

# Tribo-corrosion behaviour of composites and coatings: An overview of influencing factors, evaluation methods and inhibitors

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KEYWORDS	ABSTRACT
Tribocorrosion Corrosion Wear Passive film Inhibitors Coatings Surface treatments Sea water	Tribocorrosion studies have attracted increasing attention in recent decades due to their economic significance in terms of the durability and life of engineering materials. This paper reviews the recent literature available on the tribocorrosion properties of different materials, classifying key aspects that influence the tribocorrosion processes and behaviour. A comprehensive review of different studies conducted to examine the effect of various reinforcements, different inhibitors, and the effects of environmental conditions is presented. This work also reviews the literature on the impact of coatings and different surface treatments on tribocorrosion performance. A brief insight into the methodologies for evaluating tribocorrosion and the complexity of tribocorrosion systems is also provided. The literature revealed that the synergistic effect of wear and corrosion plays a pivotal role in the tribocorrosion performance of any material.

## **1.0 INTRODUCTION**

Almost all the metals chemically react with the environment and result in one or the other form of corrosion, thus degrading the metal. Most of the systems operate under conditions where there is a constant mechanical interaction along with the corrosive environment. Mechanical interactions such as loading, stress, and rubbing can also deteriorate the mechanical properties. Wear, which is caused due to the rubbing between two surfaces or from the hitting of solid

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particles or fluids can highly damage the material. The material loss caused by wear often gets influenced in the corrosive environment (Cao & Mischler, 2018; Landolt, 2007a; Toh et al., 2018; Villanueva et al., 2017). A corrosive environment can accelerate the wear rate and at the same time wear can enhance or complement the corrosion damage leading to shortening the service life of the materials.

A total of around 23% of the global energy is lost due to the involvement of frictional contacts. Moreover, around 1/5<sup>th</sup> of this energy is used to overcome friction and around 3% is used to remanufacture or repair the worn-out parts (Ahmad et al., 2020; Milosevic et al., 2020; Raina et al., 2021; Rouf et al., 2021). By involving good tribological practices, energy losses due to friction and wear can be decreased by around 40% and these savings could contribute to around 1.4% of the GDP of any developed nation (Holmberg & Erdemir, 2017). Similarly, corrosion losses amount to around 1-5% of the gross national product of any nation. Further, the indirect losses due to corrosion such as production, repair costs and breakdown costs add up to this cost (Javaherdashti, 2000). Figure 1 shows the surface damage caused in engineering materials caused due to corrosion.



Figure 1: Representative images of engineering equipment damage due to corrosion.

The loss of material can significantly increase because of the synergy between corrosion and wear (Landolt, 2006a; Schumacher, 1985, 1993; Watson et al., 1995). This synergistic effect between corrosion and wear is referred to as "Tribocorrosion". Tribocorrosion is the research field that studies the combined impact of wear and corrosion generated from the mechanical and chemical interactions that happen between elements of a tribological system subjected to biological conditions. Tribocorrosion is the study of wear, friction, and lubrication, all of which come under the category of tribology, as well as electrochemical processes (Z. Chen et al., 2015; Gharavi et al., 2015, 2016). Figure 2 shows the interest of the research community towards tribocorrosion in the past 5 years,

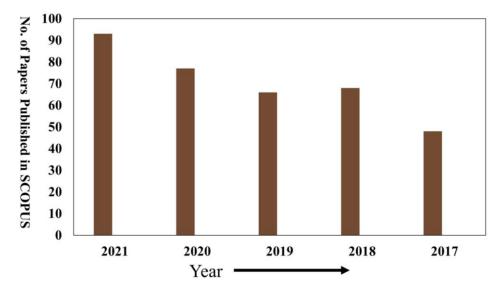


Figure 2: Year-wise number of papers published on tribocorrosion (Source: SCOPUS Keywords used "tribocorrosion").

It requires investigating the combined effects of wear and corrosion and the factors leading to change in any one of the phenomena as it can get affected with change in any one of the factors influencing either wear or corrosion (Mischler, 2013). Figure 3 shows a representative image of the tribo corrosion in a machine element caused by the joint effect of corrosion and sliding



Figure 3: Representative images showing the combined effect of corrosion and sliding in engineering parts.

Tribocorrosion has been proven to contribute considerably to material deterioration, potentially leading to material failure and expensive maintenance and replacement costs.

#### 1.1 Complexity and Relevance of Tribocorrosion Systems

Tribocorrosion systems are dependent on a variety of elements including mechanical, material, chemical, and electrochemical and are very complex in nature (Mischler & Munoz, 2018). Figure 4 represents a typical tribo-mechanical system.

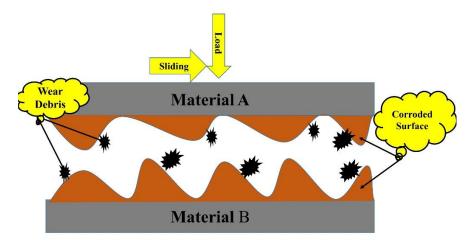


Figure 4: Tribocorrosion between two sliding surfaces.

The main reason for the complexity of the tribocorrosion systems is that the mechanical and chemical material deterioration processes are not independent of one other and influence each other, thus ensuing in the accelerated rate of material loss (Landolt et al., 2001). The separate study of wear or corrosion is not sufficient to determine the overall material loss (Mischler & Munoz, 2018). For example, Titanium Nitride (TiN) coatings that have excellent corrosion and wear properties but perform poorly in tribocorrosion applications (Barril et al., 2001). Thus, indicating that under the simultaneous wear and corrosion effect, they behave differently despite their good individual wear and corrosion properties.

