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Surface engineering of Ti6Al4V surfaces for enhanced tribocorrosion performance in artificial seawater

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A B S T R A C T

Titanium and its alloys are materials with excellent corrosion resistant properties, but under sliding contact exhibit poor wear and friction performance. Therefore, the aim of this study was to find suitable surface treatments for titanium alloy substrates to be used under saline environmental conditions. Various surface engineering techniques have been applied to Ti6Al4V substrates, and the static corrosion performance of these surface treatments in presence of artificial seawater was evaluated using potentiodynamic investigations. Furthermore, the combined sliding-corrosion performance was investigated using a micro-tribometer coupled to an electrochemical cell. Using this set-up, the selected samples were tested in order to check the synergistic effect of wear and corrosion, also known as tribocorrosion. The results clearly revealed a poor tribological performance of the untreated Ti6Al4V substrate, thus highlighting the need for surface treatments. Furthermore, it was highlighted that some of the compared surface engineering treatments applied to Ti6Al4V although exhibited improved corrosion resistance under static conditions, they showed a radically different behaviour under tribocorrosion. The underlying reasons leading to a different tribocorrosion performance are discussed and the main mechanisms associated with surface degradation under combined wear and corrosion are revealed.

1. Introduction

Tribocorrosion is a surface degradation process resulting from simultaneous tribological and electrochemical actions in a corrosive environment [1–4]. The synergism between wear and corrosion may lead to an accelerated degradation of passive metals. For instance, the mechanical removal of a passivation layer usually leads to wear-accelerated corrosion due to chemical reactivity of the nascent metal surface exposed to the corrosive environment. Therefore, it is important to identify the contribution of corrosion and wear to material removal during a tribocorrosion process in order to minimize material degradation [1,4]. Over the past two decades, significant work has been done regarding to tribocorrosion as previously reported in several reviews [1,2]. Various triboelectrochemical techniques have been applied on a variety of sliding contact conditions such as unidirectional or reciprocating motion, fretting or spinning contacts. In an attempt to identify the fundamental tribocorrosion mechanisms, the most investigated materials were model alloys [3,5,6], followed by biomedical alloys [7,8,9], sealing materials [10,11], materials for nuclear reactors [12] and materials used in chemical mechanical polishing process [13,14].

It is widely known that the synergistic action of wear and corrosion can also lead to premature failure of engineering components in seawater environments. Nevertheless, some crucial components used in marine equipment, such as pumps, valves, gears and propellers have to be directly lubricated by seawater [15,16]. Their safety, reliability and service life greatly depend on their combined tribological and corrosive performance in harsh marine environments [17]. Common corrosion resistant materials used in seawater environments, such as titanium alloys, offer a very poor tribological performance and failed to meet the mechanical requirements of highly-demanding applications [18]. One of the most cost-effective approaches for improving the tribological properties of titanium alloys is to include advanced surface engineering technologies in the component design. By doing so, surface engineered titanium components could be able to withstand seawater environment while simultaneously offering an improved wear protection.

The work regarding tribocorrosion of engineered surfaces is rather limited and only a few studies have been reported in literature [17–26]. Moreover, understanding the tribocorrosion of surface engineered surfaces is often more difficult in comparison to bulk metals due to the porosity and oxide pockets that are usually formed during the

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coating process [2]. In this case subsurface corrosion can occur at the interface with the substrate or interlayers.

In recent years, diamond-like carbon (DLC) films have been the subject of extensive investigations due to their potential of attaining a combination of highly desirable properties such as high hardness, low friction and wear, electrical insulation and chemical inertness [21,22]. Azzi et al. investigated the tribocorrosion behavior of DLC-coated 316 L stainless steel exposed to the Ringer's solution in the context of biomedical applications [21]. Two different bond layers were studied, namely amorphous hydrogenated silicon nitride (a-SiNx:H) and plasma nitrided layers. It was found that the nitrided bond layer showed a significant improvement in wear resistance of the DLC coatings in dry conditions. However, under sliding wear in simulated body fluid conditions, this bond layer proved to be insufficient, mainly due to the infiltration of the liquid through the pores and the weakening of the interface due to corrosion processes. On the other hand, the use of a-SiNx:H as an interface layer significantly improved the wear resistance of DLC films in Ringer's solution. Costa et al. studied the friction and wear rate of DLC films under seawater and saline solutions using two different tribological systems, a stainless steel vessel and a PTFE one [23]. Although the 20% hydrogenated DLC film confirmed to be effective in terms of corrosion and wear resistance under saline solutions for both vessels, better results were achieved using the stainless steel vessel.

Another effective method to reduce wear and corrosion of metallic components is using ceramic-metallic (cermet) or hard oxide coatings. High Velocity Oxygen Fuel (HVOF) coatings with compositions of 86WC-10Co-4Cr or corrosion resistant alloys such as nickel aluminum bronze have been considered for wear-corrosion applications [27–29]. In general, a particular concern for these coatings is their level of porosity (>2%) that can accelerate crack propagation and coating removal under erosive conditions. Moreover, the permeation of the electrolyte through the interconnected pores into the coating/substrate interface could lead to corrosion-driven coating-substrate disbondment [2].

