Bio and nanomaterials in tribocorrosion systems

Lidia Benea

Competences Center: Interfaces – Tribocorrosion and Electrochemical Systems,
Faculty of Engineering, "Dunarea de Jos" University of Galati, Galati, Romania

E-mail: Lidia.Benea@ugal.ro

Abstract. The growing attention that the scientific community has paid in the last decades to the corrosion phenomena, including tribocorrosion is related to the huge economic, social and environmental losses (3,5 % GDP in industrialized countries as USA, UK, Japan and Germany), that result from the spread of damage of several metal constructions and devices. Tribocorrosion is defined as the chemical-electrochemical-mechanical process leading to a degradation of materials in sliding, rolling or erosion contacts immersed in a corrosive environment or even in water. That degradation results from the combined action of corrosion and wear are higher compared with addition of corrosion and wear degradation separately. This synergism between chemical, electrochemical, and mechanical processes on materials in sliding, abrasive or erosive contacts immersed in a liquid requires a multi-disciplinary approach (material science, electrochemistry, tribology, mechanics, and surface engineering). This paper presents few summary results obtained by studying the materials degradation by complex tribocorrosion processes in terms of two broad categories of applications: tribocorrosion in industrial systems with improved behaviour of nanomaterials as hybrid and nanocomposite layers and tribocorrosion in living systems with improved behaviour by surface modifications of biomaterials applying electrochemical techniques. The purpose of this paper is to provide information on the surface conditions of materials in sliding contacts and also on the kinetics of reactions that control the corrosion component in the material loss during tribocorrosion tests.

1. Introduction

There is a strong relation created between materials degradation (corrosion, tribocorrosion) and sustainability, with the aim to avoid excessive damage to our planet, to mitigate the effect of heavy industrialization, and this goal should be also transmitted to the future generations. Both the public and private sectors appreciate the need for engineers who have been taught corrosion engineering so that they have to take into account corrosion and tribocorrosion properties for well designing and manufacturing. The importance of materials degradation (corrosion, tribocorrosion) education in today's world continues to increase as the limits of material behaviour are stretched to improve the performance of engineered structures and devices. The basis of the academic subjects related to materials degradation is scientific, but we cannot ignore its effect on every industrial process or metallic implants and the correlation of this phenomenon with sustainability. It is necessary not only provide students with knowledge about the behaviour of materials but to raise their awareness of the importance of ecological considerations due to: metallic resources which are overexploited, the environmental impact resulting from any failure in service which is unpredictable and the necessity to point out the recycling importance. Different industries that may be affected by tribocorrosion include:

petrochemical and chemical, aerospace, automotive, marine, mining, food and biomedical. In orthopaedic field, metallic implants are often exposed to simultaneous chemical/electrochemical and mechanical stresses due to each simple or complex movement performed with the arms or legs. During the motions of the artificial joints exposed to the synovial fluid, wear debris are generated which can cause several reactions in the surrounding tissue in which they are deposited leading to implant loosening. In industry corrosion and wear are responsible for maintenance expenses and loss of productivity resulted from the shortened life of components and catastrophic failure leading to massive costs of the replacement and litigation [1,2]. Tribocorrosion is defined as the chemical-electrochemical-mechanical process leading to a degradation of materials in sliding, rolling or erosion contacts immersed in a corrosive environment or even in water. Therefore tribocorrosion is the science of surface transformation by electrochemical and mechanical synergy. That degradation results from the combined action of corrosion and wear are higher than that of adding separately the corrosion and wear. The mechanism of tribocorrosion is not yet fully understood due to the complexity of the chemical, electrochemical, physical, and mechanical processes involved. Examples of the occurrence of tribocorrosion in service are the accelerated corrosion of steel conveyors exposed to ambient air of high relative humidity, the fall out of electrical connectors in the automotive industry, the degradation of orthopedic prosthesis and dental fillers, the erosion wear of turbine blades, etc. The evidence of tribocorrosion wear in pressurized water reactors (PWR) was reported recently by Lemaire and al. [3]. Some authors have reported on a modification of the surface state of materials in sliding contacts, which results from mechanical, chemical and electrochemical processes [4-6]. That interaction is of increasing interest since it may result in a new concept of operating materials under lubrication-free sliding or rolling conditions. Indeed, such tribo-reactive surface layers may modify the corrosion process on contacting materials that in turn may modify friction and wear of materials. Recently, there has been an increase in the interest on the investigation of the combined corrosion-wear degradation of materials (tribocorrosion) by electrochemical methods [7-22].

This paper presents few summary results obtained by studying the materials degradation by complex tribocorrosion processes in terms of two broad categories of applications: tribocorrosion in industrial systems with improved behavior of nanomaterials as hybrid and nanocomposite layers and tribocorrosion in living systems with improved behaviour by surface modifications of biomaterials applying electrochemical techniques. Essential information on the surface conditions of materials in sliding and friction contacts, but also on the kinetics of reactions that control the corrosion component in the material loss during tribocorrosion tests are shown. In-situ electrochemical analysis measurements and mechanical parameters for studying tribocorrosion process were monitorized simultaneously.