Tribocorrosion has expanded and evolved as a discipline as a result of its practical importance and commercial value to science, technology and engineering. The problem of tribocorrosion is encountered in various industries such as nautical or marine (Barik et al., 2005; Johnson & Von Der Ohe, 2011; Wood, 2017), aeronautical and aerospace (Dalmau Borras, 2015), mining (Katiyar et al., 2021; Madsen, 1988), automotive (Baba et al., 2019; Maleque & Abdulmumin, 2014), nuclear (Benea et al., 2004; Chitty et al., 2011; Lemaire & Le Calvar, 2001), offshore (López-Ortega, Arana, et al., 2018; López-Ortega, Bayón, et al., 2018), biomedical (Büscher et al., 2005; Lanza et al., 2019; Mathew et al., 2009), and many others where it degrades the components and results in the loss of millions of dollars every year (Wood, 2007a). Degradation by tribocorrosion has consequences for human health in the field of bio-tribocorrosion in prosthesis and restorative dentistry (Dini et al., 2020; Wood, 2007a; Wood & Wharton, 2011). In certain applications, tribocorrosion can be useful as well. In microelectronics, tribocorrosion is employed for the fabrication of integrated circuits, chemical mechanical polishing of silicon wafers and interconnects for multilevel metallization, or coated MEMS components (Mischler & Munoz, 2018; Steigerwald et al., 1997; Wood & Wharton, 2011).

## 2.0 FACTORS AFFECTING TRIBOCORROSION

Tribocorrosion is a multidisciplinary study that is usually linked to synergy or antagonism caused by mechanical (wear) and environmental/chemical (corrosion) interactions. Both wear and corrosion can take many different forms, and both of them can occur either separately or simultaneously in the material. Wear mechanisms involve abrasive, adhesive, oxidative, fretting, fatigue mechanisms, hence tribocorrosion combines the interactions of all these processes with corrosion as well as erosion and solid particle wear, tribo-oxidation and solutions of biological type (Abolusoro & Akinlabi, 2020; Sharifian, 2018; Wood, 2010). Also, the interaction between the corrosion and wear processes can occur under many different conditions with different contact modes (two body or three body contacts such as entrapped wear debris) (Mathew et al., 2009). Tribocorrosion is thus a very wide field of study that encompasses nearly all wearcorrosion interactions. Hence, it requires a multi-disciplinary approach and integration of researchers and scientists from various fields ranging from tribology, material science, mechanical engineering, chemistry, biology and even medicine to understand the various parameters and factors influencing the tribocorrosion (Celis & Ponthiaux, 2006; Mathew et al., 2009; Menezes et al., 2013; Yamamoto et al., 2007). It is quite evident from the above discussion that tribocorrosion behaviour of any material will depend on a large number of parameters which influence wear, corrosion, etc. individually and eventually tribocorrosion as a whole (Mathew et al., 2009; Wood, 2007b). All the parameters are grouped into four major groups namely (i) Material Properties (ii) Electrochemical Properties (iii) Mechanical Contact or Tribological properties and (iv) working environment or solution (Figure 5). It is evident from Figure 5 that the various factors affecting the process of tribocorrosion are related to various elements of a tribological system such as the material, environmental conditions and the contact geometry and conditions. The factors being interrelated makes the process of tribocorrosion more complex as the synergistic effects of various factors makes it difficult to study the individual contribution of each factor. Furthermore, monitoring and sensing each of the factors is also a challenging task and lot of factors vary with time such as temperature, humidity, etc.

#### 2.1 Materials Properties

It is important to consider the properties of all materials involved in the tribological contact, including the reaction products created on the rubbing surface. The material properties such as hardness, elasticity, microstructure and surface roughness affect the wear performance as well as the frictional performance. Further, these properties have a significant role to play in determining the corrosion rate at the surface of a material. In case of wear, a large number of wear models have been reviewed and they depict the diversity of material properties influencing the wear equations. In the absence of corrosion, however, wear resistance is frequently associated with parameters like hardness, stiffness, ductility, and yield strength (Rabinowitz E, 1965). These parameters may also affect tribocorrosion behaviour, however in a different manner. The mechanical behaviour of materials is greatly influenced by the microstructure and various defects such as inclusions, segregations, and dislocation density present in the material, and thus all of these characteristics are also likely to influence the material's tribocorrosion behaviour (Landolt, 2006a).

The chemical and electrochemical properties of the materials involved in a specific corrosive environment also play a significant role in tribocorrosion. The topography and chemical composition of the material surfaces, including surface roughness, growth and characteristics of oxide layers, and the formation of reaction products and their adsorption, all have an effect on the tribocorrosion rate. Besides these, a material's thermodynamic properties and electrochemical kinematics determine the corrosion rate and hence affect the tribocorrosion rate. The mechanical and chemical properties of the thick oxide coatings developed on metals subjected to high temperatures, determine the tribocorrosion rate. (Ammar et al., 2018; Landolt, 2006a; Levy, 1995; Mathew et al., 2009; Nazir et al., 2018; Stott, 1998)

On the surface of many materials, a passive layer is formed through the reduction of Gibbs free energy that functions as a barrier and can reduce the corrosion rate. However, when subjected to tribological contact, this layer can be mechanically damaged, resulting in significant material loss, which can sometimes exceed the sum of material loss under pure wear conditions and pure corrosion (Ponthiaux et al., 2004; Wood, 2007a). Therefore, the passivation behaviour of metals which includes parameters like rate of passivation, the mechanical properties of the passive film and its stability towards oxidation, reduction and pitting plays a significant role and crucial role in tribocorrosion (Landolt, 2006a, 2006b).

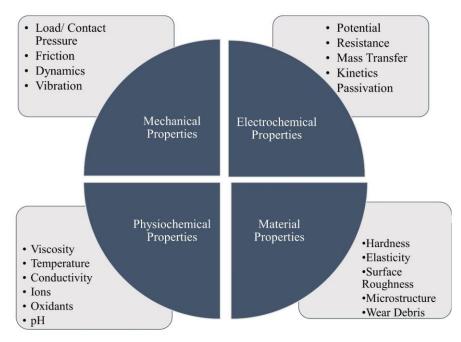


Figure 5: Factors affecting tribocorrosion.

