THE INFLUENCE OF SALIVA AND ITS SUBSTITUTES ON CORROSION OF SOME IMPLANT ALLOYS

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Abstract: The purpose of this paper is evaluation of the influence of human saliva and its substitutes on the corrosion resistance of some implant alloys used in stomatology, which included: austenitic steel (316L), titanium alloy (Ti6Al4V), and cobalt alloy (CoCrMo). Corrosion studies were conducted by means of the potentiodynamic method with the application of the VoltaLab 21 kit with VoltaMaster 4 software. The reference electrode was a saturated calomel electrode (SCE), whereas the counter electrode was a platinum electrode. The results of conducted studies indicate an increased current density in the passive range on potentiodynamic curves of studied alloys in the environment of human saliva, and also in a commercial saliva solution – Mucinex. On the basis of conducted corrosion studies, it can be stated that in terms of corrosion resistance the developed saliva substitutes may constitute competitive solutions to commercial saliva substitutes. The prepared substitutes should be studied further from the perspective of practical application for patients. The original value of the paper is a proposition of new saliva substitutes.

Key words: Metallic Alloys, Corrosion, Human Saliva, Saliva Substitute, Prosthodontia

1. INTRODUCTION

Human saliva fulfills many important functions in the human organism (e.g. digestive, protective, excretory, buffering, demineralizing, nutritional). However, it can also be the cause of health problems for patients (Dodds et al., 2005; Amerongen et al., 2002; Rantonen, 2003; Brosky, 2007; Zalewska et al., 2007; Kaczmarek, 2007). Disadvantageous processes leading to an increase in the intensiveness of destruction of metallic elements in the human stomatognathic system can be observed in the oral cavity Chatuverdi (2009). The most often cause of this phenomenon is the aggressiveness of the contact environment, which may lead to initiation of corrosive processes in metallic biomaterials, and thus, to worsening of their biofunctional properties (Sharma et al., 2008; Upadhyay et al., 2006). In this case, it pertains to contact of human saliva with metallic biomaterials used in stomatology. As a result, the phenomenon of corrosion takes place.

Processes of destruction of stomatological implants, orthodontic apparatus, metallic fillings or elements of stomatological prostheses mainly result from biological metabolic reactions occurring in a living organism. These are phenomena that result from the reaction of hydrogen emission and oxygen absorption from the tissue surrounding the implant, variable body temperature, changes in the pH of body fluids, factors of exploitation (e.g. friction processes, mechanical damage, overload, incorrect implant geometry, and the presence of specific ions (e.g. chlorine, sodium, potassium, calcium, and magnesium phosphate) (Sharma et al., 2008; Upadhyay et al., 2006; Święczko-Żurek, 2005; Hansen, 2008). They also include the influence of proteins, enzymes, fluoride ions, and bacteria from biofilms present in saliva (Lee and Newman, 2003, Jayaraman et al., 1997a, b). Other pathogenic factors include: improper diet and oral cavity hygiene, or medication taken by patients (Canay and Oktener, 1992; Wataha, 2000). Metallic biomaterials are exposed to pitting, fatigue, fretting, and crevice corrosion (Reclaru et al., 2005; Blackwood, 2010; Manivasagam, 2010). It is worth noting that many types of corrosion may be present in a single implant. The development of this process causes toxic and allergic reactions, inflammatory states, development of tumors or metalosis in the human organism (Chatuverdi, 2009; Santonen et al., 2010; Marciniak and Paszenda, 2005). In addition, metal ions released from metallic stomatological implants as a result of corrosion may travel to the digestive tract and accumulate in the stomach, liver, spleen, kidneys, bones, lungs, brain, or in the mucous membrane. In stomatology, local toxicity of metals and their alloys is encountered most often. The effect of suction of human saliva (of an increased acidity) into the interiors of contraction cavities found in metallic biomaterials caused by pulsatory changes in their volume (during cyclic deformations, e.g. of prosthetic implants during chewing), accelerates corrosion of prostheses due to the formation of a concentration cell. In relation with this, conduct of corrosion resistance studies of implants in a tissue or body fluid environment is very important, and the results of these studies should be used to develop chemical compositions of alloys used in stomatology and artificial saliva solutions (Mareci et al., 2007, 2011; Rajendran et al., 2010). A lack of activity of corrosive processes is considered to be one of the most important parameters for biocompatibility of materials used in medicine (Bedi et al., 2009).