2. Materials and methods

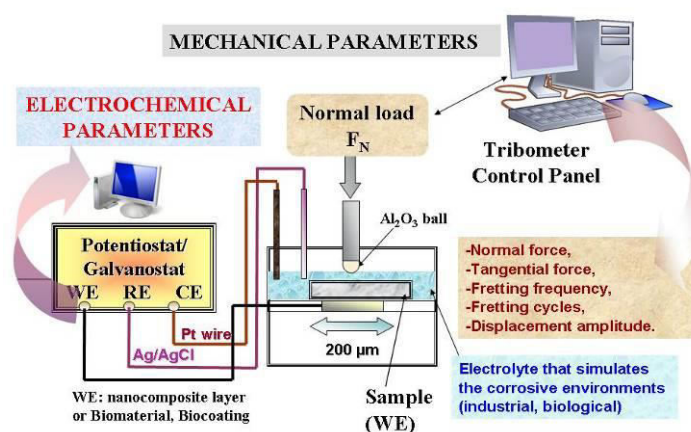### 2.1. In-situ electrochemical and mechanical parameters

Uni-directional pin-on-disk or bidirectional ball-on-flat contact geometry can be used and an electrochemical cell connected with a tribometer. Schematic diagrams of the experimental set-ups are given in figures 1 and 2.

The active surface of the working electrode is well defined by isolating with epoxy resin being the same for every experiment. The counter body (pin) usually is a hard ceramic like alumina (Al_2O_3) or zirconia (ZrO_2) cylinder (7 mm in diameter), mounted vertically on a rotating head, above the sample. The lower spherical end (radius = 100 mm) of the pin is then applied against the material surface (disc) with an adjustable normal force, correlated with the real application. When rotation is applied, the end of the pin draws a circular wear track (16 mm in diameter) on the working surface (for the uni-directional contact geometry) or a wear track with an amplitude of about 200 μm (for bi-directional contact geometry).
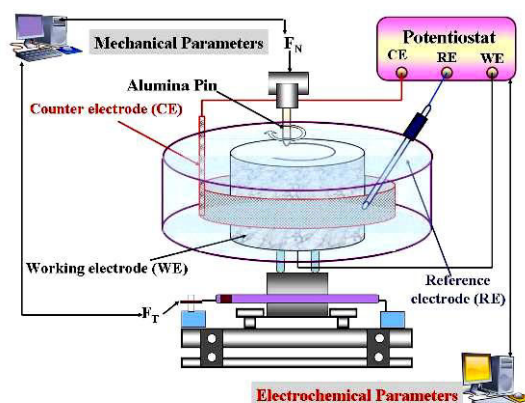
Figure 1. Schematically description of the pin-on-disc set-up used to study the tribocorrosion behaviour of materials and coatings in aqueous solution containing the electrochemical cell connected to potentiostat with reference electrode (RE), counter electrode (CE), working electrode (WE) which is the sample with the coating or a biomaterial on the top of a cylinder, counterbody (pin), made by corundum (Al_2O_3) and the wear track drawn by counterbody on the sample surface.

After the electro-codeposition of WC nanoparticles into nickel matrix the obtained Ni/ nano-WC nanocomposite layers were characterized to tribocorrosion process in pin-on-disc system, figure 1. The electrochemical protocol used for the tribocorrosion experiments in wet conditions consisted of two steps: (1) measuring the open circuit potential (OCP) of the sample for 60 min. before starting up the friction tests in order to reach a stable potential and (2) after that the Al_2O_3 pin was brought in contact with the tested sample and a constant normal force was applied using controlled mechanical parameters. After the end of fretting tests the normal force was released and for a period of 60 min. the OCP was monitored in order to observe its evolution without any force applied or friction motion.

Figure 2. Schematically description of bi-directional fretting corrosion system with computer controlled electrochemical and mechanical parameters.

After surface modification of titanium alloy by controlled oxide film formation, the friction of untreated Ti-6Al-4V alloy and anodized formed porous TiO_2 layer is studied in a ball-on-flat configuration using a MUST micro-tribometer, figure 2, under reciprocating sliding condition. Alumina balls (G 10 grade - Ceratec, The Netherlands) of 10 mm diameter were used as counterbody

in the fretting corrosion tests. The choice of alumina ball as the counter face material was made because of its high hardness, high wear resistance, chemical inertness and electrical insulating properties. Prior to any sliding test, the counterbodies were degreased with ethanol followed by hot air drying. After this, the alumina balls were loaded on top of the test samples at the normal forces of 400 mN, 600 mN and 800 mN, with a displacement amplitude of 500 μm and sliding frequency of 3 Hz for 1000 cycles. The mean Hertzian contact pressures which correspond in these tests were of 210 MPa at 400 mN, 240 MPa at 600 mN and 260 MPa at 800 mN. Each experiment was repeated at least twice to check for reproducibility.

