Passivity of Some Dental Materials in Ringer's Solution

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Summary

In this paper corrosion resistance of two experimental dental alloys, Co-Cr-Mo and Co-Cr-Ni, one commercial Co-Cr-Mo (Wironit®) alloy, high purity titanium and Ag-amalgam (Permite®) was studied in Ringer's solution. On the basis of electrochemical measurements, the relevant indicator of local corrosion - pitting potential E_{pitt}, at which the break-down of passive layer and the effects of local corrosion start, was determined. By ranking of materials according to pitting potential, it was found that pure titanium is the most stable material followed by commercial alloy Wironit®, Co-Cr-Mo and Co-Cr-Ni alloys, while amalgam showed the lowest resistance in the experimental conditions of model oral cavity medium.

Key words: passivity, dental materials, Ringer's solution, corrosion resistance, local corrosion.

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Introduction

Alloys which are used in dentistry are permanently exposed to changeable conditions of the oral environment, which is practically ideal for corrosion and chemical disintegration of often used materials (1). Implant materials must be wear resistant, chemically inert in many basic and acid food components, and also in the oral fluids.

If the materials used in dental practice are not resistant to dissolution in the oral cavity, the developed products are harmful for the tissue (ions, etc.) and can cause pathological changes (2). The influence of a such metal prosthesis reflects on the remaining teeth, on the mucus of the oral cavity and even on distant organs. Other teeth can be damaged when a prosthesis creates conditions beneficial to caries and parodontosis.

For prosthetic practice alloys of silver, gold, chromium, cobalt, nickel, molybdenum, iron and carbon are mostly used in various combinations (3). Dental alloys should have an optimal ratio of hardness and ductility, and cosequentualy a high hardness value is not always desirable (4). For example, alloy of iron and carbon, i.e. steel, is inapropriate for fixed-prostheses because its high value of hardness leads to abrasion of the natural teeth in the opposite jaw.

Co-Cr alloys, because of their high strength, hardness, corrosion resistance and biocompatibility, have wide use for various implants in dentistry and medicine (5). However, their drawbacks are low ductility and possible cancerogenic influence (6). Namely, there is a possibility that the corrosion products of Co-Cr alloys can cause health problems inside the body. It is known that cobalt inhibits the absorption of iron in the blood and causes anemia, while chromium species lead to disturbances in the central nervous system.

As that all metals corrode more or less in the oral cavity environment, it follows that their corrosion is

almost impossible to prevent. The solution to this problem is the reduction of corrosion i.e. corrosion products quantities by applying materials of better quality, such as titanium which does not corrode noticeably and does not create harmful effects in the body (7). It is well known, that titanium has excellent biocompatibility, elasticity and corrosion resistance, and is therefore recommended for dental and orthopedic implants (8). As a high-strength biomedical alloy Ti-6Al-4V is mostly used. However, it was found that vanadium, as an alloying element, is very citotoxic (9). Namely, corrosion reaction is unavoidable when the metallic material is exposed to body fluids for longer time. As Ti-6Al-4V contains vanadium, which irritates the mucous membrane of respiratory organs and is also harmful for the circulatory system, a new alloy of titanium with niobium has been developed. It was found that Ti-6Al-7Nb alloy is considerably less citotoxic, more ductile and corrosion resistant than Ti-6Al-4V alloy.

Corrosion resistance of dental materials could be evaluated according to distinct criterions. In this study the corrosion resistance of pure titanium, the Co-Cr alloys and Ag-amalgam has been investigated in Ringer's solution. The quality of the mentioned metals was estimated on the basis of pitting potential E_{pit}, at which passive film breakdowns and pitting corrosion begins.

Materials and Methods

In this study the experimental Co-Cr-Mo and Co--Cr-Ni specimens, prepared in an electric arc furnace (Laboratory of Physical Metallurgy-Faculty of Metallurgy) were used as well as commercial specimens of pure titanium, Wironit® (Bego, Bremen, Germany) and Ag-amalgam Permite® (Southern Dent. Industries Ltd., Australia). Chemical composition of the tested materials is presented in Table 1.

