FRETTING AND FRETTING CORROSION OF 316L IMPLANTATION STEEL IN THE ORAL CAVITY ENVIRONMENT

Processes of mechanical destruction of implants, dental prosthetics elements, and orthodontic apparatus considerably limit their operating lifetime and the comfort of patients. Processes of destruction of kinematic joint elements caused by fretting and fretting corrosion processes are an important problem, albeit one that is not yet fully understood. This paper presents the results of fretting and fretting corrosion studies conducted on 316L implantation steel, which is used in dentistry, particularly in prosthetic and orthodontic applications. Tests were performed by means of an original device of the authors’ own design, with the application of methodology developed by the authors. Fretting and corrosion tests were carried out in phosphate buffered saline (PBS) as well as in the presence of natural saliva and its substitutes. Own compositions of artificial saliva were developed for the purposes of studies. Observations of sample surfaces were performed using a scanning electron microscope (SEM) and a confocal microscope. Test results indicate a significant influence of fretting on the corrosion of 316L steel (fretting corrosion) as well as the important role of the studied fluids (saliva and its studies) in these processes. It was stated that the saliva substitute containing mucin III was characterized by the most favorable tribological characteristics. During fretting tests, intensive phenomena of materials conveyance into the friction contact area were observed.

Keywords: tribology, fretting, fretting corrosion, artificial saliva, implants, dentistry.

1. Introduction

Fretting is defined as a complex process of relative, oscillating micro-displacements of contacting surfaces, as a result of which destruction of the surface layers of these contacting elements takes place [33, 34]. Adhesive damaging of surfaces and the formation of fatigue cracks causes the creation of wear particle as well as their subsequent oxidation and hardening. These products act as an abrasive and are broken up, and their amount increases until the contacting surfaces are separated by a layer of oxide particles and wear conditions are stabilized. Materials conveyance processes, which take place with intensive oxidation, are also observed in the contact area [19]. Four primary mechanisms are responsible for fretting wear processes: adhesion, fatigue, abrasion, and corrosion [20]. Depending on the type and direction of motion, fretting is divided into: tangential, radial, torsional, and rotational fretting [36–38]. Its main consequence is a drastic reduction of the durability and the operational reliability period of devices.

The phenomenon of fretting applies to most biomaterials, including metals, polymers, as well as ceramic materials [5, 14, 22, 37]. Advances in implantology impose the application of materials fulfilling ever-greater requirements concerning biofunctionality, with preservation of full biotolerance of implants in the human body [10, 25]. Metallic materials are widely used in dental prosthetics and surgery. They are used, among other things, to reconstruct or replace missing teeth and as elements of orthodontic apparatus for correction of malocclusions [2, 23]. The most commonly used materials are precious metals (gold, platinum, palladium), alloys of cobalt, titanium, and nickel, as well as austenitic steels [3, 5, 6, 11]. It should also be mentioned that, due to the toxic properties of some of these materials...
(nickel, vanadium), new compositions of metallic alloys with similar characteristics but which cause less harm in the human body are sought for. Components made from implantation steels have found wide applications in dentistry and orthodontics because of their good technological and strength properties as well as their low production costs [25, 8]. AISI 316L and AISI 316LVM stainless steels are mainly deserving of attention. They contain molybdenum, which stabilizes the chromium compounds forming the passive layer on the surface of the alloy, thus increasing its resistance to pitting and crevice corrosion, which are responsible for the degradation of multi-component implant systems [15, 35].

Many works concerning fretting and fretting corrosion relate to the field of orthopedics and are focused on components of prostheses and bone fixations [12, 16, 30]. Only a few works pertain to processes occurring in the oral cavity [4, 24, 28, 30]. Processes of destruction of metal prosthetic elements (intraoral distractors of maxillofacial bones, dental implants, orthodontic apparatus) resulting from their fretting corrosion are still little known. There are known cases in which wear products of orthodontic elements (mainly ligatures) are adsorbed onto dental plaque, causing stains. A part of the wear products is sent to the digestive system, from which they pass through to the organism in the form of metal ions (iron, chromium, nickel), which exhibit toxic activity [10, 13, 29].

The influence of the environment is of large significance in processes of fretting and corrosion destruction. Its aggressiveness is largely caused by active chemical substances, particularly chlorine, sulfur, oxygen, and phosphorus compounds [9, 17]. Human saliva, which fulfills a series of protective and supporting functions, including lubrication functions, also has a large influence on corrosive and fretting wear processes in the oral cavity [7, 26, 27]. Persons suffering from abnormal salivary gland secretion (xerostomia) are exposed to fretting wear processes, which are responsible for the degradation of multi-component implant systems [15, 35].

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The goal of this paper was to study the processes of fretting and fretting corrosion of 316L implantation steel in the presence of human saliva and its substitutes – developed at the Department of Materials and Biomedical Engineering of Białystok Technical University. A special testing station and research methodology, as described further in the paper, were developed in order to achieve this goal.