# 2.2 Electrochemical Parameters

The electrochemical elements of tribocorrosion are extremely important since corrosion control and monitoring are dependent on electrochemistry. Electrochemists have been studying the kinetics of passivation initiated by scratching in order to better understand the role of electrochemical parameters in tribocorrosion. Similarly, tribologists have been looking into how surface oxidation during rubbing affects the rate of mechanical wear. Lately, the mutual

reliance on mechanical and electrochemical processes has been introduced. Applied potential, growth of passive coatings, active dissolution, ohmic resistance, and so on are the basic and most significant electrochemical parameters impacting tribocorrosion (Basak et al., 2006; Keddam & Wenger, 2011; Landolt et al., 2001; Mathew et al., 2009; Mischler et al., 2001; Zhu et al., 1994).

## 2.3 Mechanical Contact or Tribological Properties

Tribocorrosion rates for a given material in a certain environment are determined by applied forces and the type of contact—sliding, fretting, rolling, or impact (Landolt, 2006a; Mathew et al., 2009). The rate of tribocorrosion is influenced by a varied set of characteristics depending on the type of contact or mechanical action. For example, in sliding contact, stiffness of test equipment, as well as the residence time of wear particles, are critical parameters. Likewise, in fretting corrosion, small amplitude oscillations play a critical role in influencing tribocorrosion rate. (Barril et al., 2004; Landolt, 2006a). Sliding velocity, which influences the rate of depassivation, is another important and more prevalent characteristic that affects the tribocorrosion rate. Another key factor that impacts tribocorrosion is contact geometry. Vibrations, surface alignment, contact zone size, and type of motion are among the other considerations. Figure 6 depicts the interaction and relationship between wear and corrosion.

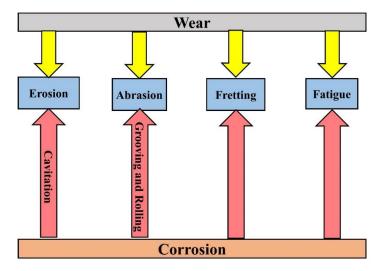


Figure 6: Relationships and Interaction between wear and corrosion.

# 2.4 Environment

Corrosion of a metallic surface occurs as a consequence of interaction with the environment. The corrosivity and mode of corrosion attack in any environment are related to environmental parameters such as chemical composition, pH, dissolved oxygen, flow conditions, temperature, salinity, and so on (Alamiery, 2021) Figure 7 shows the various corrosive environments for various engineering materials.

The corrosion rate mechanism in metals exposed to air is determined by relative humidity. Similarly, pH, oxygen content, and other variables influence corrosivity in aquatic systems. In high temperature applications, the physical nature of scales formed is a crucial characteristic. All of these environmental conditions, however, have a system-dependent effect on erosion-corrosion (Landolt, 2006a; Mathew et al., 2009; Wood, 2010). Environmental conditions can also modify the wear mechanism, hence affecting the wear rate and, consequently, the tribocorrosion rate (Wei, J. J.; Xue, Q. J.; Wang, 1993). Therefore, the environmental parameters have a very significant and major role in tribocorrosion behaviour.

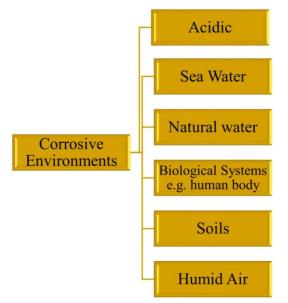


Figure 7: List of various corrosive environments.

## 3.0 MATERIALS SUSCEPTIBLE TO TRIBOCORROSION

In water and air, the vast number of metals and alloys used in industrial applications are thermodynamically unstable however, the system is going to be stable due to reaction with the environment. This situation was verified by a thin surface oxide film formed in many metals and alloys, called passive film when coming in contact with air or water (Landolt, 2007c). This passive film protects the material from any further degradation due to corrosion by separating the metal from its environment if the film stuck on substrate as well. The better corrosion resistance of many metals and alloys used in marine (Irfan Ul Haq et al., 2018; Wahid et al., 2019), biomedical, automotive, and other fields is due to the passivity (Cao & Mischler, 2018; Virtanen, 2011). Stainless steel, Aluminum, Titanium, Nickel Chromium-based super alloys, tantalum are examples of passive metals and hence resist well against the corrosion (Cao & Mischler, 2018; Landolt, 2006a; Wood, 2017). Metals that are used in engineering, industrial applications are mostly under the mechanical loading that can deteriorate the protective film. Further, rubbing and other such phenomena may increase the corrosion by degrading the passive film. It is due to these reasons that tribocorrosion is more critical and severe for metals in passive state (Landolt, 2006a, 2007a).

Passive films are typically just having 1-3 nm thickness (Landolt, 2007b; Olsson & Landolt, 2003). Even so, it still provides excellent corrosion resistance and protection against degradation, because they spontaneously self-heal and get restored due to metal oxidation when accidentally damaged. However, the self-healing process may not be enough when a metal surface is damaged

excessively and continuously if subjected to rigorous rubbing and impingement of particles (Landolt, 2007a, 2007c, 2007b; Menezes et al., 2013). Also, it requires a high oxidation rate of metal which will corrode the underlying metal prior to restoring passive protective film. It may not be reformed at all, thus promoting corrosion (Landolt, 2006a). In this case, as mentioned earlier also, the overall loss of material will be greater (Bradford, 2003). This again indicates that the tribocorrosion rate cannot be only calculated by summing the wear rate and corrosion rate measured separately. It is highly influenced by the effects of synergy or antagonism between mechanical and chemical processes (Menezes et al., 2013).

