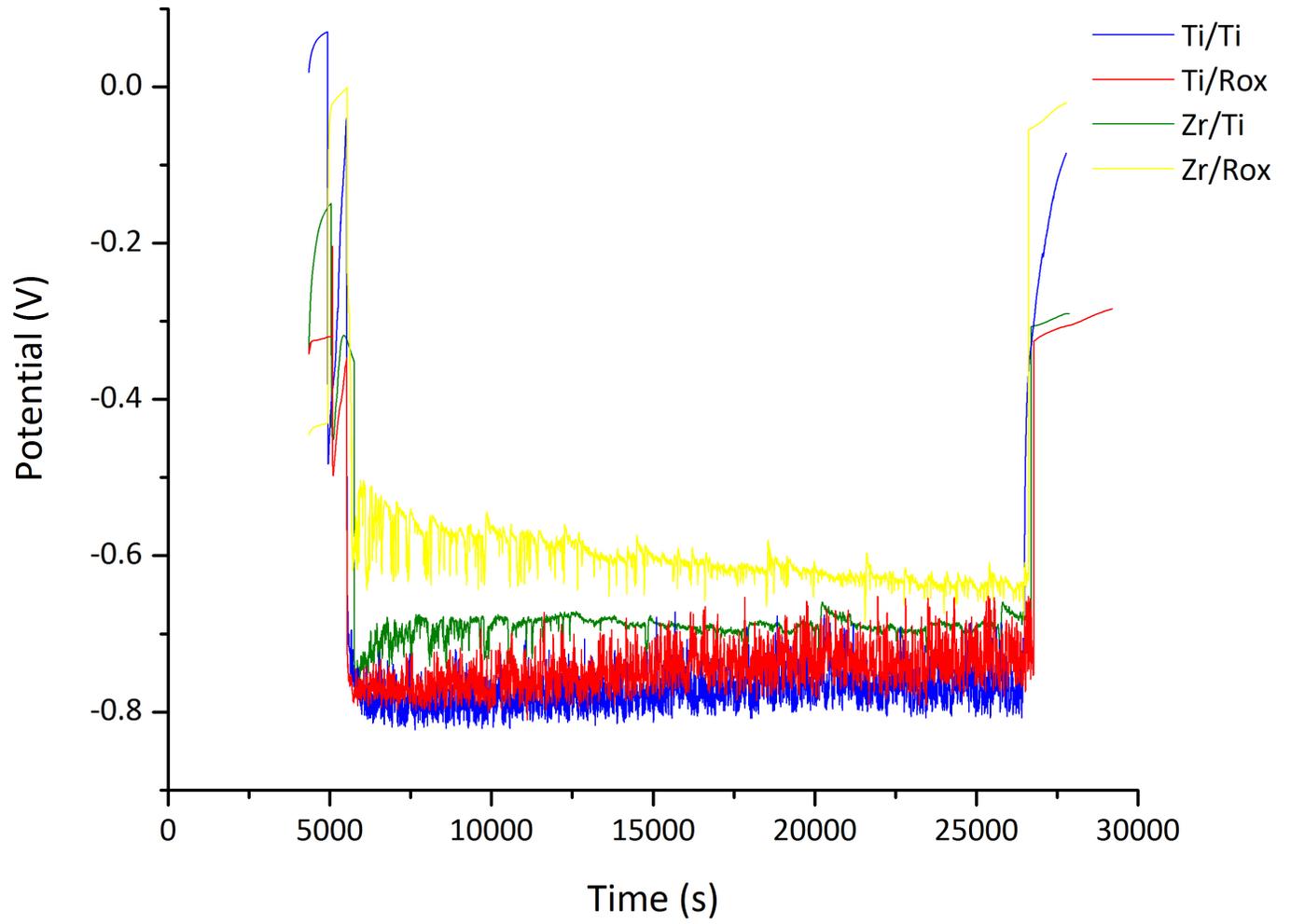


Figure 8: Average Voltage Drop

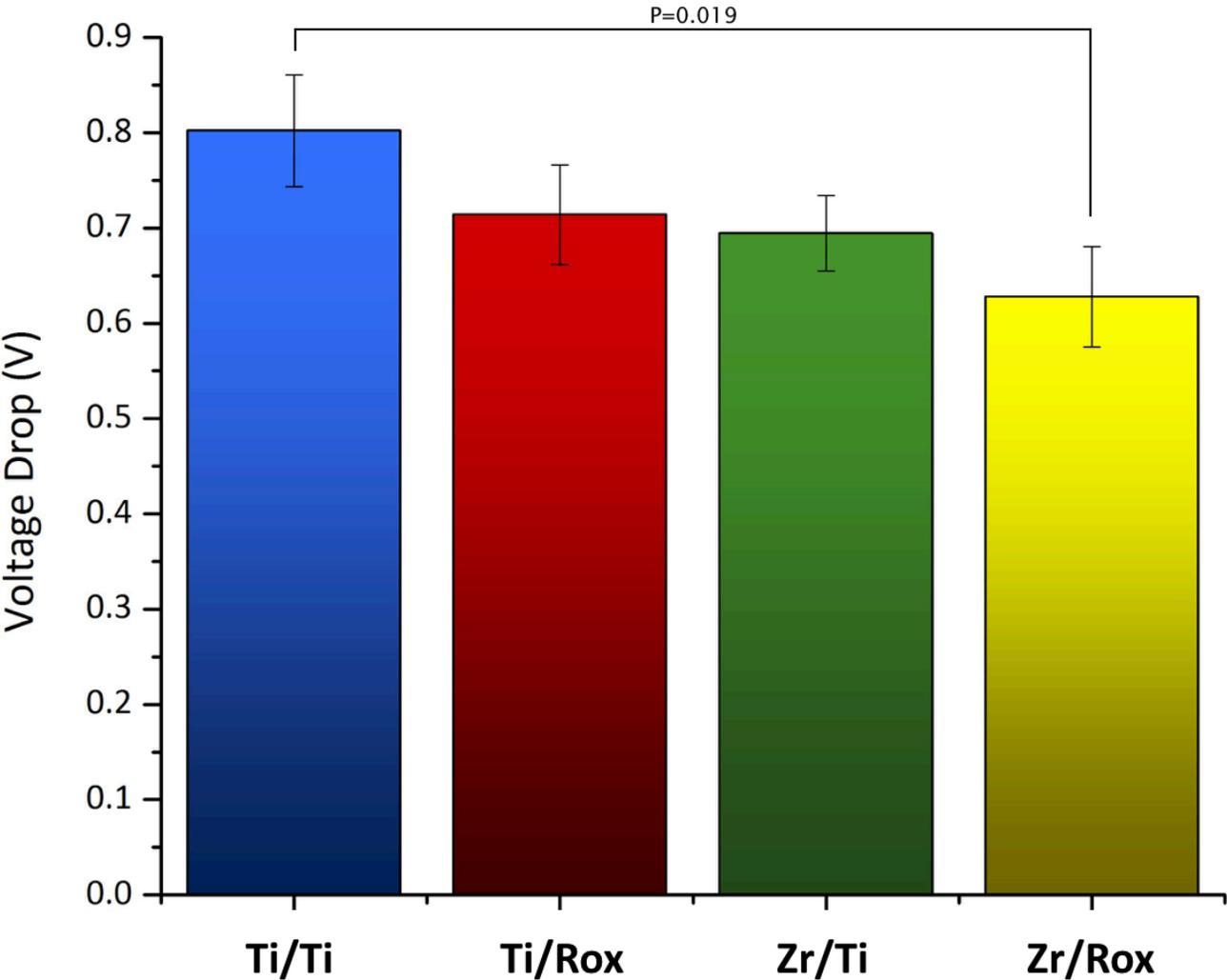


Figure 9: Average Wear Volume Loss