One of the methods of treatment and prevention of the destructive processes in the oral cavity (dryness of the oral cavity, use of prostheses, etc.) is the application of e.g. lubricants (vaseline or glycerin, etc.) or substitutes in the form of fluids or gels (Kaczmarek, 2007).
In many scientific centers, attempts are being made to create preparations with properties that are as similar as possible to those of human saliva, for the purpose of improving the comfort of life for a certain group of patients. In addition, these substitutes are to positively impact the utilitarian properties of dental fillings as well as ceramic and metallic biomaterials in the oral cavity. An important criterion for admission of such substances for use by patients is their lack of aggressiveness towards metallic biomaterials (Wang, 1996; Surowska, 2009; Unalan et al., 2009; Manivasagam et al., 2010; Grogogeat et al., 1999; Ayda et al., 2005; Barao et al., 2011; Kocjan and Conradi 2010).

Because of their properties, metal alloys are the materials generally used to produce dental implants. Due to the nature of the human body, it is necessary to learn about the electrochemical properties of applied biomaterials, which facilitates their selection for the purpose of ensuring the best biocompatibility (Bundy, 1994).

Evaluation of corrosion resistance of metallic biomaterials used in stomatology is included in the group of accelerated electrochemical tests.

The aim of this work was to evaluate the corrosion properties of human saliva and its substitutes under in vitro conditions, using the example of metallic materials most commonly used in dental implantology, such as: steel (316L), a titanium alloy (Ti6Al4V), and a cobalt alloy (CoCrMo).

2. MATERIALS AND RESEARCH METHODOLOGY

Human saliva, its commercial substitutes, and three preparations with compositions developed at the Department of Materials and Biomedical Engineering of the Białystok University of Technology (Tab. 1), were subjected to tests. The selection of the ingredients of the developed saliva substitutes was based on the wide application of these ingredients in the pharmaceutical industry (toothpastes, mouthwashes, etc.) (Kaczmarek, 2007).

Tab. 1. Lubricants used in the corrosion tests

| Solution A | human saliva |
| Solution B | PBS (phosphate buffered saline, pH=7) |
| Solution C | hydrated tetra-sodium pyrophosphate (Sigma-Aldrich) + di-sodium dihydrogen phosphate (Sigma-Aldrich) + tetra-potassium pyrophosphate (Sigma-Aldrich) + xanthan gum (Sigma-Aldrich) in PBS (phosphate buffered saline) of pH=7.0 |
| Solution D | type II mucin solution (Sigma-Aldrich) in PBS of pH=7.0 |
| Solution E | type III mucin solution (Sigma-Aldrich) in PBS of pH=7.0 |
| Solution F | Mucinox (PARNELL PHARMACEUTICALS) |
| Solution G | BioXtra (BIO-X HEALTHCARE) |

For the purpose of achieving repeatable test conditions for human saliva, a previously developed method for its acquisition was applied (Andrysewicz et al., 2008).

Corrosion resistance tests of 316L steel, Ti6Al4V titanium alloy, and CoCrMo cobalt alloy in the environment of saliva and its substitutes were conducted on the basis of methodology based on the PN-EN ISO 10993-15 standard (“Biological evaluation of medical products. Identification and quantitative determination of products of degradation of metals and alloys”) (PN-EN ISO 10993-15:2009).

Before the test started samples were polished and burnished. For corrosion tests using the potentiodynamic method, the VoltaLab 21 kit with VoltaMaster 4 software was applied, along with measuring vessels with an electrode system and an ultrathermostat (Fig. 1).

The temperature of solutions during tests was equal to 37°C. The reference electrode was a saturated calomel electrode (SCE). The counter electrode was a platinum electrode with a contact surface of 128 mm² with the electrolyte. During a time of one hour, the potential of an open system was tested in Solutions B-G. However, tests in Solution A (human saliva) were conducted directly after assembly of the test system, without hourly registration of the potential of the open system (due to precipitation of protein morphotic elements of the saliva and disruptions of the flow of electric current through the tested system). Every kind of sample was tested three times. The middle result of investigations was presented at the work.

Using VoltaMaster 4 software, the values of corrosive potentials and electrical current densities of corrosion (using the Tafel method), corrosion resistance, and yearly loss of material were determined. Samples were polarized in the range of potentials from about open circuit potential ($E_{ocp}$) – 100 mV to +4 V at a set rate of potential increase of 1 mV/s.

3. DESCRIPTION OF ACHIEVED RESULTS OF OWN RESEARCH

The results of corrosion tests for the tested alloys have been presented in Figs. 2–4 and in Tab. 2–4. Comparisons of corrosion test results for: Solution C have been presented in Fig. 5, for Solution D – Fig. 6, for Solution F – Fig. 7, for Solution A – Fig. 8. Tab. 5–8 contain a list of tested quantities for individual charts, respectively.