There are numerous examples where tribocorrosion causes failure of the components and thus the system. Gear failure is one of the main examples where tribocorrosion is involved (Menezes et al., 2013). In real life, tribocorrosion occurs under highly complex conditions and environments, like Bio-tribocorrosion of the human joints. At the interface, corrosive fluids along with tribology act simultaneously and thus playing an important role (Langton et al., 2011; Liao et al., 2011; Menezes et al., 2013; Yan et al., 2006). The reduction in the life duration of bio joints due to tribocorrosion is of major concern. Also, for implants and hip replacements, long-term durability is an issue (Essner et al., 2005; Hall et al., 2001; Yan et al., 2006). Another example of tribocorrosion is the degradation of tooth structure where processes like adhesion, abrasion, attrition, chemical degradation, and fatigue occur simultaneously and lead to failure (Lambrechts et al., 2006; Lim et al., 2002; Pallav, 1996).

## 4.0 METHODS TO EVALUATE TRIBOCORROSION

Since, tribocorrosion is a complex interaction of two different processes of wear and corrosion and is determined by a number of factors, including mechanical, chemical, material, and electrochemical factors. Thus, it requires a deeper understanding of all these factors to determine the tribocorrosion rate. As already mentioned, the separate study of wear and corrosion is not adequate to evaluate tribocorrosion as it can give misleading results. The example of TiN coatings clearly gives an idea of this problem. They have outstanding wear and corrosion properties but irrespective of this, their tribocorrosion properties are found to be unsatisfactory depending on the coating thickness. (Barril et al., 2001; Mischler & Munoz, 2018).

In a detailed review by (Mischler, 2008) the author has presented various examples wherein the tribocorrosion experimental methods have been done. The author has given examples of various materials evaluated for tribocorrosion in different environments. Based on the results obtained the author has suggested the need for various theoretical models to evaluate the tribocorrosion effects.

Tribocorrosion analysis thus requires a system that involves the combination of tribological contact with a conductive electrolyte. This is to achieve control on both the mechanical and chemical aspects of the system. This configuration is accomplished by adding a tribometer and an electrochemical measurement device together (J. Chen et al., 2018). This gives rise to the triboelectrochemical experiment, which is nothing but a tribological experiment under controlled electrochemical tests in an ionic conductor (Mischler, 2008). These triboelectrochemical techniques provide the prospect of applying the potentials thus simulating the corrosion conditions and simultaneously measure the real-time reaction kinetics of the rubbing material (Mischler & Munoz, 2018). Open circuit measurements, potentiostatic tests, are widely used triboelectrochemical tests to evaluate tribocorrosion. Further, methods such as potentiodynamic polarization testing and electrochemical impedance spectroscopy (EIS) are also used.

The first standard introducing triboelectrochemical test was published in 1995 under ASTM G119 (ASTM, 2009). ASTM G119 is the most widely used standard for evaluating tribocorrosion. This standard comprises procedures for preparation of samples, machine setup, tribocorrosion testing, and calculations after testing.

This standard is helpful in not only determining the material deterioration caused by tribocorrosion but also in determining the wear and corrosion synergism. This wear-corrosion interaction is assessed as the synergistic constituent as described by Watson et al (Watson et al., 1995) in Equation (1):

$$T = W + C + S \tag{1}$$

In this equation, T denotes the overall total degradation of the material, W denotes the degradation or loss of material because to wear only, C is loss of material owing to corrosion only and S is the material loss due to the synergistic effect of wear and corrosion

ASTM standard G119, provides the guide to determine and calculate the synergistic effect, S from the above equation. A wear test under the corrosion conditions is to be carried out to determine the total material loss, T. Individual corrosion tests are performed out to evaluate Corrosion rate, C from the potentiodynamic test, and finally Wear rate, W from the Cathodic protection test (ASTM, 2009; J. Chen et al., 2018). The values can then be used to determine the synergistic effect, S as shown in Equation (2);

$$S = T - W - C \tag{2}$$

# 5.0 TRIBOCORROSION OF VARIOUS MATERIALS

Tribocorrosion is a complex phenomenon that occurs in many materials when mechanical and corrosive conditions coexist. In this section, the diverse causes, factors, and mechanisms investigated by numerous authors on tribocorrosion study in various materials in different environments are provided and the literature available is reviewed.

## 5.1 Tribocorrosion in Different Composites

The addition of reinforcements has proven to be beneficial in enhancing material wear resistance (Haq & Anand, 2018; Singh et al., 2019; Sureshkumar & Uvaraja, 2018; Ul Haq & Anand, 2019; Yuan et al., 2016). However, the corrosion and wear accelerated corrosion behaviour generally requires a more comprehensive understanding of the underlying elemental mechanisms. In certain situations, the inclusion of reinforcement is unfavourable to the material's corrosion while improving the wear-corrosion behaviour of the material (Alaneme, 2011; Medelien, 2002; Ramachandra & Radhakrishna, 2007; Sureshkumar & Uvaraja, 2018; Vasudevan et al., 2019).

For instance, Vieira et al. (Vieira et al., 2011) examined the influence of silicon carbide particle inclusion on the corrosion and tribocorrosion performance of Al- SiCp FGMs. An alloy (Al-10Si-4.5Cu-2Mg) was used as the matrix of the functionally graded composites which were produced by centrifugal casting technique. The experiments were conducted in a 0.05M NaCl solution with an alumina counter ball sliding against the prepared specimen in a reciprocating motion tribometer. The findings of the tests revealed that the addition of SiC particles did not alter the corrosion behaviour of the material. It is obvious that much finer grain size achieved with

increasing the second phase in the metal matrix composites leading to growth of grain boundary and chemical activity Therefore, greater density of active sites at grain boundaries aid the metal dissolution thereby decreasing the stability of the corrosion product layer formed on the surface.