All reciprocating sliding tests were performed at room temperature (23°C) in Fusayama–Mayer bio-simulated saliva. The composition of this electrolyte is 0.4 g/L NaCl, 0.4 g/L KCl, 0.8 g/L $CaCl_2$ $2H_2O$, 0.69 g/L NaH_2PO_4 and 1 g/L urea having a pH of 4.8. This solution was selected because this pH condition is much more aggressive than would be normal for natural saliva and its use is expected to be able to enhance the corrosion-wear process and to distinguish the effect of surface modification of titanium alloy. During the sliding test, the normal force, tangential force, coefficient of friction, number of cycles and the linear contact displacement were continuously monitored.

2.2. Preparation of Ni/nano-WC nanocomposite layers

Ni/nano-WC composite layers were obtained by electro-codeposition from a standard nickel Watts plating bath to which WC nanoparticles with a concentration of 10 gL^{-1} was added. The tungsten carbide (WC) nanopowder with a purity of 99,95%, grain size of 60 nm was purchased from MK Impex Corp.(Ontario, Canada).

Electro-codeposition was carried out in a typical three-electrode cell with double walls to keep constant temperature of the solution, where 304L stainless steel plates with exposed surface area of 4 cm^2 were used as working electrodes, a nickel plate was used as an auxiliary electrode (counter electrode) and a saturated calomel electrode (SCE - Hg/Hg_2Cl_2) with KCl saturated solution (E= + 244 mV vs. normal hydrogen electrode - NHE) was used as a reference electrode. Tungsten carbide as a hard phase can be included into the Ni matrix to improve the wear resistance of Ni-based coatings.
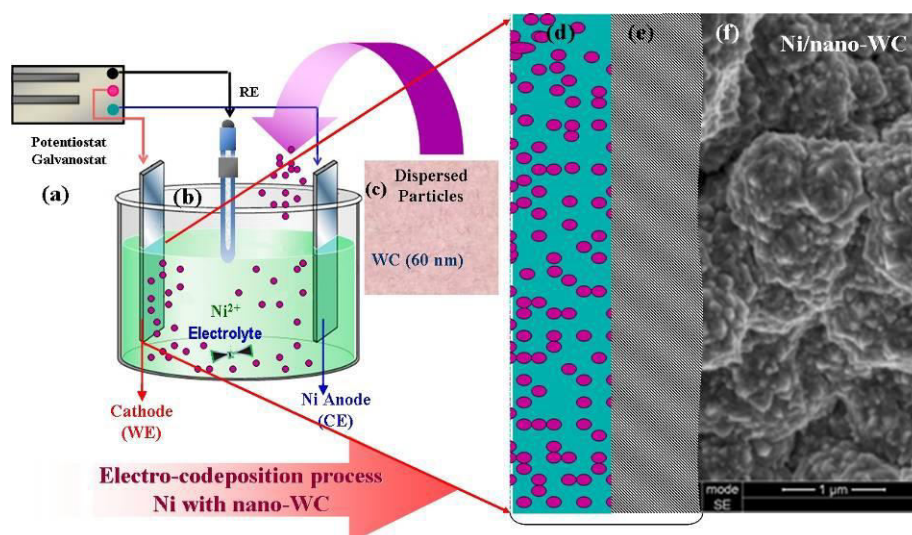

Figure 3. Schematic drawn of WC nanoparticles electro-codeposition into nickel matrix to obtain Ni/nano-WC nanocomposite layer: (a) the electrochemical workstation; (b) electrochemical cell with cathode (-) as the working electrode support for coatings to be electrodeposited, the anode (+) or counter electrode as nickel plate, the reference electrode, nickel plating solution and WC nanoparticles; (c) dispersed WC nanoparticles (60 nm diameter); (d) schematic cross section of Ni/nano-WC nanocomposite layer; (f) stainless steel support material; (f) SEM micrograph of Ni/nano-WC layer surface.

Schematic presentation of the electrolytic cell and electro-codeposition process is shown in figure 3, where (a) represent the electrolytic cell with cathode (-) as the working electrode support for coatings to be electrodeposited, the anode (+) or counter electrode as nickel plate in order to maintain an constant content of nickel ions into nickel plating bath and in the middle is the electrolyte or the plating solution having an homogenous dispersion of WC nanoparticles maintained by stirring. In figure 3 it is shown a schematic cross section of electrodeposited nanocomposite layer(d) as well as the SEM micrograph of nanocomposite layer surface.