Experimental alloys Co-Cr-Mo and Co-Cr-Ni were produced by the melting process under argon atmosphere and by subsequent casting in the copper mould. The Co-Cr-Mo specimen was heat treated in order to eliminate residual stresses. Heat treatment was performed by heating the specimen in a quartz tube filled with argon at 950°C. After 2 hours cooling in air to the room temperature followed.

In vitro measurements were done in Ringer's solution (10). During the experiment the working medium was aerated (flow rate 30 L/h) while pH was 8.0 at 37°C. As Ringer's solution composition is close to body fluids, it was chosen in order to simulate the oral cavity medium.

In this study corrosion resistance was tested with laboratory potentiostat Wenking 68FR0.5. The method of cyclic anodic polarization was used for potentiodynamic measurements which were realized going from E_{corr} to +1200 mV versus saturated calomel elecrode (SCE) and reverse, while scanning rate dE/dt was 2 mV/s (Figure 1).

Cyclic anodic polarization was performed with the aim of determining characteristic parameters from experimental polarization curves: pitting potential E_{pitt}, repassivating potential E_{rep} and hysteresis potential E_{hys}.

Local corrosion (pitting) resulting from stimulating anodic procedure can be stopped by the passivating process in reverse polarization. Such repassivation phenomenon is coupled with current intensity decrease so that potential at which hysteresis loop is closed can be referred to as repassivating potential E_{rep} (protection potential). Furthermore, hysteresis potential E_{hys} is also a corrosion related parameter and can be calculated as: $E_{hys} = E_{pitt} - E_{rep}$.

Measurements were done at constant temperature in a three-electrode double wall glass cell equipped with working electrode (specimens investigated), reference electrode (SCE) and counter electrode (platinum net). Immediately before the start of an experiment, the surface of the working electrode was ground by abrasive papers No. 400, 500 and 600, subsequently flushed with distilled water and degreased in ethanol. In order to eliminate the possible errors caused by ohmic potential drop in electrolyte, the reference electrode was equipped with Luggin's capillary. Its end was situated 2-3 mm from the working electrode surface so that elimination of the mentioned errors was possible. The measurement started with placing the working electrode in aerated solution for 30 minutes, e. g. until the stabilization of electrode potential was achieved. In this stationary state the value of rest potential E_{mir} (open circuit potential) was registered by laboratory potentiostat and compensated. The polarization of work-

ing electrode was performed by Wenking scanning potentiometer SMP72 capable of increasing/decreasing the potential. The actual potential of the electrode was followed with precise potentiometer Wenking PPT70 while the results of potentiodynamic measurements were plotted by a two-coordinate recorder (Servogor XY BBC Goerz) as the E-i curves in real time. At least three polarization experiments were done with each specimen and average values are presented here. All potentials are expressed according to saturated calomel electrode.

Results

The chemical stability of the examined materials relies on the passive, spontaneously formed surface layer. However, because of the adsorption of chloride ions from Ringer's solution the breakdown of the protective film results and the appearance of pitting starts. This can be observed as an extreme increase in the current on forward anodic polarization curves (Figures 2-4) of the registered cyclic voltammograms. For the sake of a better resolution the reverse curve is shown only in Figure 2 for the Co-Cr-Mo specimen.

The rapid increase in the current can be noticed at the pitting potential E_{pitt} at which the breakdown of the passive layer and local corrosion begin. Since a material with higher pitting potential can be considered as corrosion resistant, E_{pitt} was used as the criterion for comparison between the tested dental materials. The values determined from the curves of cyclic anodic polarization are shown in Table 2.

Discussion

The excellent biocompatibility of titanium is connected with the properties of the surface which is in contact with the biological environment, i. e. with the stable, passivating oxide layer formed on its surface. The natural oxide layer on commercially pure titanium is predominantly composed of TiO_2 with minor amounts of Ti_2O_3 and TiO (11). TiO_2 provides the corrosion resistance under static conditions, and it has often been reported that titanium is not susceptible to pitting and/or crevice corrosion

(12). Thus in this study, among other examined materials, titanium has shown the best corrosion performances. It follows from the fact that the appearance of pitting in the potential range from E_{corr} to +1200 mV vs SCE was not noticed (Figure 5.). This extraordinary corrosion resistance of titanium is obtained due to the extreme stable passive layer in Ringer's solution. Thermodynamic stability and passivity of this layer on the titanium surface have a protective role in the corrosion process.