The tribocorrosion behaviour, on the other hand, is dependent on the silicon carbide content, as the metal matrix is substantially protected against both wear and wear-corrosion damage in samples containing more than 18% SiC particles. No such effect is seen below 18% SiC content and high wear and wear-accelerated corrosion are prevalent. Above 18%, the improvement is attributed to the SiC particles extruding from the surface which in turn protects the material. Similar works were done by Velhinho et al. (Velhinho et al., 2004) on tribocorrosion of Al-SiCp FGPs. The experiments were carried out against cast iron pins under both dry conditions and in the presence of water on an inverted configuration pin-on-disc tribometer. The findings observed that the composite's wear is substantially raised in the water. This was attributed to the SiC particle pull-out due to the water which precludes the load-carrying capacity of reinforcements. In a related study, Toptan et al. (Toptan et al., 2016) developed Ti-B<sub>4</sub>C composites for orthopaedic implants and investigated their corrosion and tribocorrosion properties. Hot pressing technique was employed to produce the 24% vol. B<sub>4</sub>C particle reinforced composites. Electrochemical impedance spectroscopy was employed to examine the corrosion activity. Tribocorrosion testing was carried out using a reciprocating tribometer under both open circuit potential as well as potentiodynamic polarisation. The findings of the tests revealed that the composite samples were less prone to corrosion. In addition, when sliding against an alumina ball, the composites demonstrated lower corrosion kinetics when compared to unreinforced samples. This behaviour was attributed to the load-carrying capability of B<sub>4</sub>C particles, which further resulted in lower composite wear. However, localized corrosion occurs at higher volume fractions of reinforcements due to agglomeration, which causes porosity in the material. In a similar study, Toptan et al. (Toptan et al., 2013) examined the corrosion and tribocorrosion performance of Al-Si-Cu-Mg alloys and B<sub>4</sub>C reinforced composites. The study was carried out for 15 vol.% and 19 vol.% B4C reinforced composites and also the bare alloy in 0.05 M NaCl solution. The authors reported that the inclusion of  $B_4C$  particles was not able to greatly alter the corrosion behaviour. However, tribocorrosion was reduced in composites, and the alloy was protected from wearcorrosion damage. This was mainly because the counter material slides on B<sub>4</sub>C particles. Moreover, the wear debris got accumulated and entrapped between reinforcing particles.

Farías et al. (Farías et al., 2020) evaluated the tribocorrosion behaviour of Ti-based composites reinforced with three different volume percentages of Titanium Carbide. The composites were prepared by the spark plasma sintering process. A potentiostat coupled together with a ball-on-plate reciprocating type micro tribometer performed the tribocorrosion testing in a simulated body fluid at a 2 N load. The findings of the tribocorrosion tests revealed that the inclusion of TiC particles minimized wear-corrosion risk. Wear resistance increases with a rising volume percentage of TiC, with the highest wear resistance found in samples with 30% vol TiC, nearly three times that of unreinforced composites. The main reason for the occurrence of such phenomenon is that electrolyte act as a lubricant; particularly at the interface of the exposed TiC and the ball.

Gordo et al. (Gordo et al., 2016) also investigated the corrosion and tribocorrosion performance of Ti reinforced with 1% wt.  $Al_2O_3$  particles. Colloidal techniques along with powder metallurgy were used to create the composites. Both corrosion and tribocorrosion experiments were performed in two separate NaCl solution concentrations (0.9% and 3.5%). The results of the experiments demonstrated that the inclusion of alumina had no effect on corrosion activity,

implying that Ti and Ti- $Al_2O_3$  have identical corrosion behaviour. However, in both NaCl solution concentrations (0.9% and 3.5%), composites exhibit a nearly 60% reduction in wear as compared to unreinforced Titanium.

The tribo corrosion behaviour of a biocompatible material, Ti-6Al-4V alloy has been investigated by researchers (Rasool et al., 2020). The micro abrasion corrosion of the developed material has been explored against a ceramic counter face in ringer solution in presence and absence of SiC particles. The findings have revealed that the loss of material as a result of micro abrasion is predominant than that of the material loss due to electrochemical process. It has also been observed that, without SiC particles, the total and micro-abrasion mass loss was found to be much greater (Figure 8), however decrease in mass due to corrosion was considerably lower both in the presence and absence of solid particles. Fig. 9 shows the wear mechanism of the substrate with abrasive particles, and no micro abrasion is observed in the SEM images. The wear scars depict the incorporated solid particles along with plastic deformation which indicates the development of a composite layer resulting in decreased abrasive wear. Without the abrasive particles, the diameter nearly doubles as shown in Figure 8 suggesting that two-body abrasive wear is more extreme than when solid particles are present (Figure 9).

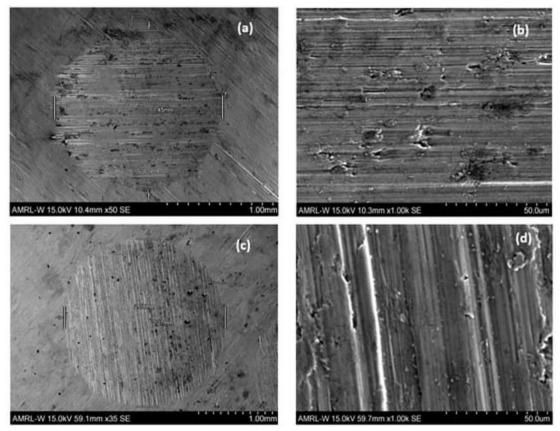


Figure 8: SEM images of Ti-6Al-4V alloy exhibiting the dominance of micro abrasion wear a) at 0.5N load b) at 0.5N at x1000 magnification c) at 4N load d) at 4N at x1000 magnification (Rasool et al., 2020).

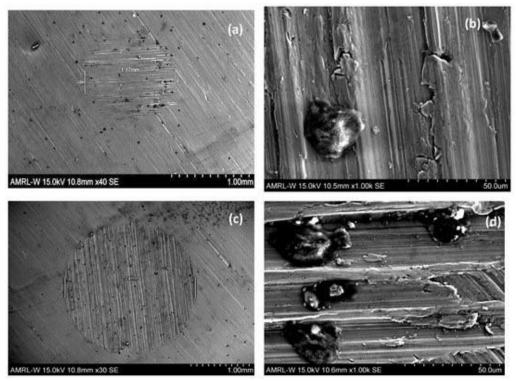


Figure 9: SEM images of Ti-6Al-4V alloy with abrasive particles a) at 0.5N load b) at 0.5N at  $\times$ 1000 magnification c) at 4N load d) at 4N at  $\times$ 1000 magnification (Rasool et al., 2020).