2.3. Surface modification of titanium alloy to improve the tribocorrosion resistance
The preparation method of untreated Ti-6Al-4V alloy, nanoporous anodic oxide films were described more in detail previously [18,23]. In figure 4. there is presented a schematic drawn of controlled formation and growth of porous titanium oxide film on titanium alloy. The alloy is immersed in an anodization electrolyte connected at anode in an electrochemical cell (a). By varying the parameter as voltage, current density, temperature and time it could be obtained a porous film on titanium alloy with a given thickness, usually between 30 to 100 nm.
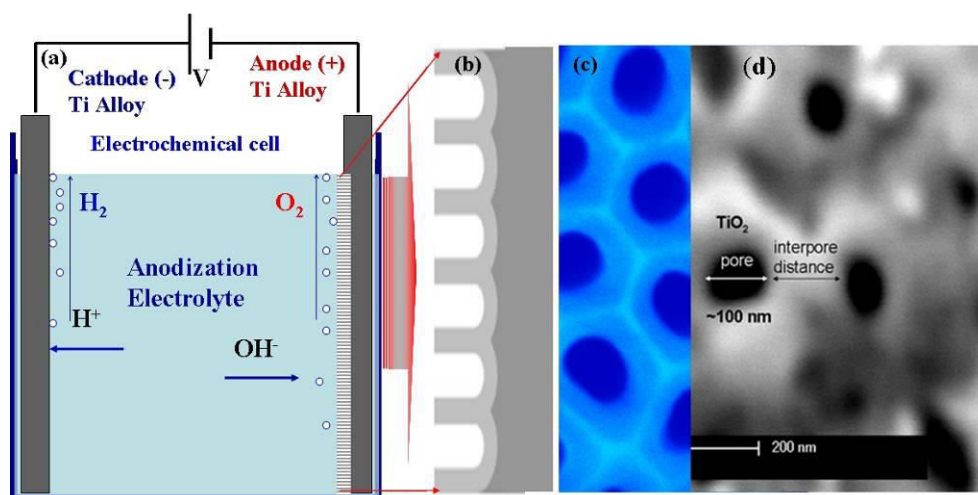
Figure 4. Schematic presentation of surface modification of titanium alloy by electrochemically controlled growth of TiO_2 nanoporous film: (a) electrochemical anodization cell; (b) cross section of TiO_2 film; (c) schematic surface of nanoporous TiO_2 film; (d) SEM micrograph of titanium oxide film

The obtained nanoporous film with estimated pore diammeter of 100 nm, figure 4 (c, d) is expected to improve the wear corrosion properties of titanium alloy in biologic solution.

3. Results and discussion

3.1. Nanocomposite layers in tribocorrosion systems for energy applications
In the nuclear power plants there is a need of wear resistant materials which work in wet conditions like primary circuit solution formed from a mixed lithium hydroxide and boric acid dissolved in purified water. Parts of nuclear pressurized water reactors (PWR), immersed in the cooling water, are submitted to both mechanical perturbation as well as corrosion. Therefore passivable alloys with high mechanical properties are used for their manufacture. The gripper latch arms (GLAs) of the control rod drive mechanisms are protected from wear and corrosion by a layer of 5 mm thickness of cobalt chromium alloy with 28 wt. % chromium which is deposited by plasma spraying.

   The electrochemical analysis techniques were applied for studying specifically in-situ tribocorrosion process of cobalt chromium alloy hard coating 5 mm thick on 304 L stainless steel support [20]. It was found that this alloy is supporting a tribocorrosion mechanism consisting in a

periodical destruction by friction of the Cr_2O_3 oxide film formed during stopping the friction (stationary time).

In this research work it was obtained a Ni / nano-WC (60 nm mean diameter) nanocomposite layer by electro-codeposition process on 304 L stainless steel support in order to be tested in the same tribocorrosion conditions as Co-Cr alloy. The nanocomposite layer with good adherence to stainless steel support, having a thickness of 10 micrometers and about 13.12 wt % of tungsten carbide included into nickel matrix was characterized to tribocorrosion process in bidirectional fretting conditions, as presented in figure 2. The Ni / nano-WC nanocomposite layers obtained by electrodeposition were comparatively characterized to nanohardness and wear corrosion by immersion in Water +Li +B, the simulated cooling water reactor.

The surface morphology and chemical composition of Ni/nano-WC composite layer is presented in figure 5. WC nanoparticles are homogeneously dispersed in the Ni matrix. This means that nickel ions from the electrolyte are adsorbed on WC nanoparticles and then are reduced on the WC surface and their deposition on the surface is totally uniformly. The SEM morphology of Ni/nano-WC composite layer also reveals a cauliflower structure [24].

The incorporation percentage of WC into Ni matrix is determined by transformation of W element wt % in molecular mass of WC, considering the standard atomic weight of W element which is 183.84.
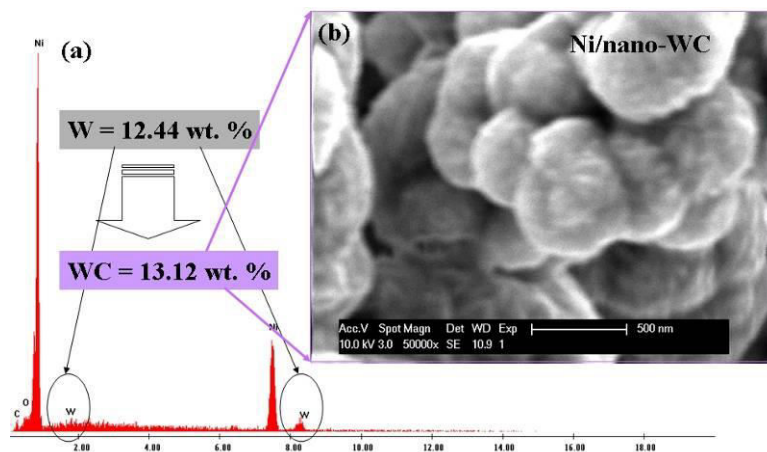
Figure 5. EDX-SEM analyzes and calculation of amount of reinforcing WC phase into nickel matrix (a) EDX elemental analyze of the entire surface corresponding to SEM micrograph; (b) - SEM surface morphology.