The below charts (Fig. 2, Tab. 2) show that 316L steel has the greatest polarization resistance (138 kΩcm²) in solution C, which, combined with the high value of corrosion potential (-294 mV) and small annual loss of thickness (0.004593 mm/Y), means that this alloy is the most resistant to corrosion in this environment. It is also worth noting, that despite having an identical corrosion
potential as in solution C, 316L steel exhibits the lowest corrosion resistance in natural saliva (solution A), and this is also indicated by the lowest value of polarization resistance (4 kΩcm²) and by the greatest annual loss of thickness (0.1637 mm/Y).

From analysis of Fig. 3 and Tab. 3, it results that the Ti6Al4V alloy is characterized by the greatest polarization resistance in solution E (1629 kΩcm²) and exhibits, at the same time, a small annual loss of thickness (0.000405 mm/Y) and the greatest corrosion resistance. It should be emphasized that a stable passive range, not exceeding 10 μA/cm² for small current densities, was achieved in the environment of all saliva substitutes. The most corrosive environments for the titanium alloy turned out to be the commercially available formula, Mucinox (solution F), and natural saliva (solution A).

It results from Fig. 4 and Tab. 4, that the cobalt alloy in Solution E, is characterized by the highest polarization resistance (2500 kΩcm²) and breakthrough potential (1829 mV), as well as by a lowest negative corrosion potential (-346 mV). These parameters are decisive of the high corrosion resistance of the alloy in Solution E, manifested in the lowest yearly decrement of thickness (0.000146 mm/Y).

The second part of the work concerns analysis of the influence of the type of solution on the corrosion properties of the three tested metallic materials.
Despite the fact that 316L steel is characterized by the highest corrosion potential (-294 mV) in solution C, it is the CoCrMo cobalt alloy that exhibits the highest corrosion resistance due to its high polarization resistance (1480 kΩcm²) and low annual loss of thickness (0.000219 mm/Y).

Studies showed, that similarly as in the case of solution C, the cobalt alloy also exhibits the highest corrosion resistance in solution E. This solution constitutes the environment that is most aggressive to 316L steel (Fig. 6, Tab. 6). This is indicated by the low value of polarization resistance (50 kΩcm²) and the low value of breakthrough potential (615 mV).

In solution F, the studied Ti6Al4V titanium alloy is characterized by the best anti-corrosion properties in comparison with other materials, as made evident by its having the greatest corrosion potential (-298 mV) and the lowest annual loss of thickness (0.009404 mm/Y). However, its polarization resistance is small and similar to the resistance of the CoCrMo cobalt alloy (14 kΩcm²), as illustrated in Fig. 7 and Tab. 7.

The low polarization resistance value and high values of yearly decrement of thickness achieved through the application of Solution A (Fig. 8, Tab. 8), may be the cause of rapidly advancing corrosion processes in the studied metal alloys.

4. DISCUSSION AND CONCLUSIONS

The success of medical procedures related to the use of metallic implants is dependent on the optimal selection of utilitarian properties of biomaterials and of their physicochemical properties, because the aggressiveness of bodily fluids may lead to the initiation of corrosive processes. Metals used in the human body must be highly resistant to corrosion, which is why in vitro assessments of the corrosion resistance of implant alloys in the environment of artificial bodily fluids are being carried out in many scientific centers (Paszenda, 2010; Reza, 2011; Bellefontaine, 2010).

The authors of this work assessed the corrosion resistance of implant alloys in formulas developed by them at the Department of Materials and Biomedical Engineering. The developed preparations are meant for use by persons with salivary gland disorders.

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### Tab. 5. Corrosion properties of materials in Solution C

<table>
<thead>
<tr>
<th></th>
<th>$E_c$ [mV]</th>
<th>$R_p$ [kΩcm²]</th>
<th>Corrosion rate [mm/Y]</th>
<th>$E_b$ [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 LV</td>
<td>-294</td>
<td>138</td>
<td>0.004593</td>
<td>515</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>-466</td>
<td>775</td>
<td>0.000521</td>
<td>2356</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>-447</td>
<td>1480</td>
<td>0.000219</td>
<td>387</td>
</tr>
</tbody>
</table>