# 5.2 Tribocorrosion of Coatings

The requirement for prolonging the life of various components in many industries, as well as decreasing operational and other expenses in tribocorrosive environments, has prompted researchers to develop new approaches for enhancing the wear and corrosion performance of materials. One of the most prevalent ways for enhancing tribocorrosion performance is the use of coatings. Coatings help to protect the substrate material from the adverse effects of corrosion and tribology (Abdollah et al., 2012) by acting as a barrier for chemical as well as electrical processes taking place at the surface of the metals. Rather than developing strategies to change the bulk material, tailoring the surface by application of protective coatings is an age-old method to improve the corrosion behaviour of material e.g., application of paints in metals. However, tribocorrosion being a dual effect, developing coating with both anticorrosive properties as well as good tribological behaviour is a challenge. Further, the poor strength of the substrate and the coating interface is a limiting factor in widespread use of coatings in tribocorrosion applications.

The most pioneering work has been done by Wood (Wood, 2007a) who extensively reviewed the behaviour of coatings under the synergistic impact of wear and corrosion deposited using various techniques. Coating degradation processes have also been discussed. Furthermore, postcoating procedures for increasing coating performance have been reviewed in great detail.

Cai et al. (Cai et al., 2021) evaluated the tribocorrosion performance of TiSiN-Ag composite coatings with varied Si doping levels (5% and 8%). The composite coatings were prepared using

multi-arc ion plate technology and deposited on three different copper substrates (316L, TC4, and H65). The results of different tests conducted in simulated seawater demonstrated that 8 wt.% Si doped coatings outperform coatings with a 5 wt.% Si doping concentration under tribocorrosion conditions. Furthermore, coatings with an 8 wt.% Si doping level demonstrated improved mechanical characteristics, smaller grain size, and increased corrosion resistance. Furthermore, among all samples, the 8 wt. % Si doped TiSiN-Ag coating on TC4 substrate demonstrated the best tribocorrosion performance in artificial seawater.

In Ringer's solution, Naghibi et al. (Naghibi et al., 2014) performed a study to evaluate the tribocorrosion performance of Ti/TiN composite coatings on 316L stainless steel substrates. The physical vapor deposition method was used to deposit the 2  $\mu$ m thick coating. The results showed that the application of Ti/TiN coatings increased the material's corrosion resistance. After the sliding is stopped, both the stainless steel and Ti/TiN coated samples show repassivation, indicating that the passive layer has been repaired. Moreover, the total volume loss for coated samples was found to be lower in all conditions than that to uncoated stainless steel samples because of high hardness of coating i.e. ~2600 HV obtained using nanoindentation. The authors concluded that, as compared to mechanical wear and/or anodic dissolution, the synergistic effect of wear and corrosion has a significant impact in the deterioration of Ti/TiN coated samples.

Fu et al. (Fu et al., 2020) developed CrMoSiCN nano-composite coatings with a low carbon concentration on Ti-6Al-4V alloy to investigate their tribocorrosion performance. The coatings were developed with the help of an unbalanced magnetron sputtering process. The tribocorrosion findings indicated that the CrMoSiCN nano-composite coated sample outperformed the Ti-6Al-4V alloy in artificial seawater. The primary cause of Ti-6Al-4V failure was determined to be the synergistic action of wear and corrosion followed the high hardness of coating through solid solution strengthening mechanism. i.e. (Cr, Mo) N. However, in the case of CrMoSiCN coatings, the major reason for failure was altered to pure wear behaviour. The CrMoSiCN coating greatly reduces material loss due to tribocorrosion.

#### 6.0 TRIBOCORROSION INHIBITORS

Inhibitors are chemical compounds used to prevent material from corrosion. Table 1 provides the list of various corrosion inhibitors.

Table 1. Examples and Types of Corrosion minorors			
S.No	Type of corrosion inhibitor	Examples	
1	Cathodic Inhibitor (Inorganic)	Zinc Inhibitors	
2	Anodic Inhibitor (Inorganic)	Nitrates, Phosphates	
3	Film Forming (Organic)	Amines and Amine salts	

Table 1: Examples and Types of Corrosion inhibitors

Corrosion is either avoided or reduced as they have the potential to reduce the rate of corrosion (Dariva & Galio, 2014; Plieth, 2008; Sastri, 1998; Schweitzer, 2009). Inhibitors are directly added to the corrosive environment to inhibit corrosion. In some cases, inhibitors are mixed with phosphate compositions to make anti-corrosion coatings and paints (Pokhmurskii et al., 2012).

In simulated seawater, H. Zhao et al. (Zhao et al., 2018) examined the inhibition effect of sodium octanoate (C8Na) on the tribocorrosion of aluminium alloy 5052. The tribocorrosion tests were performed out at various concentrations of C8Na (0.0025 M, 0.005 M, 0.01 M, and 0.02 M)

and at different potentials to study the influence of applied potential along with C8Na concentration on the inhibition effect on total tribocorrosion. The authors stated that increasing the concentration of C8Na up to 0.01 M improves the corrosion resistance of aluminium. The wear volume again increased after 0.01 M C8Na concentration due to aggregated micelles in solution. The results explicitly demonstrate that C8Na serves as an effective inhibitor of tribocorrosion of aluminium in NaCl solution. Furthermore, the authors indicated that corrosive wear is affected by the applied potential.