2. Materials and testing methodology

Table 1. Chemical composition of 316L steel

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe (remainder)</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>22.00</td>
<td>15.00</td>
<td>4.25</td>
<td>3.00</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0.80</td>
<td>0.50</td>
<td>0.50</td>
<td>0.08</td>
<td>0.03</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Materials and Biomedical Engineering of Białystok Technical University (table 2), were used in tests. All artificial saliva preparations were based on phosphate buffered saline (PBS) with pH=7 and had the chemical compositions presented in table 3.

Table 2. Solutions used in tests

<table>
<thead>
<tr>
<th>Designation</th>
<th>Composition</th>
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<tbody>
<tr>
<td>A</td>
<td>human saliva</td>
</tr>
<tr>
<td>B</td>
<td>phosphate buffered saline (PBS)</td>
</tr>
<tr>
<td>C</td>
<td>mucin III (2% mass) in PBS</td>
</tr>
<tr>
<td>D</td>
<td>mucin III (2% mass) + xanthan gum (0.35% mass) in PBS</td>
</tr>
</tbody>
</table>

Table 3. Chemical composition of PBS (content of ingredients in 1 dm³ of water)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Content [g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride (NaCl)</td>
<td>6.72</td>
</tr>
<tr>
<td>Disodium phosphate (Na₂H₂PO₄)</td>
<td>2.27</td>
</tr>
<tr>
<td>Monopotassium phosphate (K₂HPO₄)</td>
<td>1.11</td>
</tr>
</tbody>
</table>

Analysis of data from the literature and the results of preliminary studies conducted by the authors were the basis for selection of model saliva substitutes. The selection of mucins was related to the favorable tribological characteristics of this substance. Xanthan gum is a natural ingredient in many compositions destined for use in the oral cavity. Its addition enabled correction of the rheological properties of the developed compositions relative to natural saliva.

A diagram of the kit used for fretting and fretting corrosion tests is shown in fig. 1. Friction processes were performed at a small amplitude on the order of 100 μm, a frequency of 0.8 Hz, and with unit pressing forces of: 5, 15 and 30 MPa. The moving table of the device, on which disk-shaped samples with a diameter of 8 mm were fastened, was in reverse motion. A counterparts in the shape of a truncated code was pressed to the surface of the disk, and the diameter of the contact surface was equal to 1.3 mm. Disks and cones were made from 316L steel.

Assessment of fretting wear was performed according to a method developed by the authors by measuring the volume of material decrement as well as of the material accumulated during the friction process (excess material). A LEXT OLS4000 with 3D imaging capability was used in these studies. It enabled accurate measurement of the surface and of the volumes of decrements and excess material. The applied method makes it possible to measure only areas of interest, the statistics of which are calculated in real time. An illustration of the developed method of fretting wear assessment is presented on the diagram in fig. 2.

Fretting corrosion tests were conducted at a pressure of 15 MPa. The tester was connected to a PGP201 potentiostat from the Radiometer company along with a tri-electrode system. The working electrode was the tested sample, and the reference electrode was a saturated calomel electrode (SCE). The auxiliary electrode was a platinum electrode with a surface of 128 mm².

Pitting corrosion resistance tests were carried out using the potentiodynamic method according to standard PN-EN-ISO 10993-15 [20]. Every test was started by determining the open circuit potential open circuit potential. Fretting corrosion tests were divided into three trials. All trials were repeated five times. The first trial
was a reference test, during which pitting corrosion resistance was assessed. At the start of potentiodynamic tests, potential was set at the level \( E_{\text{init}} = E_{\text{OCP}} - 100 \text{ mV} \). Potential change took place in the direction of the anode at a rate of 3 mV/s. After the achievement of the maximum value in the measuring range +4094 mV or after the achievement of anode current density at 1 mA/cm², a change in the polarization direction took place. In the second trial, the fretting process was started after the determination of \( E_{\text{OCP}} \) potential, and changes of potential were recorded over one hour (2880 cycles). Next, a potentiodynamic test of samples with damaged surfaces was conducted. The final test involved the registration of the electrochemical processes occurring during fretting (approx. 900 cycles).

The registration of anode polarization curves during individual stages of fretting corrosion made it possible to determine characteristic quantities describing the resistance of steel to pitting corrosion in the environment of saliva and its substitutes. Open circuit potential \( (E_{\text{OCP}}) \), corrosion potential \( (E_{\text{cor}}) \), repassivation potential \( (E_{\text{rep}}) \), and polarization resistance \( (R_p) \) were registered. The value of polarization resistance was determined using Stern’s method by analyzing the range of ±10 mV relative to the corrosion potential. This was conditioned by the requirements of maintaining a linear dependency between current density and sample potential. The value of repassivation potential was read at the coordinates of the point of intersection of the anode curve with the return curve.

Observations of sample surfaces were carried out using a Hitachi S-3000N (SEM) scanning electron microscope and a LEXT OLS4000 confocal microscope.

3. Test results and discussion

Measurements of friction forces and estimated friction coefficients were performed under stable conditions during fretting tests. Tests were performed in the environment of natural saliva and developed substitutes. Obtained results are presented in fig. 3.