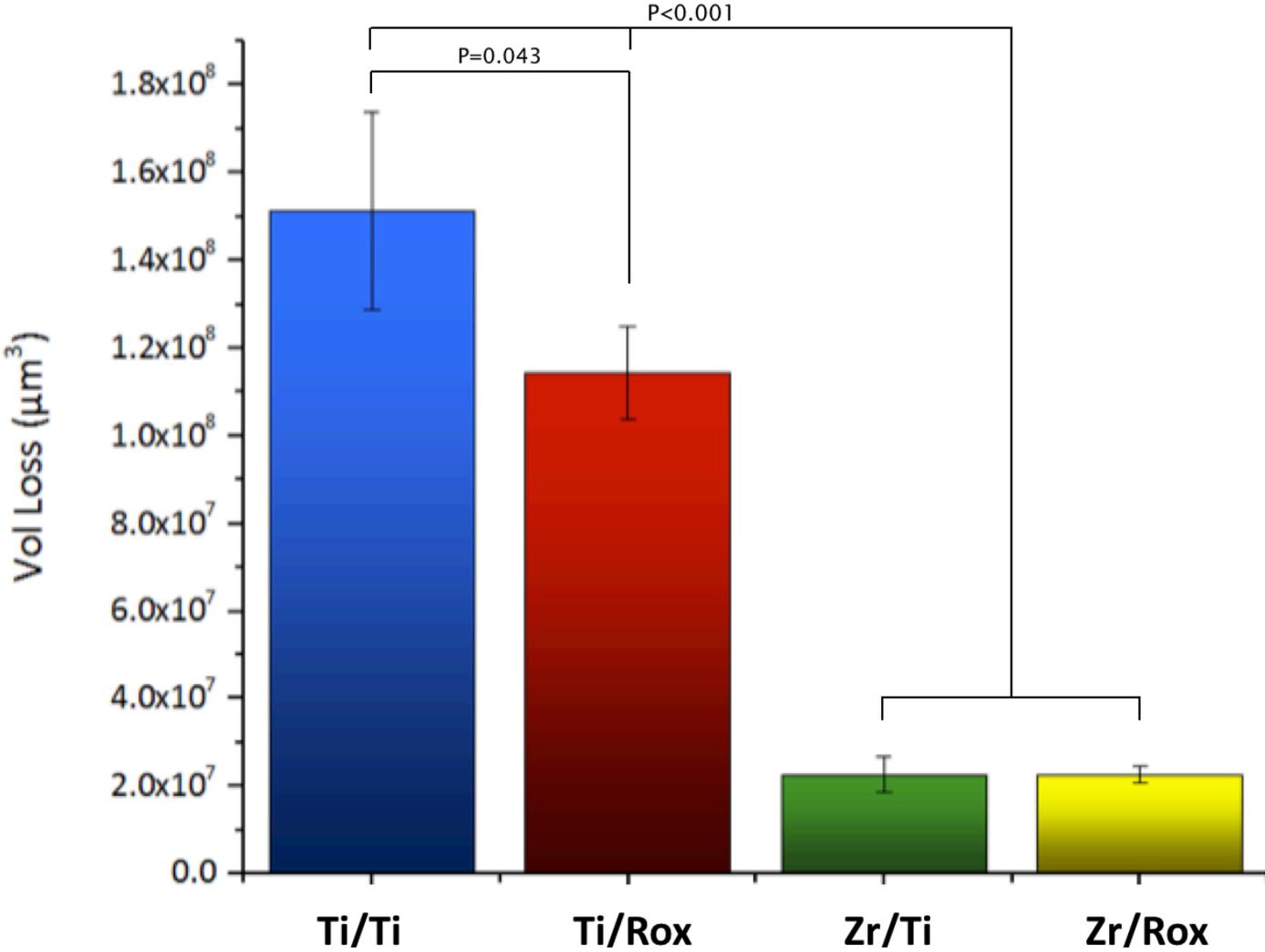


Figure 10: White Light Interferometry Images of the Wear Scars

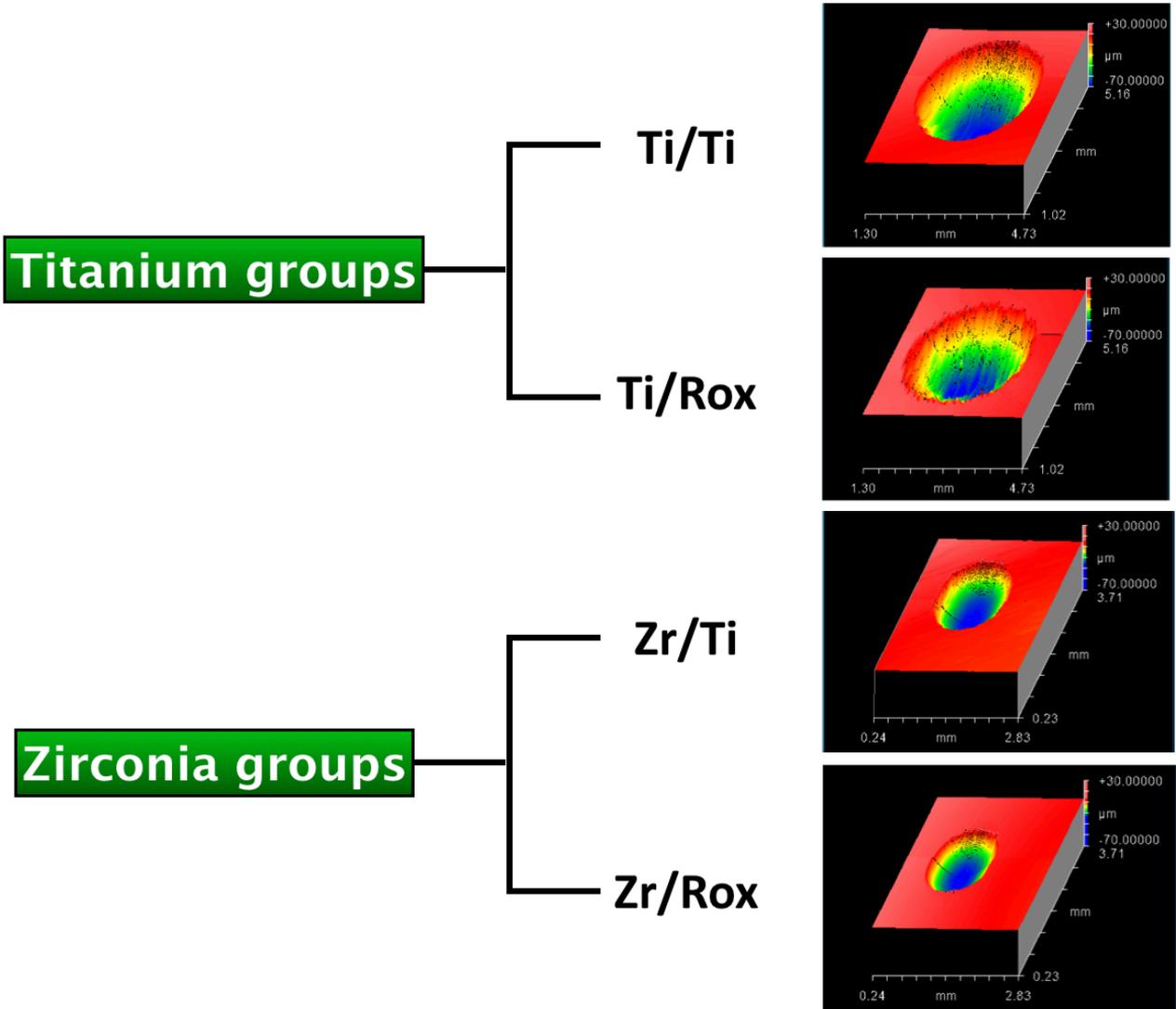


Figure 11: Surface Roughness