Surface engineering of metals by plasma nitriding techniques can be used to improve tribocorrosion [18,25]. Galliano et al. investigated the tribocorrosion performance of a plasma nitrided Ti6Al4V alloy coating in 0.9 wt% NaCl solutions under reciprocating alumina ball-on-flat sliding wear [18]. It was found that samples nitrided at higher temperatures (1173 K) showed better wear resistance without crack formation compared to samples nitrided at lower temperatures (973 K) which microcracked causing failure. The improvement in anti-wear properties was attributed to a surface hardened layer of TiN-Ti_2N.

It is noteworthy that, in general, the various tribocorrosion studies previously reported in literature mostly focused on the assessment of a single surface engineering technology. Furthermore, the investigated surface technology was often evaluated in terms of the role of process parameters or was simply compared with the untreated substrate material. A systematic approach that investigates the wear and corrosion protection of different surface engineering techniques in artificial seawater seems to be lacking in the existing literature. Such a study is essential for providing design rules for components able to withstand operations under offshore environments. For this reason, the aim of the present work is to investigate and compare the tribocorrosion behavior of DLC coatings, HVOF coatings and Ion implantation treatments applied to titanium substrates exposed to artificial seawater in the context of offshore applications.

2. Experimental

2.1. Surface technologies

The substrate investigated was a titanium alloy (Ti6Al4V), commercially available from Alba Industrial AS (Bekkestua, Norway). Three different surface engineering treatments were applied to the substrate and are summarized in Table 1.

Table 1
Sample pre-treatments and their corresponding hardness and roughness.

Sample	Treatment	Hardness (GPa)	Roughness, Ra (μm)
Ti6Al4V	None	3.3	0.3
W-DLC	CrN + a-C:H:W Topcoat	15.9	0.3
HVOF	Cr_3C_2 in Ni/Cr matrix	14.0	0.3
Ion implantation	Low pressure nitriding	16.0	0.4

The first surface treatment (referred as W-DLC) comprised of a multifunctional coating applied in a single-pass Physical-Vapor Deposition process at temperatures between 180 and 350 °C and was commercially available from Oerlikon Balzers Coating Austria GmbH (Stainz, Austria). The multifunctional coating consisted of a tribologically effective tungsten-doped hydrogenated DLC top layer and a CrN intermediate layer for corrosion resistance.

The second surface treatment (referred as HVOF), commercially available from TeroLab Surface GmbH (Vienna, Austria) consisted of a hard metallic structure made of chromium carbides with a content of 75% weight. The carbides were embedded in a metallic matrix made of nickel and chromium. The coating was deposited using a HVOF thermal spray process to obtain a dense, homogenous and ultra-hard coating.

The third surface treatment (referred as Ion implantation), commercially available from Bodycote SAS (Pusignan, France) was based on nitrogen diffusion into titanium performed under vacuum at low pressure, without the use of a plasma. The diffusion of nitrogen created a compound layer of TiN + Ti_2N and a diffusion layer of Ti (N) underneath. The chemical composition of the samples is given in Table 2.

2.2. Tribocorrosion investigations

Tribocorrosion experiments were performed at room temperature using a using a linear reciprocating ball-on-flat tribometer TETRA BASALT®-N from Falex Tribology N.V. (Rotselaar, Belgium) described in a previous publication [30]. The detailed experimental parameters are displayed in Table 3. The average contact pressures for all the tested materials have been estimated from the Hertzian contact stress theory. The calculated average contact pressures for Ti6Al4V, W-DLC, HVOF and Ion implantation are 200 MPa, 230 MPa, 160 MPa and 240 MPa, respectively.

During a typical experiment an alumina ball (5 mm diameter) slides against the sample specimen fully immersed in artificial seawater (2.5% NaCl, pH = 7.6) made according to ASTM Standard D1141-13. The testing sample serves as the working electrode (WE) and its potential is monitored using a potentiostat VERSASTAT 3F from AMETEK GmbH (Meerbusch, Germany). The reference electrode (REF) was an Ag/AgCl in 3 M saturated NaCl solution and the counter electrode was a platinum plate (Fig. 1).

The tribocorrosion method used consisted of four sequences: cathodic cleaning of the samples at −1.2 V (vs. Ag/AgCl) for 60 s for dissolution of air-formed oxides [1]; stabilization of the system under Open Circuit Potential (OCP) for 8000 s (in absence of rubbing) to achieve a stable passive surface; rubbing under OCP for 6500 s, and finally, restabilization of the system under OCP (after rubbing was stopped) for

Table 2
Chemical composition (at%) of the samples.

Sample	Chemical composition (atomic %)								
	C	O	Ti	Cr	Ni	W	Al	Si	N
Ti6Al4V	–	–	91.0	–	–	–	8.2	–	–
W-DLC	64.6	15.8	1.2	4.3	2.6	11.5	–	–	–
HVOF	36.0	11.2	–	43.6	9.1	0.1	–	–	–
Ion implantation	–	–	41.5	–	–	–	1.6	1.0	55.9