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TRIBOCORROSION DEGRADATION OF PROTECTIVE COATINGS ON STAINLESS STEEL

TRIBOKOROZIJSKA DEGRADACIJA ZAŠČITNIH PREVLEK NA NERJAVNEM JEKLU

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Wear, erosion, corrosion and other forms of material deterioration lead to a significant decrease in the performance of industrial production and thus increase the production cost. The PVD protective coatings based on nitrides, carbides and oxides of transitional metals have been developed in order to reduce these problems. Further progress in this field, however, depends on the understanding of the surface and interface effects, especially in the case of tribocorrosion when degradation of materials results from a combination of tribological and electrochemical processes.

This work focuses on the methodology that allows one to conduct the sliding wear and corrosion tests simultaneously and to follow in situ the degradation processes of the coating systems by controlling (in real time) the friction coefficient, corrosion current and corrosion potential. Using practical examples from the area of biomedical applications, i.e., the stainless-steel 316L substrate and the stainless-steel substrate protected with the TiAgN and TiSiN hard coatings, it is shown that tribocorrosion experiments can be used to design and predict the properties of new coatings with an enhanced performance and stability.

Keywords: tribocorrosion, PVD coatings, stainless steel, ball-on-disc, electrochemical method

Obraba, erozija, korozija in druge oblike degradacije materiala vodijo do manjše produktivnosti in s tem do večjih stroškov proizvodnje. Da bi zmanjšali omenjene težave, so bile razvite različne PVD-prevleke. Nadaljnji napredek na tem področju je odvisen od razumevanja procesov na površinah in faznih mejah, še posebej v primeru tribokorozije, kjer gre za degradacijo materiala zaradi triboloških in elektrokemijskih procesov.

V delu se osredinjamo na metodologijo, ki omogoča hkrati merjenje parametrov drsne obrabe (npr. koeficienta trenja) in elektrokemijskih parametrov (korozijski potencial, korozijski tok). Tako lahko in-situ spremljamo degradacijo prevlek ali pasivne plasti na pasivnih kovinah. Na praktičnih primerih tribokorozijskih preizkusov (dveh prevlek TiAgN in TiSiN ter podlage 316L) smo pokazali, da je mogoče tribokorozijske preizkuse uporabljati za načrtovanje in napovedovanje lastnosti prevlek z optimalnimi lastnostmi.

Ključne besede: tribokorozija, PVD-prevleke, nerjavno jeklo, pin-on-disc, elektrokemijske metode

1 INTRODUCTION

Wear and corrosion of materials are the most important failure mechanisms in industry.[1] Significant efforts have been made to combat wear and corrosion. Hard coatings such as nitrides and carbides are successful examples in protecting surface against dry wear.[1,2] Passivation techniques were shown to improve significantly the corrosion properties of passive materials.[3,4] However, when wear and corrosion are involved simultaneously, the synergistic action of wear and corrosion may deteriorate the performance of the materials. For instance, hard coatings may perform poorly in a corrosive medium due to defect growth.[5–7] On the other hand, corrosion-resistant materials, such as stainless steels and titanium alloys, may lose their corrosion resistance and corrosive-wear conditions as the passive layer continuously abrades away by wear.[8–10]

In general, tribocorrosion is defined as a degradation of materials that results from a combination of tribological and electrochemical processes.[11,12] The material-degradation rate, whether expressed as a loss in the component performance or a loss in the material, is very often higher than the sum of the rates of corrosion and wear acting separately. The synergy of corrosion and wear is still poorly understood due to the complexity of the problem and a lack of appropriate experimental techniques. The material resistance to tribocorrosion is very often evaluated using the conventional wear testers such as pin-on-disc and simply immersing the contact in a specific electrolyte. These testers can be used to rank the materials but not to investigate the mechanism responsible for tribocorrosion. Until recently, no effective analytic methods have been available to investigate the separate roles of the wear and corrosion in the corrosive wear, which are crucial for understanding the corrosive-wear synergy. Currently, in industry, the selection of the material to resist corrosive wear is mainly based on experience and trial-and-error testing. Therefore, it is useful to develop the guidelines for materials selection and design.

In this paper, we present the characterization of material resistance to tribocorrosion. Electrochemical techniques are combined with tribological testing in order to assess the roles of wear and corrosion. Additionally, microhardness was measured.