Vieira et al. (Vieira et al., 2006) analyzed titanium tribocorrosion in artificial saliva to comprehend the degradation mechanism of the tribocorrosion system used in dental implants. The authors investigated the effect of pH variance on fretting corrosion by introducing citric acid to artificial saliva. Further, the inhibition effect of three different inhibitors was also investigated. The electrochemical noise technique findings during fretting experiments indicated a slight improvement in tribocorrosion with the incorporation of citric acid to artificial saliva. With the inclusion of an anodic inhibitor (sodium nitrate), similar findings were obtained. Lower wear volume was primarily due to lower corrosion rate in both of these situations, as only a negligible variation in wear rate per dissipated energy was observed. The inclusion of a cathodic inhibitor or an organic inhibitor, on the other hand, is detrimental to titanium tribocorrosion. Higher wear volume loss and significantly higher corrosion rates were observed in these situations.

In a 0.5 M sulphuric acid medium, Ouknin et al. (Ouknin et al., 2019) looked into the impact of a Populus nigra var italica propolis (PP) essential oil on the tribocorrosion efficiency of 304L stainless steel. The tribocorrosion performance was studied using weight loss measurements with and without 600 ppm of essential oil to determine the impact of Corsican Poplar Leaf buds essential oil. The findings showed that after the addition of essential oil, low values of frictional coefficient and energy dissipated are obtained. Furthermore, SEM-EDX findings show that the inclusion of essential oil results in a much-improved surface than the surface that is exposed to acidic medium without the addition of essential oil. The results clearly show that Corsican Poplar Leaf Buds essential oil is an effective tribocorrosion inhibitor in acid medium.

Ouknin et al. (OUKNIN et al., 2020) in another study examined the influence of Thymus willdenowii Boiss & Reut essential oil (TW) on AISI 304L Stainless Steel tribocorrosion in a 0.5 M  $H_2SO_4$  solution. After adding 3g/L of Thymus willdenowii oil, the results showed that low friction coefficients and energy dissipation values were obtained. Furthermore, a potentiodynamic study confirms that phenolic components primarily function as cathodic inhibitors, as cathodic reactions are significantly more affected than anodic reactions. In addition, the worn volume in the sliding surface is decreased from 2752 um to 1403 um. Also, surface analysis confirms the significant improvement in surface morphology. The inhibition efficiency value of 83.20 % demonstrated unequivocally that TW essential oil is an outstanding tribocorrosion inhibitor in acid medium of  $H_2SO_4$ . Furthermore, the authors argue that TW oil is suitable for use in the food industry as a natural product.

Panagopoulos et al. (Panagopoulos et al., 2009) assessed the tribocorrosion performance of aluminium alloy 6082 with 0.01M NaCl and varying sodium molybdate dihydrate (Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O) concentrations (0, 0.01, 0.1, and 0.5 M). The findings showed that as the concentration of Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O increased, it acted as a corrosion inhibitor. The wear tests revealed a substantial decrease in wear volume due to the inhibiting effect of Na<sub>2</sub>MoO<sub>4</sub>.2H<sub>2</sub>O. The inhibition was caused by MoO4-2 ion adsorption from the corrosion medium onto the oxidized surface layer of the samples. Furthermore, plastic deformation and abrasive wear were

discovered to be the most prominent wear mechanisms, which occurred in tandem with pitting corrosion.

## 7.0 TRIBOCORROSION UNDER DIFFERENT ENVIRONMENTS

The tribocorrosion of a material depends greatly on the environment. Sodium chloride solutions have mostly been used by researchers to investigate tribocorrosion mechanisms and behaviour. Researchers have mostly investigated the tribocorrosion behaviour and mechanism in sodium chloride solutions to simulate environmental conditions. However, tribocorrosion is prevalent in many other environments where it is more critical such as tribocorrosion in tooth structure, human joints, dental implants, or other implants in body fluids. Tribocorrosion can occur in many other industries such as biomedical, food, marine, offshore, and so on. Other environments have been reviewed to get a better insight of the impact of environments on the tribocorrosion behaviour of different materials.

For example, Borrás et al. (Dalmau Borrás et al., 2019) researched the tribocorrosion of titanium/zirconia dental implants in artificial saliva for biomedical applications. Metal and ceramic degradation mechanisms were investigated by means of a ball-on disc tribometer coupled with potentiostat. Tribocorrosion experiments conducted at various applied potentials revealed that at high passive potential, increased wear volume and tribocorrosion are observed, whereas, at OCP, the lowest wear volume was observed. Further, at cathodic applied potential, a very thin or no passive layer is formed, and no transfer of titanium to zirconia counterpart is observed. In a similar study, Licausi et al. (Licausi et al., 2013) explored the mechanism and behaviour of tribocorrosion in Ti6Al4V biomedical alloy for use in dental implants. The cast and sintered alloys were examined in solutions of artificial human saliva with differing pHs (3,6, and 9) as well as in acidic saliva with 1000 ppm fluorides. As per the results of different electrochemical processes, a spontaneous passive layer develops on the Ti6Al4V alloy independently of the pH of the solution, and material damage is mostly caused by mechanical wear in the artificial saliva. However, as fluorides are added, the alloy actively corrodes, and the degradation mechanism is changed to active dissolution of titanium alloy, with corrosion being the predominant cause of damage. The material loss is also one order greater in acidic saliva with fluorides than in the other three solutions. Further, the authors have stated that the effect of fabrication processes on corrosion and tribocorrosion mechanisms, as well as the degree of material loss, is not substantial.

Pina et al. (Pina et al., 2015) examined the tribocorrosion of  $\beta$  titanium biomedical alloys -Ti30NbxSn, with varying Sn content (0, 2, and 4 wt. %). Powder metallurgy was used to sinter the titanium alloy, and the experiment was carried out in phosphate buffer saline solution. The results of various mechanical and electrochemical testing showed that all alloys (0, 2, and 4% Sn) deteriorated by a similar tribocorrosion process of passive dissolution and plastic deformation, with the rate of passive dissolution increasing with the amount of Sn in the alloy. Wear accelerated corrosion is 1.5 times greater in the alloy with 4% Sn than in the alloys with 2% and 0% Sn, implying that corrosion resistance decreases above 2% Sn content. Furthermore, the authors claimed that the alloy with 2 wt. % Sn (Ti30Nb2Sn) was the most suited under tribocorrosion.