The weight percentage for W element included into Ni matrix, as shown in figure 5 was determined by EDX analyses being equal to 12.44 wt % (mean value). Therefore the wt. % of WC reinforcing the Ni/nano-WC composite layers resulted at an average value of 13.12, percentage that improved the properties of the nanocomposite layer.

The roughness of obtained layers was measured with a high resolution microtopograph STIL with optical fiber. The results of 2D and 3D surface profiles are presented in figure 6.
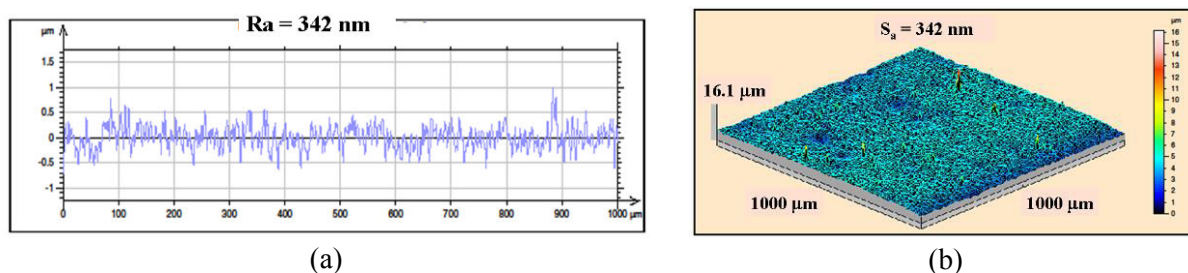

Figure 6. Roughness of Ni/nano-WC nanocomposite layer: (a) 2D profile; (b) 3D surface profile

The nanohardness testing of the obtained layers were done in order to get the values of hardness (H) and elastic modulus (E), presented in figure 7 and Table 1.

Table 1. Nanoidentation results as hardness, elastic modulus and H / E ratio for Ni/nano-WC composite and pure Ni coatings

| Type of coating	Identation hardness (H) [GPa]	Vickers hardness [Hv]	Elastic modulus [GPa]	H / E ratio [GPa]
Pure Ni	3.06	220.42	180.82	0.0169
Ni/nano-WC nanocomposite layer	3.98	416.84	194.52	0.0204
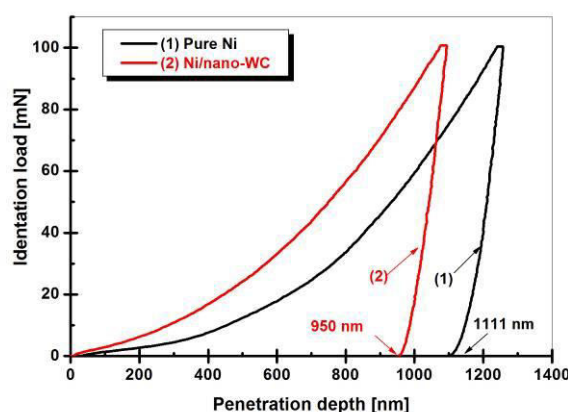
Figure 7. Typical cyclic nanoidentation load-displacement curves for (1) pure Ni layer and (2) Ni/nano-WC layer obtained with a Berkovich indenter.

Hardness is commonly regarded to be a significant mechanical property for evaluating wear resistance [24]. However, several authors have recognized that the ratio between the hardness and the elastic modulus is a more adequate guideline for predicting wear resistance than the hardness itself [24]. This H / E ratio is related to the elastic strain to failure [24]. Leyland et all. [25] have assumed that the most durable coatings can be obtained if the elastic strain to failure has a high value and this can be done by obtaining layers with sufficiently high hardness in order to resist at plastic deformation and simultaneously with a low elastic modulus (similar to, or slightly below, that of the substrate material).

Figure 8 provides the mean values for coefficients of friction monitored in wet conditions as a function of normal forces of 1 N, 2 N and 5 N, at the fretting frequency of 1 Hz, for a number of cycles equal to 10000 and 200 μm displacement amplitude corresponding to pure Ni coating and Ni/nano-WC nanocomposite layer.

Figure 8 shows a general behaviour of friction coefficient recorded under wet condition of Ni/nano-WC nanocomposite layers being smaller than that of pure Ni layers for all three normal forces applied.