2 EXPERIMENTAL WORK

Tribocorrosion experiments were conducted using a CSM tribometer with a pin-on-disc configuration. A special configuration of a cell (**Figure 1**) allowed us simultaneous measurements of the wear (the friction coefficient) and electrochemical parameters (open-circuit potential – OCP). The ball-sample contact was fully immersed in the test electrolyte. The sample served as the working electrode and its potential was measured with respect to a standard Ag/AgCl electrode. A platinum wire was used as the counter electrode.

The test electrolyte was Hank's solution which simulates the body fluid environment with the composition of NaCl 8 g/L, Na_2HPO_4 0.0475 g/L, $NaHCO_3$ 0.35 g/L, KCl 0.5 g/L, KH_2PO_4 0.06 g/L, $MgCl_2 \cdot 6H_2O$ 0.1 g/L, $MgSO_4 \cdot 7H_2O$ 0.10 g/L, $CaCl_2$ 0.18 g/L and 1 g/L glucose at pH = 7.2. As the test samples stainless-steel AISI 316L discs were used as the substrates with two types of coatings (TiAgN and TiSiN) deposited on the AISI 316L substrates.

The coatings (with the thickness of 1.6 µm for TiSiN and 1.9 µm for TiAgN) were deposited with the plasma-beam-sputtering technique in a Sputron (Balzers) apparatus. The polished stainless-steel samples (R_a = 25 nm) were used as substrates. The vacuum chamber was evacuated to the base pressure of approximately 2 mPa. The nitrogen (with the purity of 99.995 %) flow remained constant at 5 sccm. During the deposition the bias voltage was –30 V and the temperature not did not exceed 130 °C. For enhancement an adhesion layer of pure titanium (around 100 nm) was sputtered on the substrate at the beginning of the deposition.

The wear tests were conducted with an alumina ball sliding on the plate of a sample at a fixed normal load of 8 N. The sliding was performed for 1800 laps at a sliding radius of 2 mm. The corresponding Hertz contact pressure was around 1.5 GPa.

The hardness was measured using a Fischerscope H100 indenter with the loads of 10 mN to 1000 mN.

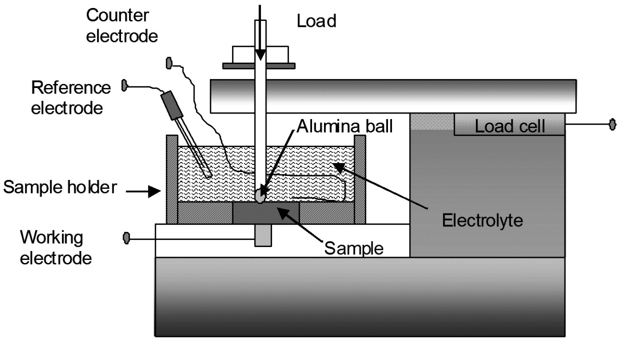

Figure 1: Scheme of the experimental cell that allowed us simultaneous measurements of wear (friction coefficient) and electrochemical parameters (open-circuit-potential – OCP)

Slika 1: Shema eksperimentalne celice, ki omogoča hkratno merjenje obrabnih in elektrokemijskih parametrov

3 RESULTS AND DISCUSSION

Tribocorrosion involves tribological and corrosion processes. Due to the synergistic interaction between them, the material loss can be larger than the sum of the losses due to the wear and corrosion acting separately. The total mass loss is expressed as:

$$M_{tot} = M_{mech} + M_c + M_{syn} \tag{1}$$

where M_{tot} is the total mass loss, M_{mech} is the mass loss due to the pure mechanical wear in the absence of corrosion, M_c is the mass loss due to the static corrosion in the absence of wear and M_{syn} is the mass loss due to the synergy effect. Friction and wear change the corrosion behavior of a material and vice-versa; corrosion may change the condition of friction.[13] Therefore, M_{syn} can be expressed as the sum of the two components, $M_{c\text{-}w}$ and $M_{w\text{-}c}$, where $M_{c\text{-}w}$ is the increase in the corrosion loss due to a tribological action, called the wear-enhanced corrosion, and $M_{w\text{-}c}$ is the increase in the mechanical wear due to the corrosion, called the corrosion-enhanced wear. Therefore, equation (1) can be expressed as:

$$M_{tot} = M_{mech} + M_c + M_{c\text{-}w} + M_{w\text{-}c} \tag{2}$$

$M_{w\text{-}c}$ could be attributed to the inhomogeneous distribution of strain, defect and surface irregularities caused by the mechanical wear. In such a way microelectrodes (cathodic and anodic places) are generated at the surface. This leads to an increase in the material dissolution. A destruction of the passive film by wear can also lead to the material dissolution. $M_{c\text{-}w}$ is more relevant in coated substrates, where the electrolyte penetrates through the pores and defects in the coatings. These can lead to a reduction of the tribological properties of the substrate/coating system.