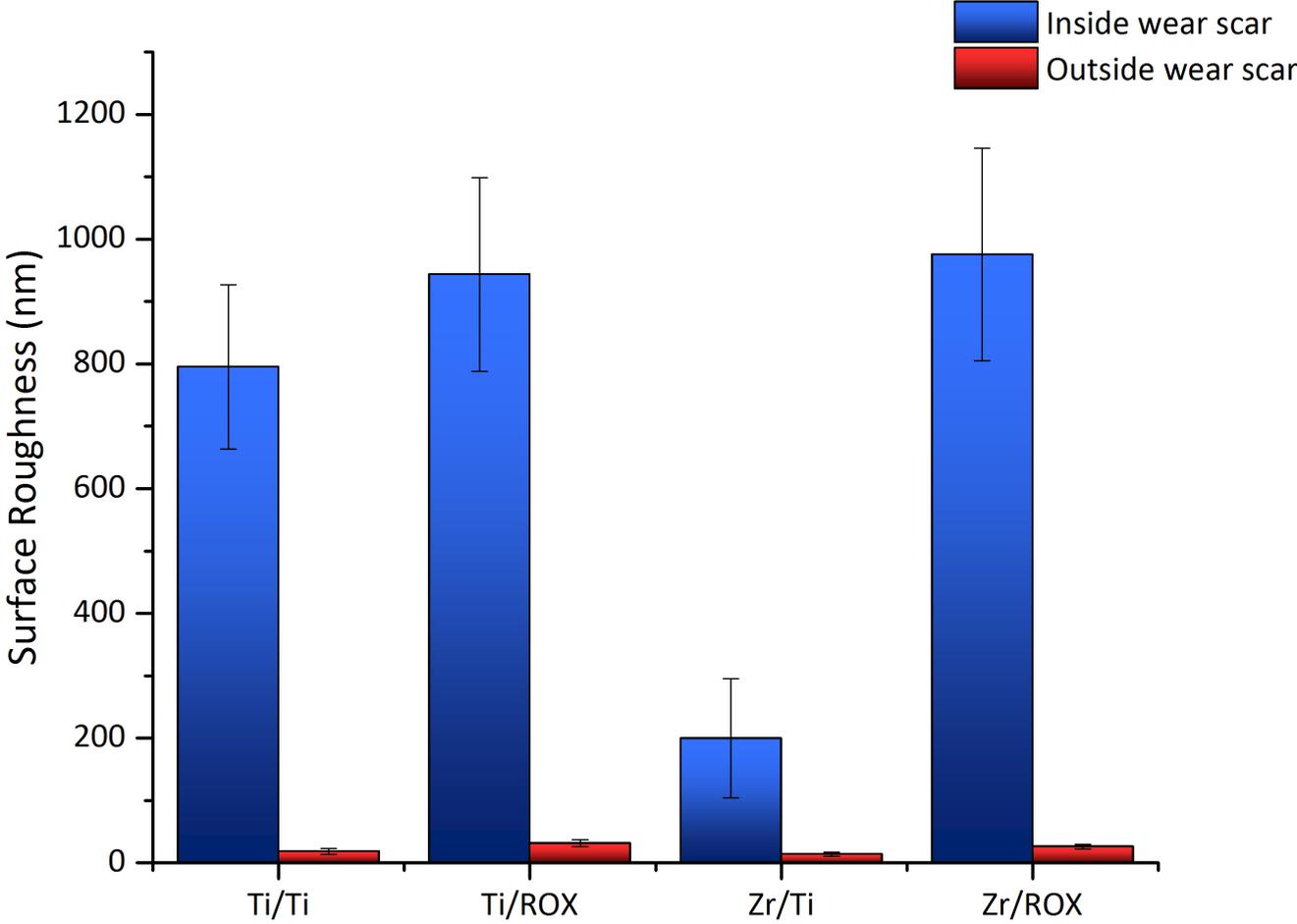


Figure 12: Scanning Electron Microscopy of Wear Scars

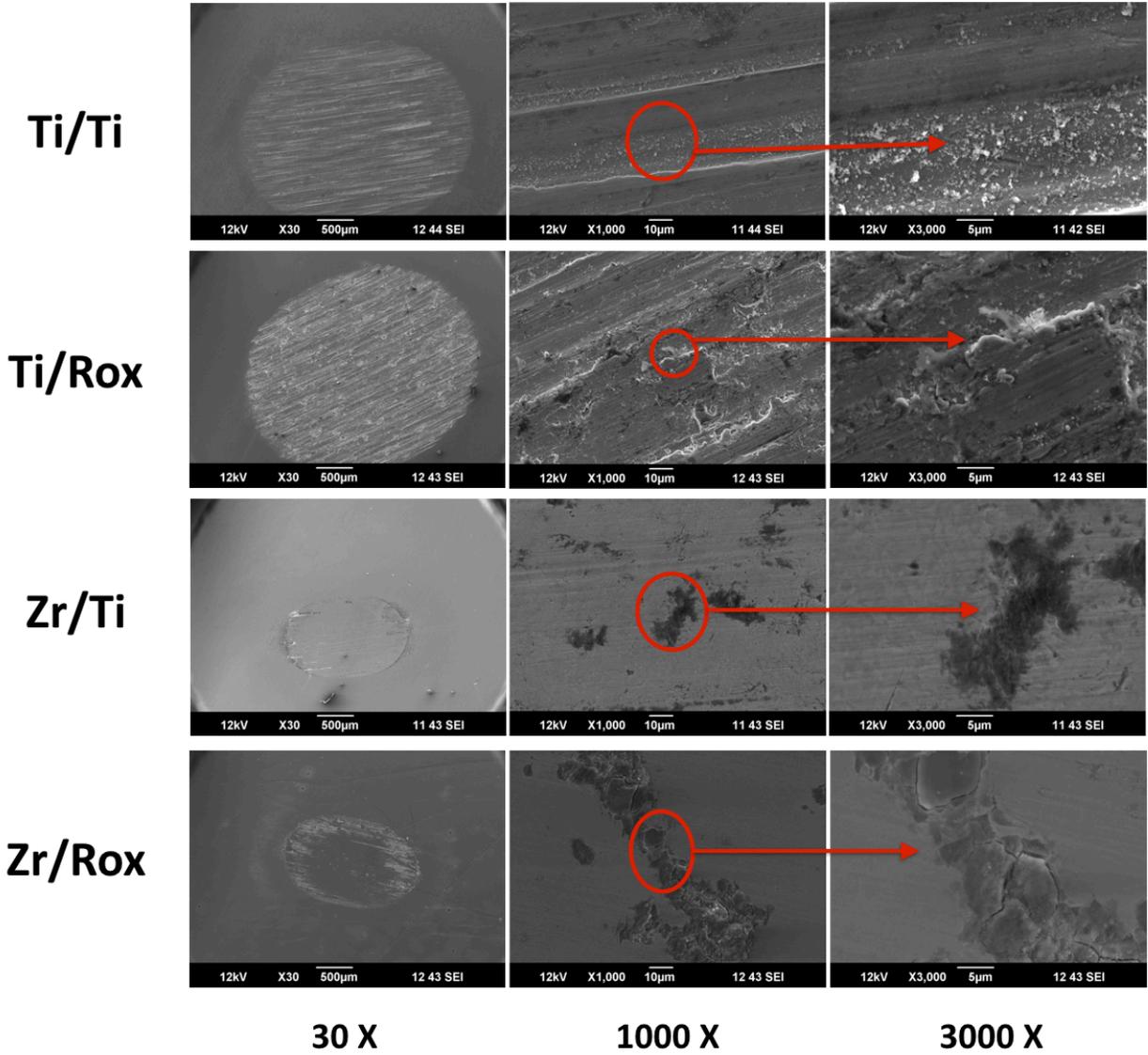


Figure 13: Scanning Electron Microscopy Spectroscopy