### Tab. 6. Corrosion properties of materials in Solution E

<table>
<thead>
<tr>
<th></th>
<th>$E_c$ [mV]</th>
<th>$R_p$ [kΩcm²]</th>
<th>Corrosion rate [mm/Y]</th>
<th>$E_b$ [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 LV</td>
<td>-367</td>
<td>50</td>
<td>0.004851</td>
<td>615</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>-305</td>
<td>1620</td>
<td>0.000405</td>
<td>2416</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>-346</td>
<td>2500</td>
<td>0.000146</td>
<td>1829</td>
</tr>
</tbody>
</table>

### Tab. 7. Corrosion properties of materials in Solution F

<table>
<thead>
<tr>
<th></th>
<th>$E_c$ [mV]</th>
<th>$R_p$ [kΩcm²]</th>
<th>Corrosion rate [mm/Y]</th>
<th>$E_b$ [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 LV</td>
<td>-598</td>
<td>5</td>
<td>0.028970</td>
<td>962</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>-298</td>
<td>14</td>
<td>0.009404</td>
<td>-</td>
</tr>
<tr>
<td>CoCrMo</td>
<td>-379</td>
<td>14</td>
<td>0.021660</td>
<td>1066</td>
</tr>
</tbody>
</table>

The developed preparations are meant for use by persons with salivary gland disorders.
and wearing dental prostheses, particularly to reduce friction and its effects (bruxism, dental prosthetics). The saliva substitutes in which in vitro studies were conducted have novel formulas, and in relation to this, no articles were found in which the results of other authors could be compared to the results of this study.

Analysis of the obtained results of studies indicates that natural saliva constitutes the most aggressive environment. This is indicated by unequivocally low values of polarization resistance and high annual losses of thickness for all of the studied implant alloys. The authors’ own composition – type III mucin solution in PBS, was characterized by the lowest corrosiveness and exhibited low current densities in the passive range and high polarization resistance for the selected biomaterials.

The CoCrMo cobalt alloy proved to be the most resistant to corrosion in most of the studied environments, followed closely by the Ti6Al4V titanium alloy. CoCrMo alloys have been used in implantology for many decades due to their high resistance to abrasion. The corrosion resistance of this material is improved by increasing Cr concentration or by applying films e.g. with nitrogen ions onto these alloys (Hermawan, 2011; Dobrzański, 2011).

As regards titanium and its alloys, special attention should be paid to the composition and thickness of the surface layer in contact with the human body. The following alloys are characterized by a very high polarization resistance: Ti-6Al-4V, Ti-5Al-2.5Fe and Ti-6Al-7Nb (Paszenda, 2010; Hermawan, 2011; Ige, 2009). In the case of the Ti-6Al-4V alloy, there is now an increasingly visible tendency of eliminating vanadium and aluminium and replacing them with other elements e.g. niobium, iron, or zirconium.

Until recently, steels were the most commonly used implant materials, particularly 316L grade steel. Unfortunately, its application was limited because 316L steel is not suitable for long-term in vivo exploitation. Its low polarization resistance combined with a high and advancing loss of thickness are indicative of intensive oxidation processes and of the formation of corrosion products, which reduce the biocompatibility of steel. When using implants made from 316L grade steel, special attention is to be paid to the appropriate design and selection of materials for implants (Paszenda, 2010; Ige, 2009; Dobrzański, 2011).

On the basis of conducted corrosion studies, it can be stated that, in terms of corrosion resistance, the developed saliva substitutes may constitute competitive solutions to commercial saliva substitutes. The prepared substitutes should be studied further from the perspective of practical application for patients.

REFERENCES

12. Dobrzański L. A., Reimann L. (2011), Influence of Cr and Co on hardness and corrosion resistance CoCrMo alloys used on den-
13. Dodds M. W. J., Johnson D. A., Yehc Ch. K. (2005), Health bene-
15. Hansen D. C. (2008), Metal corrosion in the human body: the ulti-
27. Mareci D., Ungureanu G., Aeleanei D. M., Rosca J. C. (2007), Electrochemical characteristics of titanium based biomaterials in arti-
28. Paszenda Z., Walke W., Jadacka S. (2010), Electrochemical inves-
tigations of Ti6Al4V and Ti6Al7Nb alloys used on implants in boneburger, Journal of Achievements in Materials and Manufacturing En-
30. Rajendran S., Chitra Devi P., Johnmary S., Krishnaveni A., Kan-
chana S., Christly L., Nagalakshmi R., Narayanasamy B. (2010),
The Influence of Saliva and Its Substitutes on Corrosion of Some Implant Alloys

Corrosion behaviour of SS 316L in artificial saliva in presence of electrical., Zastita Materijala, 51, 149-158.


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