The tribocorrosion experiments were performed on the bare stainless-steel AISI316L substrate and on the samples coated with two nitride-based coatings. The

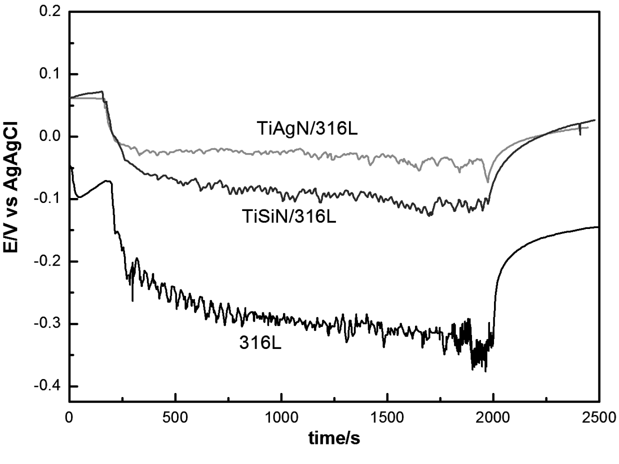

Figure 2: Evolution of the corrosion potential before, during and after the wear of the bare substrate and both coatings (TiAgN, TiSiN)

Slika 2: Spreminjanje korozijskega potenciala (OCP) pred obrabo, med njo in po njej za samo podlago in obe prevleki (TiAgN, TiSiN) measurement consisted of monitoring the OCP before, during and after the sliding wear. The drop in the potential can be the result of the destruction of the protective passive layer due to the wear mechanism. After the sliding was stopped the corrosion potential increased. Therefore, the repassivation of the passive layer occurred.

Figure 2 shows the corrosion potential (OCP) evolution of the two coated stainless-steel samples and of the bare stainless-steel substrate in Hank's solution. For the bare substrate, the OCP dropped gradually to the lowest value of –375 mV vs Ag/AgCl after almost 1700 cycles of sliding. This gradual drop in the potential suggests a gradual removal of the oxide passive layer. When the sliding ceased, the OCP increased and progressively returned to its original value. Thus, the repassivation of the passive layer occurred. For the coated samples, the OCP dropped to reach the potential values of –80 mV vs Ag/AgCl for the TiAgN and of –110 mV vs Ag/AgCl for the TiSiN coatings. The drop in the potential on the bare substrate is the result of the destruction of the protective passive layer due to the wear mechanism. After the sliding was stopped the corrosion potential increased.

The explanation for the drop and increase in the potential for the coated substrates is not as straightforward as in the case of the bare substrate. In this case there is no formation of a passive layer on the inert nitride coating. The drop in the potential suggests a reduction in the corrosion properties of the substrate/coating system due to the penetration of the electrolyte through the pores and defects in the coatings, as explained before in equation (2) ($M_{\text{c-w}}$ part). However, more data are needed to support this statement.

The evolution of the friction coefficient was analyzed during the sliding in Hank's solution for both coatings and the bare substrate. **Figure 3** shows the representative curves of the observed trends. For the bare substrate, there was an increment in the values of the friction coefficients at the beginning of the sliding process (250 laps). After the initial running-in period, the value of the friction coefficient remains stable at around 0.6. The fluctuation in the value of the friction coefficient corresponds to the removal and regrowth of the passive layer.[13] When the substrate was coated with TiSiN or TiAgN, the friction coefficient dropped by about five times to about 0.15. However, it should be pointed out, that for the TiAgN coatings the friction coefficient did not converge to a stable value during 1800 laps. An increase in the friction coefficient during the sliding was observed (**Figure 3**) for the TiAgN coating. Such behavior may be due to the formation of the corrosion products and wear debris during the sliding process, as also reported in literature.[13] In general, the tribocorrosion parameters are not the material properties, but the properties of the system. Therefore, the fiction coefficient depends on the sliding processes (i.e., parameters, electrolyte).

