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Tribocorrosion behaviour of Ti6Al4V in artificial seawater at low contact pressures

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A B S T R A C T

The tribo-electrochemical performance of Ti6Al4V in artificial seawater is investigated under reciprocating sliding conditions at three contact loads (10 mN, 100 mN, and 1 N) and three electrochemical conditions (−0.5 V, OCP and +0.5 V). The results reveal that the achieved contact pressures are not able to fully depassivate the surface. For the lowest load, no rupture on the passive film could be detected while with an increase in the load, depassivation-repassivation takes place during sliding contact. For 100 mN, an unusual higher coefficient of friction was measured for all electrochemical testing conditions. This behaviour is observed to correlate with a higher synergy between corrosion and wear and seems to be linked with the initial surface roughness of the titanium alloy.

1. Introduction

Titanium and its alloys are the one of the most extensively used materials for applications exposed to corrosive environments like offshore, bio implants, etc. [1–4]. Their resistance to static corrosion is superb and it is mainly provided by the formation of a surface protective oxide film consisting of TiO_2 with maximum film thickness of up to 10 nm [5,6]. However, in most of the above mentioned applications where corrosion is combined with mechanical wear, the surface protective TiO_2 passivation films are exposed to deterioration and rupture and hence, the nascent titanium surface is exposed to the corrosive environment, thus reducing the overall lifetime of components.

The titanium alloy Ti6Al4V exhibits superior physical and mechanical properties when compared to pure titanium thanks to its two-phase structure. A hexagonal α-Ti with aluminium in solid solution combined with β-Ti cubic lattice stabilized with vanadium results in a lower density and higher mechanical strength [7].

Although titanium alloys possess certain advantages such as corrosion resistance under static conditions, light weight, etc., over other types of engineering materials, due to their poor tribological properties (low wear resistance, adhesion), they generally miss to fulfil the necessary requirements in some tribological applications [3,4]. In order to overpass this problem, in offshore and marine applications, parts machined from titanium alloys (Ti6Al4V) are the subject of various surface engineering technologies in order to improve their hardness and wear resistance under corrosive environment. These surface treatments include (but are not limited to) the implementation of different techniques like PVD, thermal spraying, or nitriding by ion implantation [3,8–10]. Similar approaches are followed for the surface engineering of different conventional materials like various types of steels in order to improve their mechanical properties and corrosion resistance [11–15].

The combination of corrosion with mechanical wear leads to wear accelerated corrosion, a phenomenon that is commonly named tribocorrosion. Over the past 20 years, significant efforts have been invested into investigating tribocorrosion. The most salient results of these works have been summarized in several review papers [16,17]. During this period, some works have addressed the influence of normal load, among other parameters, on the tribocorrosion behaviour of passive metals. The influence of normal load on the tribocorrosion behaviour of AISI 430 ferritic stainless steel in the range of 2–10 N under point contact was investigated by Stemp et al. [18]. In their work, they concluded that the relation between wear volume and anodic current with normal load was in both cases linear. The behaviour was observed for two different roughness of the aluminium oxide ball used as counterbody, also noticing that the wear loss and anodic current rose for rougher balls. No significant dependence between coefficient of friction and applied normal load could be found. In terms of wear mechanisms, no significant variation was observed for rough alumina balls, whereas less plastic flow and slightly more disrupted surface was observed at lower loads for samples tested against smoother alumina balls.

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The friction and wear behaviour of Ti6Al4V during fretting at 10 N in point contact as function of the applied potential was addressed by Barril et al. [19]. The experiments were performed in 0.9% NaCl, using samples with a R_a of 0.6 μm, which is the typical roughness of hip joint stems and found that the wear rate depended on the prevailing electrode potential. The influence of oscillation amplitude and normal load on Ti6Al4V was addressed by the same authors using Ti6Al4V with very similar experimental conditions [20]. They found that for both investigated loads (10 and 30 N) the current was proportional to the factor $1/r_H{*}v_s{*}F_n$, being r_H the radius of the Hertzian area of contact, v_s the sliding velocity and F_n the normal load.

More recently, the influence of load on the tribocorrosion behaviour of CoCrMo alloy was addressed by Mathew et al. using two test rigs in a load range comprising 0.05–64 N, i.e. contact pressures of 138–752 MPa [21]. For each test rig a different electrolyte was used, namely phosphate buffer solution and bovine calf serum. In both cases, the total weight loss after tribocorrosion was always higher for higher normal loads, even though a linear relationship cannot be derived from their work. Interestingly, the authors analysed the influence of load on the synergistic interaction between wear and corrosion as represented by the ratio K_c/K_W with K_c and K_W being the wear loss due to corrosion and wear, respectively. They found that the ratio is initially wear dominated for smaller loads ($K_c/K_W \sim 0.1$), rises with increasing load up to 0.4 and subsequently decreases being close to 0 for the highest investigated load. A lower load regime was recently addressed by Martinez-Nogues et al. using similar CoCrMo alloys [22]. In their case, the investigated load range covered 1–30 mN, even though the contact pressures were high, ranging from 1 to 20 GPa and the experiments were performed under dry contact conditions.