The data shown in fig. 3 indicates that friction pairs in the environment of mucin III and natural saliva are characterized by the lowest resistances to motion. The greatest resistances to motion, which were reduced as pressure increased, were observed under dry friction conditions. This is probably related to the oxides that are formed on the surface of steel, which create a protective anti-adhesive layer that reduces frictional resistance after being broken up. The presence of lubricant substances in the friction pair limits oxygen access, which reduces the capability of protective oxide layer formation. In this case, the rheological properties of lubricant fluids and the content of anti-friction modifiers (mucin) capable of forming adsorbent boundary layers are decisive. These layers prevent direct metal-metal contact, thus reducing resistance to motion and wear. The worsening of the tribological characteristics of compositions containing xanthan gum, particularly under small loads, may be related to the antagonistic effect of this additive to the adsorptive capabilities of mucin and to an increase of the viscosity of the tested lubricant composition (D). A more precise explanation of the observed phenomenon requires further study.

It should be emphasized that weak removal of wear products from the friction area is characteristic of fretting processes. Disk wear test results are presented in fig. 4. This data indicates that the greatest wear occurs during dry friction. This is expressed by the accumulation of a large amount of wear products on the surface of friction (excess material). In a large degree, these are oxidized products of primary wear, mainly in the form of iron and chromium oxides (components of the steel) [32]. As a result of intensive oxidation processes, the volume of wear products in comparison
to the native material and their hardness are increased. This has an effect on further friction and tribological destruction processes. The application of lubricant fluids significantly reduced the amount of wear, particularly in the presence of saliva and of the mucin solution. The addition of xanthan gum (solution D) led to increased wear. As mentioned earlier, this is probably caused by a reduction of mucin adsorption, which limits the formation of protective boundary layers. Furthermore, an increase of fluid viscosity has an unfavorable impact on capabilities of wear product removal from the friction area. This may lead to intensification of wear processes (secondary wear).

As mentioned earlier, the significant effect of fretting on the intensification of corrosion processes is indicated in many publications [4, 17, 30]. The results of conducted tests shown in table 4 confirm these constatations.

Testing of sample potential in an open system enables preliminary assessment of the resistance of the material to corrosion processes. The influence of fretting on changes of potential is clearly visible in fig. 5. After potential was stabilized over one hour, the fretting friction process was initiated, which led to the destruction of the protective passive layer and a sudden drop of the corrosion potential value. After friction is discontinued, the oxide layer is reconstructed and potential rises in the direction of the initial state. However, the destroyed protective layer was not fully reconstructed, which has an unfavorable influence on the corrosion resistance of the tested material. Lower open circuit and corrosion potentials of studied samples are indicative of this.

Analysis of the obtained data shows that all studied saliva substitutes exhibit similar corrosion aggressiveness. However solution D had the worst characteristics, as indicated by the lowest values of corrosion potentials as well as by the slightly greater rate of current density increase. Despite similar potentials, the greatest polarization resistances are present in the environment of natural saliva - which indicates is favorable anti-corrosion properties. Registered anode polarization curves in the environment of saliva and its substitutes are presented in fig. 6. The return curve in solution A visible on the chart indicates the occurrence of repassivation processes - the formation of a secondary protective layer. This formed layer is quickly destroyed, however, and the revealed metal surface is subject to corrosion. No clear repassivation processes were observed in other environments.

Obtained data shows that, for the studied fluids, repassivation potentials are similar to corrosion potentials, which indicates a low intensity of surface repassivation processes. The processes of passive layer destruction and reconstruction are visible in the case of simultaneous testing of fretting and corrosion. This indicates a typical, jagged course of the anode polarization curve (fig. 7).

Microscope observations of the surfaces of tested samples constituted unequivocal evidence of the intensive processes of fretting and corrosion wear. Indicative images of such surfaces are shown in fig. 8. Fretting wear processes are focused in the central friction contact area (fig. 8a). Wear products remaining in the friction area are clearly visible.
Despite the difficulties in identification of the simultaneously occurring processes of tribological and corrosive wear (fretting corrosion), it was possible to observe propagation of the corrosion beyond the friction area (fig. 8b).

4. Conclusions

The results of studies confirmed the high susceptibility of 316L implantation steel to wear as a result of fretting and fretting corrosion. Test results indicate differing effects of saliva and its substitutes on the course of these processes. The lowest corrosive aggressiveness and the best lubricant properties, relative to natural saliva, were exhibited by the mucin III solution in phosphate buffered saline. The addition of xanthan gum had an unfavorable effect on tribological characteristics and corrosion resistance. 316L implantation steel exhibits the greatest resistance to fretting corrosion processes in the environment of natural saliva. This is indicated by high polarization resistances and visibly greater values of potential at which reverse polarization takes place.

Despite the fact that natural saliva still remains to be the least corrosive environment for 316L steel, it seems that the base solution of mucin III in PBS may constitute a basis for development of saliva substitutes with favorable tribological characteristics. Such preparations can be used to reduce the effects of affections in the oral cavity, such as bruxism, and may also be useful in improving the operational lifetime of dental prosthetics and orthopedic apparatus components.

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References