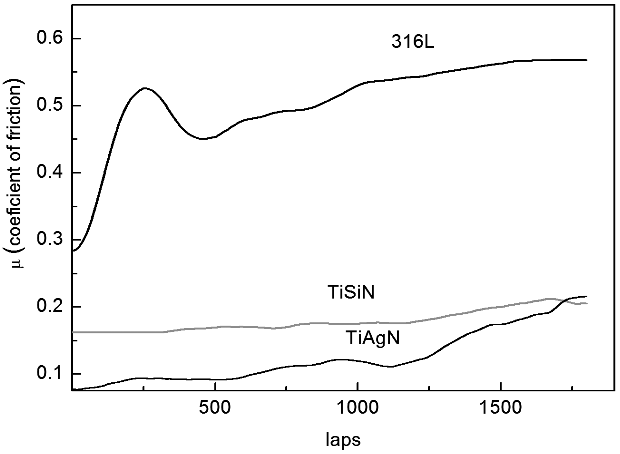

Figure 3: Evolution of the friction coefficient during the sliding in Hank's solution of the bare substrate and both coatings (TiAgN, TiSiN)

Slika 3: Spreminjanje koeficienta trenja med razenjem v Hankovi raztopini za podlago in obe prevleki (TiAgN, TiSiN)

After the tribocorrosion test, the wear track was analyzed by a profilometer (**Figures 4** and **5**). **Figure 4** shows the average depths of the worn profiles on both coatings, TiAgN and TiSiN, and on the bare substrate. The depth of the worn profile was estimated and compared to the thickness of the coatings. The wear-track depth is around 0.70 μm for the bare substrate, 0.33 μm for the TiSiN coatings and 0.15 μm for the TiAgN coatings. Based on the results, we can find out if the coatings were removed completely or not after the tribocorrosion test. In the case of the TiSiN coatings 20 % was removed, while only 8 % of the TiAgN coatings were removed. This shows that the current systems (when the coating and the substrate are considered) exhibit good tribocorrosion properties.

Hardness is one of the key mechanical properties of the protective coatings. However, the result obtained with the measurement strongly depends on the load

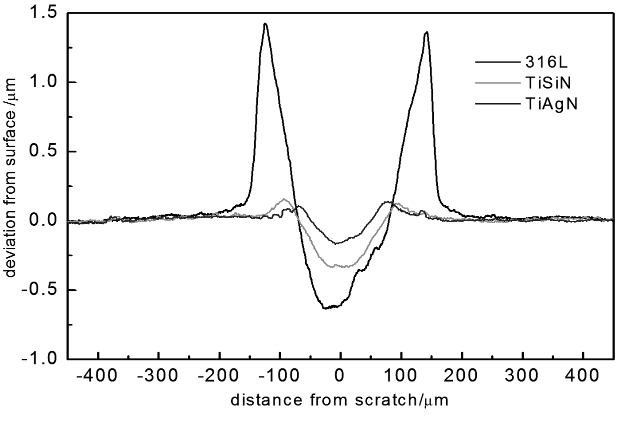

Figure 4: Average depth profile after the tribocorrosion experiment of the bare substrate and both coatings (TiAgN, TiSiN)

Slika 4: Povprečni globinski profil podlage in obeh prevlek (TiAgN, TiSiN) po tribokorozijskem preizkušanju