From figure 8 it can be seen that under wet conditions, the friction coefficient of both pure Ni and Ni/nano-WC composite coatings decreases gradually with increasing the normal force. For example in the case of Ni/nano-WC nanocomposite layer the coefficient of friction has the average value of 0.27 for 1 N normal force decreasing to 0.18 at 2 N normal force and to 0.17 at 5N normal force. The coefficient of friction for pure nickel layer is 0.42 being higher at 1 N normal force and decreases to 0.32 at 2 N normal force and respectively at 0.27 at 5 N normal force. By incorporation of WC nanoparticles into nickel matrix, the friction coefficients are reduced as compared with pure Ni coatings, demonstrating an improvement of fretting wear resistance.
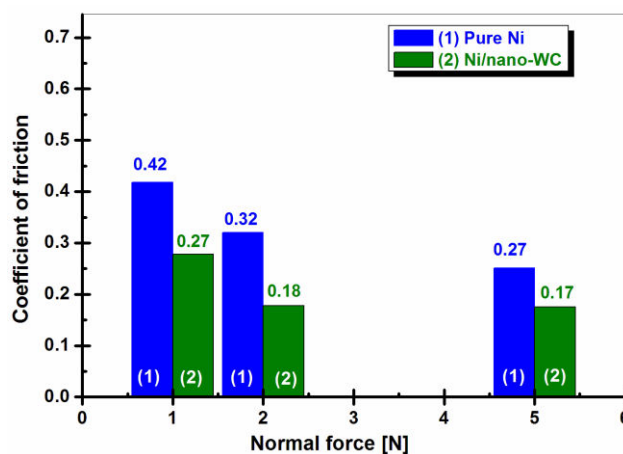
Figure 8. Evolution of the friction coefficient of Ni/nano-WC composite and pure Ni coatings during tribocorrosion tests performed in water +Li+B solution during 10000 cycles for the normal forces of: (a) 1 N, (b) 2 N and (c) 5 N.

The open circuit potential (OCP) data recorded on Ni/nano-WC layers and pure nickel layers before, during and after loading the forces in the same solution are shown in Figs. 9 and 10.
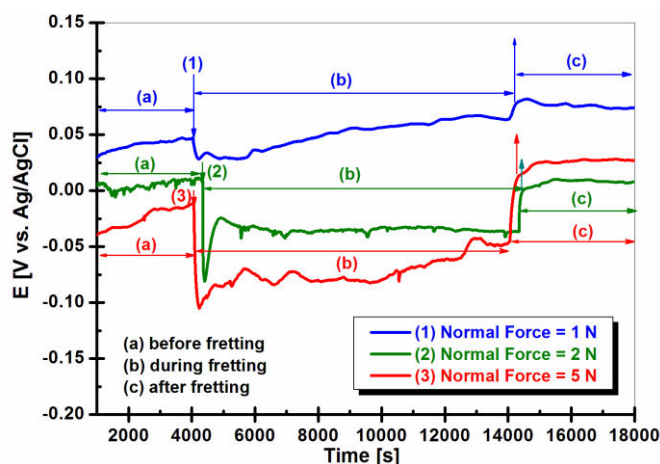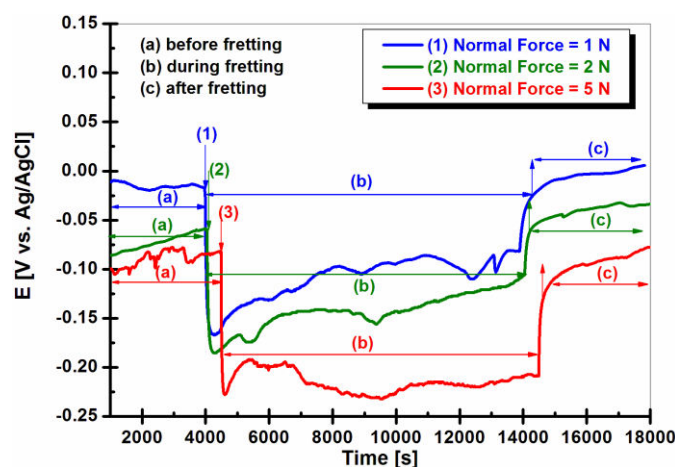

Figure 9. Evolution of the open circuit potential recorded (a) before, (b) during and (c) after loading the forces for Ni/nano-WC composite layers in water +Li+B solution during 10000 cycles for the normal forces of: (1) 1 N, (2) 2 N and (3) 5 N.

After immersion in the test solution, before loading the force, a large increase of the open circuit potential for both Ni/nano-WC composite layers and pure Ni layer could be observed, which confirm the stabilization of steady state of sample surface to a passive one. It must be mentioned that the potential measured before loading the force of Ni/nano-WC nanocomposite layers is more ennobled as compared to those of pure Ni layers, thus leading to a significant increase of anticorrosion effect. This means that an ennoblement of the nanocomposite surface occurs when WC nanoparticles are incorporated into the electrodeposited nickel layer reinforcing therefore the nickel matrix.

The suddenly shift in the cathodic domain at the moment when the normal force was loaded on the Ni/nano-WC nanocomposite layers surface took a slower leap of 0.018 V vs. Ag/AgCl (from 0.046 to 0.028 V vs. Ag/AgCl) for 1 N normal force (figure 9), confirming a better tribocorrosion resistance due to reinforcing nanoparticulate WC phase.