The present work aims to understand the role of contact loads in the sub-newton range on the tribocorrosive behaviour of Ti6Al4V alloy. The investigated contact loads lead to contact mean Hertzian contact pressures in the range of 90–430 MPa, with the advantage that a well-defined point contact is applied. Such contact pressures are found in a wide variety of applications in off-shore and biomedical applications. At such contact pressures, the metal is expected to partly repassivate during sliding contact so that the interaction between surface asperities and counterbody becomes of high relevance.

2. Experimental

2.1. Materials and electrolyte

In this study, Ti6Al4V plates were tested against Al_2O_3 balls. The Ti6Al4V plates (Vulcanium Metals International, UK) were cut into 3 × 10 × 10 mm, and subsequently polished to a final average surface roughness R_a of 44 ± 3 nm. Additional samples with higher ($R_a = 825 \pm 92$) and lower ($R_a = 15 \pm 2$) surface roughness were prepared to investigate the impact of surface roughness on friction and wear. The 5 mm diameter aluminium oxide balls with average surface roughness 100 nm were commercially available (Kugel Pompel, Austria). The mechanical properties of both tribopairs are displayed in Table 1. The selected electrolyte in this study was artificial seawater in order to address prospective off-shore applications. The seawater was prepared according to the ASTM D665-12 standard and its chemical composition is given in Table 2.

2.2. Electrochemical experiments

2.2.1. Electrochemical cell

The electrochemical experiments were performed using a three electrode electrochemical cell coupled to a microtribometer. The flat Ti6Al4V samples were set as working electrode. The counter electrode was a 0.5 m long platinum wire (99.99%) with a diameter of 0.3 mm coiled in spiral. As reference electrode, an Ag/AgCl in 3 M NaCl saturated solution (0.194 V) was used. Throughout all performed experiments, the Ti6Al4V samples were kept fully immersed in the artificial seawater. The exposed area of the Ti6Al4V samples immersed in the electrolyte was 1 cm^2. The electrochemical measurements were performed with a VersaSTAT 3F potentiostat from Ametek, Inc. (Berwyn, PA USA).

2.2.2. Potentiodynamic experiments

Potentiodynamic polarization scans were performed by applying a linear potential in the range from −1.2–1.2 V, with a scanning rate of 1 mV/s. Each potentiodynamic experiment was preceded by cathodic cleaning at −1.2 V for 5 min, followed by open circuit potential (OCP) for 60 min in order to stabilize the system. According to previous studies, by applying a cathodic potential of −1.2 V for 5 min, any air-formed passive film on passive metals should dissolve leading to similar initial surface conditions for different samples [23].

2.2.3. Tribocorrosion experiments

The friction and wear behaviour of the Ti6Al4V samples was investigated using tribocorrosion experiments on the setup presented in Fig. 1. The described three electrode electrochemical cell was mounted on the reciprocating sliding module of a FALEX-MUST precision tester (Falex tribology, Rotselaar, Belgium). The frictional and normal force were measured with a 2D-FM 1 N measurement sensor, which consists of optic displacement fibres and force transducers, with a measuring range of

Table 1
Mechanical properties of materials used in this study.

Material	Elastic modulus [GPa]	Hardness [HV]	Yield strength [MPa]	Tensile strength [MPa]	Poisson ratio [−]
Ti6Al4V	126	363	830	910	0.34
Al_2O_3	380	1900	–	–	0.23

Table 2
Chemical composition of artificial seawater according to ASTM D665-12.

Salt	g/l
NaCl	24.54
$MgCl_2 \times 6H_2O$	11.10
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.69
$NaHCO_3$	0.20
KBr	0.10
H_3BO_3	0.03
$SrCl_2 \times 6H_2O$	0.04
NaF	0.003

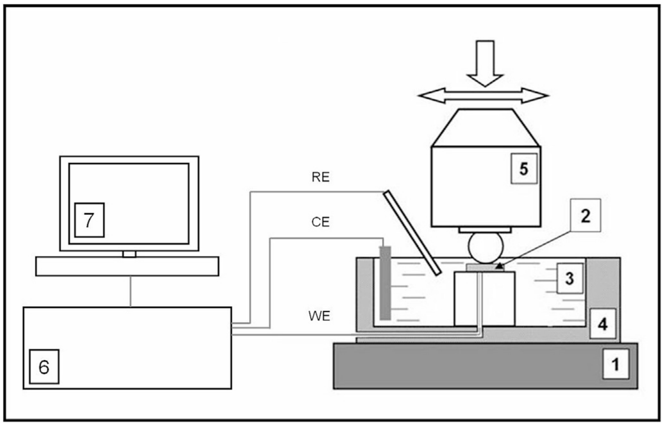

Fig. 1. Scheme of the experimental setup for the tribocorrosion experiments: 1) reciprocating-sliding movement module; 2) Ti6Al4V samples; 3) electrolyte; 4) electrochemical cell; 5) 2D-FM 1 N measurement sensor; 6) potentiostat; 7) PC controlling unit.