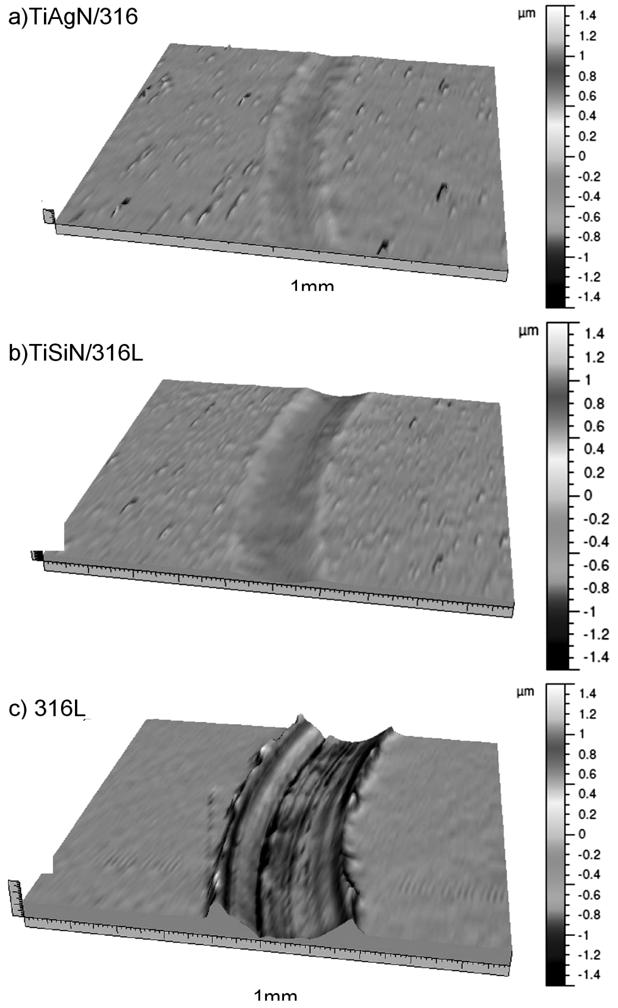

Figure 5: 3D micrographs of the wear tracks after tribocorrosion experiments for the bare substrate and both coatings
Slika 5: 3D globinski profil raze podlage in obeh prevlek (TiAgN, TiSiN) po tribokorozijskem preizkušanju

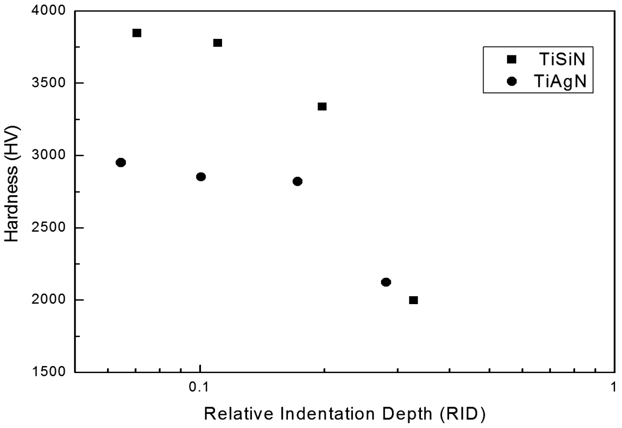

Figure 6: Vickers hardness as a function of the relative indentation depth (RID) for both coatings at the loads from 10 mN to 100 mN
Slika 6: Trodota po Vikersu v odvisnosti od relativnega globinskega profila (RID) za obe prevleki (TiAgN, TiSiN) pri obremenitvi od 10 mN do 100 mN

applied, as well as on the sample preparation. At smaller loads there is no substrate influence on the hardness (when the indentation depth is less than about 10 % of the coating thickness). Therefore, only the coating properties are measured. At higher loads, on the other hand, the substrate influence comes into sight. In our case, the measurements were taken at the applied loads from 10 mN to 100 mN. It should be noted, that, at a lower load, the error of the measurement grows because of various surface affects (roughness, defects, inhomogeneities, tip irregularities, etc.).

Figure 6 presents the hardness in dependence of the relative indentation depth (RID) for both coatings in the load range from 10 mN to 100 mN. The relative indentation depth is computed by dividing the indentation depth by the coating thickness of the corresponding system.[14] The hardness of the bulk substrate was determined to be 200 HV. The hardness, measured at the 10 mN load reached the value of around 3800 HV for the TiSiN coating, and 2900 HV for the TiAgN coatings. Thus, with a coating deposition the surface hardness increases by almost 20-fold. However, the highest value of the surface hardness does not imply the best wear resistance. One possible reason why TiSiN exhibits a lower wear resistance than TiAgN is the presence of the hard Si_3N_4 particles that increase the wear.

4 CONCLUSION

In this paper, the hardness and tribocorrosion characterization of the TiAgN and TiSiN coatings and bare stainless-steel substrate was performed. Electrochemical techniques were combined with friction tests to understand the synergy between wear and corrosion.

For the bare substrate, the drop in the potential is the result of the destruction of the protective passive layer due to the wear mechanism. After the sliding was stopped the corrosion potential increased. Therefore, a repassivation of the oxide layer occurred. The friction coefficient of the bare substrate and the depth of the wear track exhibit the wear resistance that is five times lower than that of the coated substrate.

For the TiAgN and TiSiN coatings, the drop in the potential during the wear suggests a reduction in the corrosion properties of the substrate/coating system due to the penetration of the electrolyte through the pores and defects in the coatings. Both coatings improved the tribocorrosion and mechanical stability compared to the bare stainless-steel substrate. The TiAgN coating exhibits a better wear resistance than the TiSiN coating, although the surface hardness of the TiSiN coating is higher than that of the TiAgN coatings.

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