Figure 10. Evolution of the open circuit potential recorded (a) before, (b) during and (c) after loading the forces for pure Ni layers in water +Li+B solution during 10000 cycles for the normal forces of: (1) 1 N, (2) 2 N and (3) 5 N.

According to figure 10, at the start of fretting, the potential of the pure Ni layers drops suddenly to a more negative value, its leap being of around 0.15 V vs. Ag/AgCl (from -0.016 to -0.166 V vs. Ag/AgCl) for normal force of 1 N. Similar observations were made earlier by Ponthiaux et al. [26] for stainless steel disk immersed in 0.5 M H_2SO_4, by Berradja et al. [28] for stainless steel during sliding in Ringer's solution and by Mardare et al. [19] for Ti-6Al-4V alloy during sliding in bio-simulated environment.

This potential sudden shift in the negative direction favours the damage and partial or complete removal of the passive film induced by fretting, suggesting an increase in its susceptibility for corrosion [26]. By comparing the open circuit potential of Ni/nano-WC composite layers (figure 9) with that of pure Ni layers (figure 10), it can be clearly seen that the highest drop in potential for all applied forces is observed for pure nickel as compared with Ni/nano-WC composite. This observations indicate that pure Ni layers exhibit more cathodic values of the open circuit potential before and with the onset of friction force than Ni/nano-WC nanocomposite layers. This improved behaviour of nanocomposite layer could be attributed to the presence in the nickel matrix of WC nanoparticles.

At the end of the friction test, the potential of both types of studied layers exhibit an anodic shift, reaching again their original values, indicating the progressive repassivation of the worn surface. In the present study, after the fretting motion is stopped, pure Ni layers tends to reach the steady state potential before the onset of friction, whereas Ni/nano-WC protective layers go far beyond the steady state potential reached before the start of the friction, confirming again the better resistance of nanocomposite layer to tribocorrosion degradation process.

3.2. Nanoporous thin oxide films on titanium alloy to improve the tribocorrosion resistance
Improving corrosion and tribocorrosion resistance in physiological fluids for biomaterials by electrochemical surface modification of Ti alloy was an atteint objective of this reserach work. The friction coefficients of electrochemically formed nanoporous titanium oxide film and untreated titanium alloy, measured in saliva solution are shown in figure 11.

From Fig 11, it appears that for each separately surface the lowest coefficient of friction was recorded at the highest normal force, at constant frequency and constant number of cycles, an effect also observed by Ahmad et al. for aluminium matrix composite [28]. The reason of decrease in coefficient of friction may be due to smoothening of the surface under higher load. The average values of the coefficient of friction for both surfaces studied versus applied normal forces are shown in figure 11.
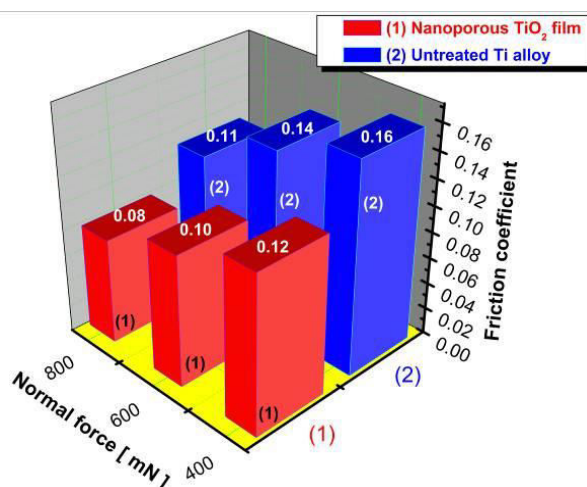
Figure 11. Average values of friction coefficients for nanoporous TiO$_2$ film electrochemically formed on titanium alloy (1) and for untreated titanium alloy (2) measured versus applied normal forces of 400, 600, and 800 mN at fretting frequency of 1Hz during 1000 cycles.