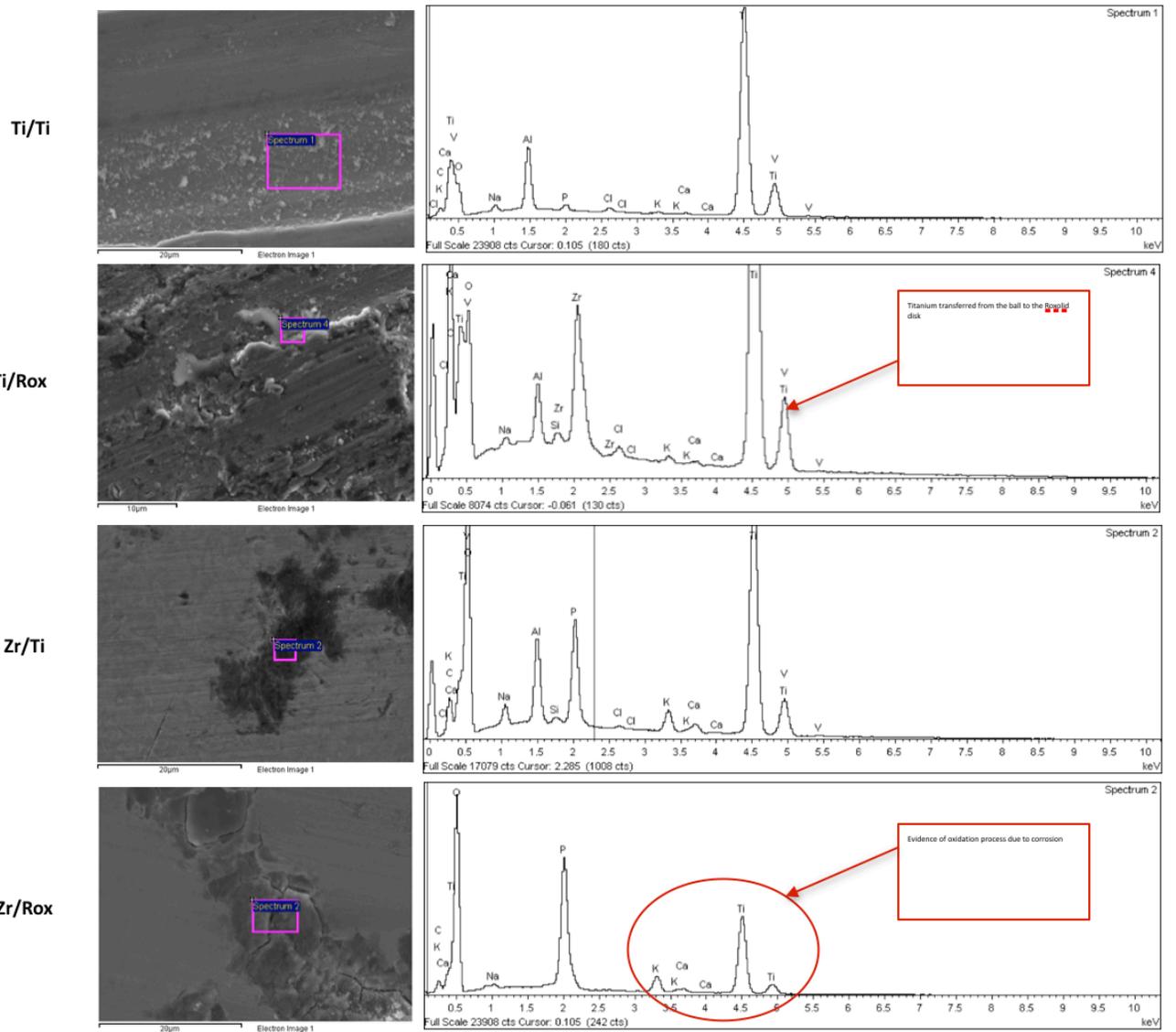
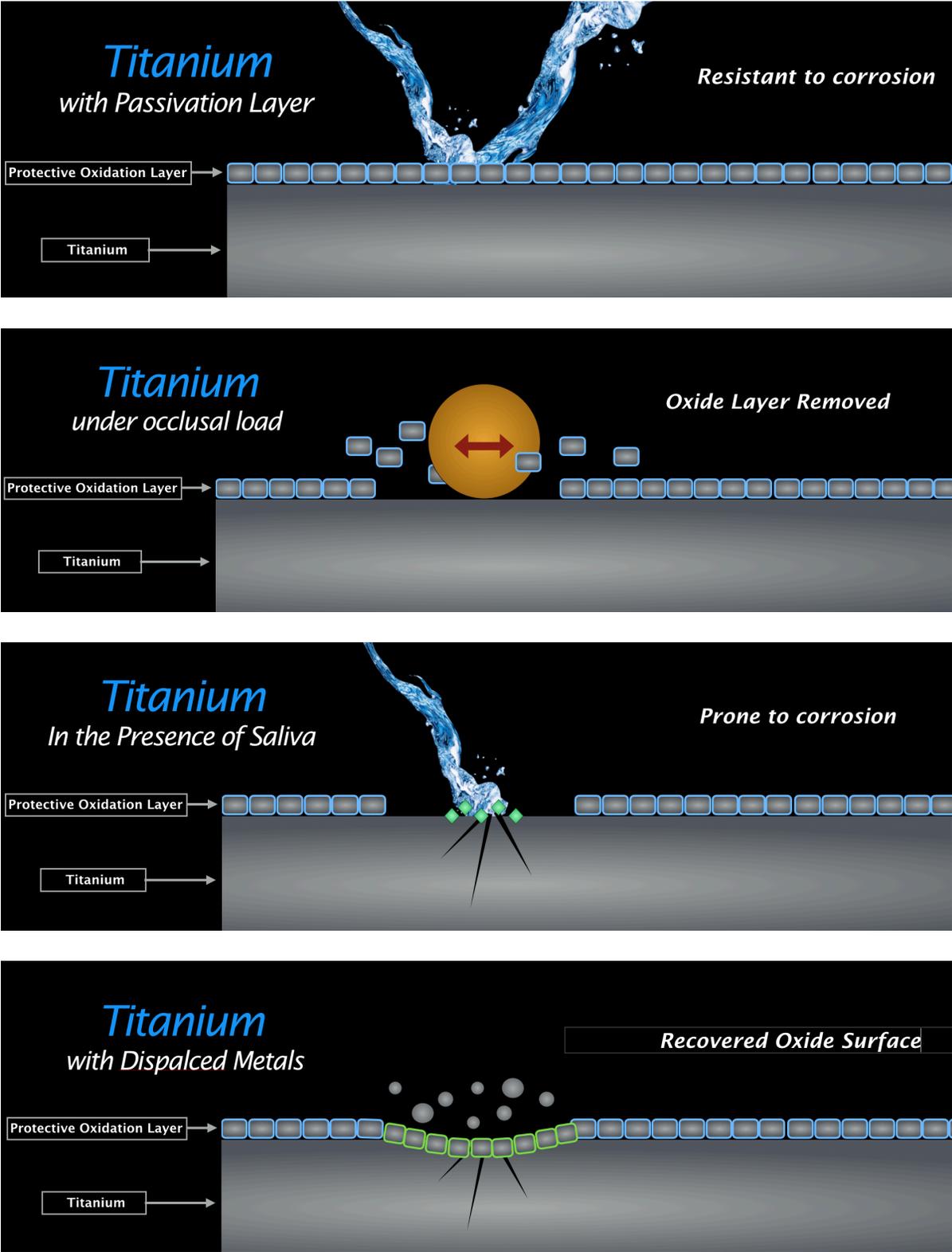


Figure 14: Titanium with intact oxide layer and under mechanical and electrochemical attack



TABLES

Table I: Titanium Grade V Composition

Element	Composition Weight %
Titanium (Ti)	~89.6%
Aluminum (Al)	~6.1%
Vanadium (V)	~4.0%
Iron (Fe)	0.16%
Oxygen (O)	0.106%
Carbon (C)	0.004%
Nitrogen (N)	0.008%
Hydrogen (H)	0.0022%

Table II: Roxolid Composition

Element	Composition Weight%
Titanium (Ti)	~85%
Zirconium (Zr)	~15%
Oxygen (O)	0.24%
Iron (Fe)	0.05%
Carbon (C)	0.05%
Nitrogen (N)	0.02%
Hydrogen (H)	0.01%

Table III: Fusayama and Meyer's Artificial Saliva Composition

Component	Concentration (g/L)
KCl	0.4
NaCl	0.4
CaCl. 2H ₂ O	0.906
NaH ₂ PO ₄ . 2H ₂ O	0.690
Na ₂ S. 9H ₂ O	0.005
Urea	1

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