Second, according to corrosion resistance is Wironit® followed by Co-Cr alloys and Ag-amalgam. Corrosion resistance of Co-Cr experimental alloys is determined by their chemical composition. It is known from the literature (13) that cobalt enhances good mechanical properties and reduces viscosity (during the casting) of the alloy. Chromium improves the chemical stability and inertness of the alloy, while molybdenum also has a favourable effect on the chemical stability of the alloy and increases its elasticity. In addition, Mo bonds the excess of unburned carbon from melt, forming molybdenum-carbide (Mo_6C) and increasing the brittleness of the alloy. Furthermore, it is known that Wironit® and other Co-Cr alloys have an inhomogenous, partial eutectic, microstructure which indicates good corrosion resistance (14). In this study, however, lower corrosion resistance of Co-Cr-Ni alloy was obtained, indicating that the poorer properties of the passive layer are probably the consequences of the negative influence of nickel present in the chemical composition. Hence, it can be concluded that the use of Co-Cr-Ni alloys in the oral cavity is not desirable because they have a greater tendency to corrosion than Co-Cr-Mo alloys. Apart from cobalt, chromium and molybdenum, Wironit® also contains carbon, silicon and manganese, which provide the formation of carbides. They increase not only the hardness of the alloy, but also may influence corrosion resistance (15, 16).

Ag-amalgam Permite® has been shown to be the least resistant material showing the lowest amount of pitting potential. Such polarization characteristics can be expected in Ringer's solution, because it is known that dental amalgams are multiphase materials with a complex metallografic structure (14). Metallic matrix mostly consists of three solid phases Ag_2Hg_3, Ag_3Sn and Sn_8Hg_8. Each one of

them contributes to the corrosion reaction in the aggressive medium of the oral cavity (17-20) resulting in mercury ions release. According to numerous investigations (21-26), health risk substantially increases because of the presence of mercury in the human organism.

By comparing the potentials of hysteresis E_{hys} (Figure 6), it can be seen that a specimen of Wironit® has the narrowest loop of hysteresis, while Co-Cr-Ni alloy has the broadest loop of hysteresis. It is known that the narrower loop of hysteresis indicates higher corrosion resistance, which is not the case here comparing E_{pit}t values. The cause of this might be complex and has not been investigated here. However, it is known (27-30) that broadness of the loop can be provoked by a change in the surface during the anodic polarization, by slow diffusion of Mez+-ions and H+-ions from the first polarization and by some other kind of local corrosion, such as at the grain boundaries or between the phases. Thus, it is important to emphasize that the most reliable criterion for corrosion resistance determination is the pitting potential E_{pitt}, which is used in this study.

Conclusions

1. Corrosion characteristics of two experimental Co-Cr-Mo and Co-Cr-Ni alloys were determined by the method of potentiodynamic polarization and compared to the relevant values of one commercial specimen Co-Cr-Mo (Wironit®), titanium and Ag-amalgam (Permite®).

2. Since the use of the most biomedical alloys is found to rely on the presence of a surface passive layer which has the property of controlling the undesirable dissolution of metal matrix, in this study the corrosion resistance was estimated on the basis of pitting potential at which the breakdown of the passive layer starts and pitting corrosion results.

3. Extraordinary high corrosion resistance of titanium was registered due to the stable passive layer of TiO2 in Ringer's solution, while for the good corrosion resistance of Wironit® as well as of Co-Cr-Mo and Co-Cr-Ni alloys chemical composition is responsible.

4. Amalgamic alloy Permite® showed the lowest value of pitting potential.

5. It has been shown that pitting potential can serve as the reliable criterion for ranking of examined specimens, and also for the selection of dental materials which can provide good corrosion resistance.