The coefficient of friction for untreated Ti-6Al-4V alloy decreases from about 0.16 corresponding to 400 mN to 0.11 according to 800 mN. The same trend is also maintained for anodic nanoporous TiO$_2$ layer surface but with lower values, starting from 0.12 at 400 mN normal force and slowing down to 0.08 at 800 mN normal force. It could be noticed that the lowest coefficient of friction is obtained at the highest normal force, remark applied to both types of surfaces studied. By comparing the coefficient of friction of untreated Ti-6Al-4V surface with anodized surface at the same normal force it can be seen that the lowest coefficient of friction is obtained for nanoporous oxide film formed on titanium alloy.
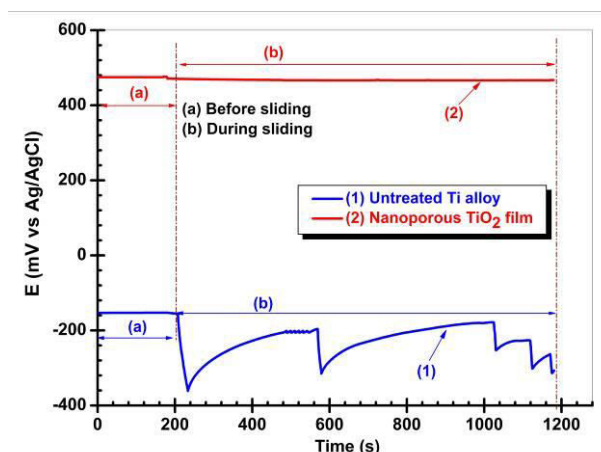
The open circuit potential measured before and during fretting, generated by reciprocating sliding tests at Fn=400 mN, displacement amplitude = 500 μm, 1 Hz fretting frequency and 1000 sliding cycles) performed in Fusayama Mayer saliva are shown in figure 12. By immersion in saliva solution and before fretting start, there is observed a clear ennoblement of open circuit potential of nanoporous TiO$_2$ film, which is 480 mV vs. Ag/ AgCl as compared with the untreated alloy having an open circuit potential of -150 mV vs. Ag/ AgCl. By controlled forming and growth of nanoporous titanium oxide on titanium alloy the open circuit potential of modified surface is ennobled with more than 600 mV, confirming a better behavior of nanoporous TiO$_2$ film.

By loading the fretting force of 400 mN at 1 Hz fretting frequency, the open circuit potential of untreated Ti alloy is shutting down to more cathodic active domain with about 200 mV vs. Ag/AgCl and show many oscillations during fretting period.

In the same fretting conditions the nanoporous TiO$_2$ film exhibits better behavior, the open circuit potential remaining practically constant, at the same noble value as before starting the fretting, as it is shown in figure 12 (curve 2).

By measuring the surface wear tracks generated after reciprocating sliding tests using a non-contact white light interferometry analysis Wyco NT3300 optical profilometer with Vision (version 2.210) software the better results of nanoporous TiO$_2$ film is confirmed, practically the wear track on nanoporous titanium oxide film is hardly to be observed, as it is shown on 3D surfaces of the resulted wear tracks, Figures 13 a and b.

As it can be observed in figure 13, the wear track on nanoporous titanium oxide film is not quantifiable being not drawn by the counter body because the surface is becoming highly resistant to extreme wear-corrosion conditions.

Figure 12. Open circuit potential of untreated Ti alloy (1) and nanoporous TiO$_2$ film (2) measured at immersion in saliva solution before fretting (a) and during fretting (b) with a normal force of 400 mN, fretting frequency of 1 Hz and 1000 cycles.
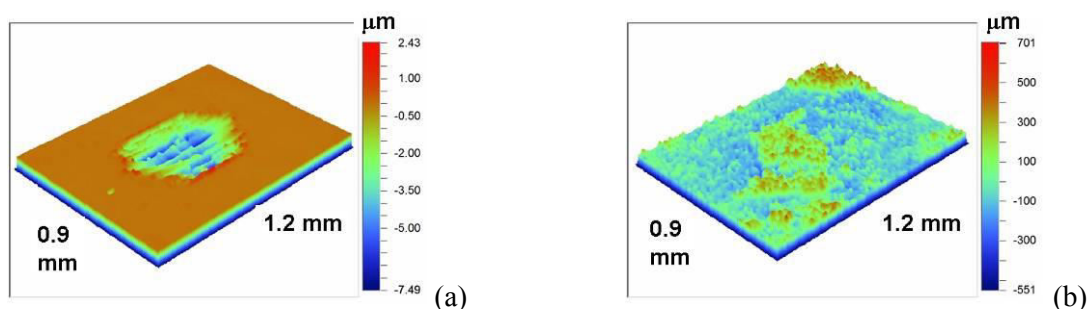
Figure 13. 3D surface profiles of wear tracks generated by tribocorrosion tests on untreated Ti alloy (a) and nanoporous TiO2 film (b) by fretting at 400 mN , 1Hz frequency and 1000 cycles

4. Conclusions

This work points out the capabilities of in - situ tribocorrosion investigations to compare the different materials and coatings in order to choose the better ones to be used under tribocorrosive conditions in sliding contacts for industrial or biomedical applications.

Electrochemical techniques as electrodeposition and controlled oxide formation and growth by anodization can lead to the a large class of nanocomposite layers as nanomaterials and nanoporous oxide films as biomaterials on different support materials and structures necessary for a future based on nanotechnology and nanomaterials to improve the resistance to aggressive environments and complex degradation processes.

Improving surface properties for corrosion and tribocorrosion resistance of materials to be used in specific environments give more valuable industrial and biomedical applications with improved life cycle.

Tribocorrosion is a complex degradation process which is present in industrial as well as in biomedical applications of materials.

The nanomaterials as nanocomposite layers having dispersed and reinforcing hard ceramic nanoparticles are an alternative possibility to increase the lifecycle of materials used in nuclear power plants in wet and moving conditions.

Functionalizing the surface of materials and biomaterials is the way to reduce or by-pass the complex degradation by corrosion and tribocorrosion processes.

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