Espallargas et al. (Espallargas & Mischler, 2010) performed an experimental study to evaluate the tribocorrosion performance of an overlay welded Ni-Cr 625 alloy. The study was carried out by sliding the alloy against alumina under potentiostatic conditions in 0.5 M sulphuric acid and nitric acid solution. Tribocorrosion experiments were conducted at -1.5 V (cathodic potential), ±

0.3 V (passive potentials). The results showed that the tribocorrosion damage in sulphuric acid is less at cathodic potential (-1.5 V) than that at passive potentials (±0.3 V). Also, there is no discernible change in tribocorrosion between - 0.3 V and + 0.3 V. In nitric acid, however, no noticeable impact of potential is detected and there is no variation in wear between cathodic and passive potentials. Moreover, the wear in HNO<sub>3</sub> solution is considerably greater than in  $H_2SO_4$  solution. This is due to the oxidizing effect of nitrate ions, which causes the development of an oxide layer. Because of the increased reactivity, this encourages wear under sliding conditions. Furthermore, the authors concluded that the use of cathodic potential would not inhibit oxidation of the metal in the presence of oxidizing ions.

#### 8.0 EFFECT OF SURFACE TREATMENTS ON TRIBOCORROSION

Similar to coatings, other methods such as surface treatment have also been researched to enhance the performance of various alloys under wear-corrosion environments (Najar et al., 2019). The various surface treatments employed to improve the tribocorrosion behaviour of materials include the surface texturing, surface hardening and improving the surface finish (Mahayuddin et al., 2020). There is a dearth of literature on the influence of surface treatment on tribocorrosion behaviour, and further study is needed to completely comprehend the impact of surface treatment on tribocorrosion. Few works on the influence of surface treatment on the tribocorrosion have been reviewed and presented below.

In a study by Sun et al. (Sun & Bailey, 2014) the impact of surface mechanical attrition treatment on AISI 304 stainless steel on tribocorrosion behaviour was investigated. Spherical shot peening is used for the surface mechanical attrition treatment. The experiment is carried out in 0.9 percent NaCl solutions. The results showed that surface treated samples reduced material loss by 2 to 4 times when compared to untreated samples under all conditions. Furthermore, surface mechanical attrition treated (SMAT) samples had a lower coefficient of friction than untreated samples. The results revealed that surface treatment reduced both wear and corrosion. The enhancement in tribocorrosion is linked to the surface hardening effect caused by surface mechanical attrition treatment.

Kossam et al. (Kossman et al., 2020) analysed the tribocorrosion performance of 316L stainless steel in NaCl solution using three different industrial surface treatments. Passivation (SSO), electro polishing passivation (SSEP), and micro-undulation (SSM mechano-chemical + electro polishing + passivation) are the three surface treatments. The results of the testing demonstrated that electro polishing deteriorates the material and is detrimental to the tribocorrosion of 316L stainless steel. The mechano-chemical technique (SSM) has proven effective, improving the tribocorrosion characteristics of 316L stainless steel. Similarly, some more studies have been performed to study the effect of surface treatments on the tribocorrosion behaviour of various materials (Alves et al., 2013; Saada et al., 2018; Siddaiah, 2020; Totolin et al., 2016). These studies suggest that surface treatments help in improving the tribocorrosion behaviour of these materials by affecting the influencing factors such as hardness, microstructure and surface roughness.

#### **CONCLUSIONS AND FUTURE RECOMMENDATIONS**

Tribocorrosion is a complex phenomenon encompassing a wide range of aspects such as mechanical, physical and electrochemical. The current study highlights the various tribocorrosion

environments, strategies for mitigating the tribocorrosion with a focus on tribocorrosion inhibitors, coatings and surface treatments. The present work shall act as a precursor for future research in the related areas of tribocorrosion and shall help researchers working in the field. The synergism of tribology and corrosion involved in tribocorrosion also makes it dependent upon various parameters. Although there are various standard methodologies provided to measure corrosion, however with the advent of new material options such as composites the evaluation of corrosion becomes a bit difficult. Corrosion in composites is improved because of reinforcement inclusion and the better tribocorrosion properties of the reinforcements. The formation of chemical layer which acts as protective film normally is broken by the sliding action of the counterface materials. The development of better coatings with improved tribocorrosion properties helps to protect the substrate material from wearing out. Different surface treatments are also employed to improve the tribocorrosion behaviour of different materials.

Due to the economic losses suffered by global economies due to the combined adverse effects of corrosion and tribology, it becomes imperative to study the joint effects of both on various materials. Future studies can be employed to study the different mechanisms of tribocorrosion in detail with special focus on biomedical and marine applications. Studies pertaining to different types of surface treatment and coatings need to be undertaken to study the effect of various parameters specific to these methods on the tribocorrosion behaviour. Owing to the complexity of the tribocorrosion phenomenon the combined effect of various influencing parameters needs to be studied in detail. Studies can be undertaken to elucidate the effect of various reinforcements, coatings, inhibitors, surface treatments on the tribocorrosion behaviour of advanced materials. Further, mathematical models be developed to predict the tribocorrosion behaviour of these systems. The advancements in nanomaterials can be exploited in use for tribocorrosion improvement by involving nanomaterials as reinforcements, additives in lubricants and coatings. Further, the advanced materials developed by additive manufacturing can also be explored for tribocorrosion applications and effect of various additive manufacturing process parameters can be studied on the tribocorrosion. Complex biological systems particularly in orthopedic and dental applications involve tribocorrosion therefore development of advanced materials and strategies for biotribological applications which help to mitigate the adverse effects of tribocorrosion can be undertaken.

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